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Zhang, Wali.

2010

Zhang, W. L. (2010). Magnetron sputtered nanocomposite films of Si nanocrystals embedded in SiO₂ for electronic and optoelectronic applications. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/44687>

<https://doi.org/10.32657/10356/44687>

Magnetron Sputtered Nanocomposite Films of Si Nanocrystals Embedded in SiO₂ for Electronic and Optoelectronic Applications

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**A Thesis Submitted to the Nanyang Technological University
in Fulfillment of the Requirements for the Degree of
Doctor of Philosophy**

2010

Abstract

Nanocomposite thin films of Si nanocrystals (nc-Si) embedded in SiO₂ have attracted intensive research for potential applications in next generation non-volatile memory device as well as Si-compatible light-emitting devices. This dissertation studies the structural, electrical and optoelectronic properties of the Si nanocomposite films. The Si nanocomposite films are synthesized by reactive radio frequency magnetron sputtering of a Si target in a gas mixture of Ar/O₂ followed by rapid thermal annealing at high temperatures. The synthesized films have been characterized with transmission electron microscopy (TEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), current-voltage (*I-V*), capacitance-voltage (*C-V*) and electroluminescence (EL).

The as-sputtered SiO_x films are amorphous. XPS analysis reveals that the as-deposited SiO_x films contain five Si chemical states (Siⁿ⁺, where n = 0, 1, 2, 3 and 4) in a wide composition range. Amorphous Si nanoclusters are formed in the as-deposited SiO_x films, and they are embedded in the SiO₂ matrix. The physical origin of the formation of the amorphous Si clusters is the high kinetic energy of the sputtered Si atoms coupled with high surface diffusivity. An atomic model has been proposed to depict the atomic structure of the amorphous SiO_x films where Si nanocluster cores are encapsulated by shell of Si suboxides, which themselves embedded in the SiO₂ matrix. Si nanocrystals are formed by rapid thermal annealing the as-deposited SiO_x films at elevated temperatures. The growth mechanism of nc-Si is found to be different from the classical nucleation and diffusion growth model. It is believed that thermal segregation of the Si suboxides provides rapid growth of Si nanoclusters,

thus is considered the responsible mechanism.

The existence of nc-Si strongly enhances the current conduction in the nanocomposite films. Three conduction mechanisms are identified, including direct tunneling via the tunneling paths formed by nc-Si, nc-Si-assisted Poole-Frenkel emission and the nc-Si-assisted Fowler-Nordheim tunneling. These mechanisms dominate the current conduction in different stage depending on magnitude of the gate bias. The charging of the nc-Si leads to significant decrease in conductance of the oxide while the discharging of the nc-Si recovers the conductance. XPS depth profiling reveals that the nc-Si plays a dominant role in the charge trapping mechanism in the nc-Si/a-SiO₂ system. Electric field-induced reversible bipolar resistive switching is observed in Al/nc-Si:SiO₂/Si MOS nanostructure. The resistive switching effect is explained by a model of conductive filament of oxygen-related defects where the filaments are formed and ruptured at the SiO_x/Si substrate electric barrier.

Intense EL spectrum has been obtained with a dominant band at ~600 nm (2.1 eV) and two shoulder bands at ~480 nm (2.7 eV) and 760 nm (1.8 eV) from both as-sputtered amorphous SiO_x films and the films after high temperature annealing. The physical origins of the light emission are the same for both as-deposited and annealed samples, believing to come from both the Si nanoparticles and the oxygen-deficient defect centers such as the neutral oxygen vacancy and non-bridging oxygen hole centers. The charging of the Si nanocrystals strongly reduces the EL intensity and gate current due to the reduction in the number of the injected carriers available for the radiative recombination. The reduced EL intensity can be partially recovered by releasing of the trapped charges.

Acknowledgments

First and foremost, I would like to express my sincere and deepest gratitude to my research supervisor, Professor Sam Zhang, for his invaluable guidance, support and encouragement throughout my PhD study. He not only introduced me to the world of scientific research and encouraged me to develop my research skills, but also taught me the disciplines in both study and life. I also would like to extend my sincere thanks to my co-supervisor, Professor Chen Tupei of School of Electrical and Electronic Engineering, NTU for providing me useful and insightful suggestions on my experimental results and writing.

I also would like to thank my seniors, Dr. Liu Yang, Dr. Wang Yong Sheng, Dr. Ong Soon Eng, Dr. Liu Qing Lin, Dr. Zhang Xiao Min and Mr. Wang Hui Li, who helped me to conquer numerous challenges during my research. Thanks also go to my fellow PhD students, Mr. Yang Ming, Mr. Liu Zhen, Mr. Cen Zhan Hong, Mr. Shang Lei, Mr. Sun Li Dong, Ms Zhang Zhe, Ms Cai Yang Li, Mr. Li Feng Ji and Mr. Wang Yu Xi, for their help, useful discussion and good ideas, which helped me overcome frustrating barriers in the course of my research. I greatly enjoyed the time working with all the members in my research group and sincerely appreciate their help.

I sincerely thank Professor Liu Er Jia and Mr. Khun Nay Win for their assistance in some sample preparation. I also would like to thank the technicians in Materials Laboratory A and B, Mr. Leng Kwok Phui, Mr. Lew Sui Leung, Ms Chow Chiau Kee, Ms Yong Mei Yoke, Mr. Chang set Chiang, Ms Seah Peng Neo, Sandy, for their Lab support, especially, Ms Chow Shiau Kee help in the XPS and Ms Yong Mei Yoke for TEM work.

I would like to thank my parents, my sister and my brother. Their love and support are the driving force for my research. My deep gratitude also goes to my parents-in-law and brother-in-law for taking care of my daily life in Singapore. Finally but mostly, I would like to express my sincere and deepest gratitude to my wife Ms Jin Min and my sons Heran, Zhuoran, because without them this dissertation neither would be possible nor worthwhile.

This thesis is dedicated to my wife and my sons.

Selected Publications

- [1] Wali Zhang, Sam Zhang, Ming Yang and Tupei Chen, Microstructure of Magnetron Sputtered Amorphous SiO_x Films: Formation of Amorphous Si Core-Shell Nanoclusters, **Journal of Physical Chemistry C** (IF: 3.6) **114**, 2414–2420 (2010).
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- [3] Wali Zhang, Sam Zhang, Yang Liu and Tupei Chen, Evolution of Si Suboxides into Si Nanocrystals during Rapid Thermal Annealing as Revealed by XPS and Raman studies, **Journal of Crystal Growth** (IF:1.9), 311, (2009) 1296-1301
- [4] Wali Zhang, Sam Zhang, Ming Yang, Zhen Liu, Zhanhong Cen, Tupei Chen and Dongping Liu, Electroluminescence of As-sputtered Silicon-rich SiO_x Films, **Vacuum**, 84, (2010) 1043-1048.
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- [7] Wali Zhang, Sam Zhang, Ming Yang, Zhen Liu and Tupei Chen, Electric Field-induced Resistive Switching Effect in the Nanocomposite Films of Si Nanocrystals Embedded in SiO₂ Films, **Journal of Physical Chemistry Letter** (under review)
- [8] Wali Zhang, Sam Zhang, Tupei Chen and Zhen Liu, Electrical Properties of the nc-Si Embedded SiO₂ films (book chapter), **Handbook of Nanostructured Thin Films and Coatings: Functional Properties**, Taylor&Francis, New York, 2010

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List of Abbreviations and Symbols

Abbreviation

CMOS	Complementary metal oxide semiconductor
$C-V$	Capacitance-Voltage
CVD	Chemical Vapor Deposition
EL	Electroluminescence
EOT	Equivalent Gate Oxide Thickness
FG	Floating-Gate
FN	Fowler-Nordheim
FWHM	Full Width a Half Maximum
HRS	High Resistance State
HRTEM	High Resolution Transmission Electron Microscopy
ITO	Indium Tin Oxide
ITRS	International Technology Roadmap for Semiconductor
$I-V$	Current-Voltage
LPCVD	Low Pressure Chemical Vapor Deposition
LRS	Low Resistance State
MBE	Molecular Beam Epitaxy
MOS	Metal Oxide Semiconductor
MOSFET	Metal Oxide Semiconductor Field Effect Transistor
NBOHC	Non-bridging Oxygen Hole Center
nc-Si	Si Nanocrystals
NOV	Neutral Oxygen Vacancy

PECVD	Plasma Enhanced Chemical Vapor Deposition
PF	Poole-Frenkel
PL	Photoluminescence
PLD	Pulse Laser Deposition
PMT	Photomultiplier Tube
RBM	Random-Bonding Model
RF	Radio Frequency
RMM	Random-Mixture Model
RRAM	Resistance Random Access Memories
RTA	Rapid Thermal Annealing
SMU	Source Measurement Unit
TEM	Transmission Electron Microscopy
ULSI	Ultra Large Scale Integration
XPS	X-ray Photoelectron Spectroscopy

Symbols

A	Surface area of Si nanocrystal
B	Magnetic Field
E	Electric Field
C	Capacitance
C^a	Composition of stoichiometric SiO ₂
C^b	Composition of the silicon cluster

C^m	Average composition of the SiO _x film
C_{dot}	Self capacitance of the quantum dot
D	Diameter of Si nanocrystal
E_c	Self charging energy of Si nanocrystal
E_q	Coulomb charging energy
E_T	Total trap energy
E_g	Band gap of Si nanocrystal
E_g^0	Band gap of bulk silicon
$E(A)$	Energy of neutral atom at the initial ground state
$E(A^+)$	Energy of the charged ion in the final excited state
$E(e^-)$	Kinetic energy of the photoelectron
E_B	Binding energy
V_{Gate}	Gate voltage bias
$h\nu$	X-ray energy
I_{Gate}	Gate current
ϕ_S	Work function of the electron spectrometer
q	Electronic charge
Q	Activation energy
r_1	Radius of the as-deposited silicon cluster
r_2	Radius of the nanocluster after annealing
R	The universal gas constant
S	Average spacing of the Si nanocrystals
T_A	Annealing temperature
ζ	Scaling exponent

ϕ	Surface potential
ϵ_0	Vacuum permittivity
ϵ_{SiO_2}	Dielectric constant of SiO ₂
γ_{cm}	Cluster-matrix interfacial energy
ΔG_v	Volume Gibbs free energy change

Chapter 1 Introduction

Semiconductor flash memory is an indispensable component of modern electronic systems. In the past decades, memory chips with low power consumption and low cost have attracted more and more attention due to the booming market of portable electronic devices such as personal computers, cellular phones, digital cameras, smart-media, networks, automotive system and global positioning systems. The current nonvolatile flash memory structure is based on floating-gate (FG), which is a polycrystalline silicon layer completely surrounded by the gate dielectric of a field effect transistor (FET). When the device operates, charges are injected into or removed from the FG by an applied electric field. The market demand of flash memory technology including high density, low cost and low power consumption results in aggressive scaling of semiconductor memory cells and dramatic increase in the density of memory array. This can be achieved by continuous scaling the tunneling oxide of the devices. However, in the conventional FG nonvolatile flash memory, the reduction in the tunneling oxide thickness has its own critical limitation. The limitation mainly results from the extreme requirements on the tunnel oxide separating the FG and the Si substrate, i.e., the floating gate memory requires a thick tunneling oxide to reduce the defect-related charge loss. This limits the further scaling down of the floating-gate flash memory device.

To overcome the limitation in the conventional FG-based memory design, a new concept of quantum dot flash memory has been proposed by Tiwari et al[1], in which the conventional FG was replaced by a layer of discrete charge trapping nodes (i.e. Si nanocrystals) [2, 3]. In a quantum dot flash memory device, charges are stored in individual nanocrystals, a single

leakage path due to a defect in the tunneling oxide can only discharge the charges stored in the particular dot near the defect. The dots further away from this defect will remain unaffected and the overall memory cell will still remain in a charged state. Hence the tunneling oxide thickness in the quantum dot memory can be reduced. The reduction in thickness enables direct tunneling hence faster write/erase operation compared to conventional flash memory devices (mainly the Fowler-Nordheim tunneling). The thinner tunneling oxide also allows lower voltage operation and less power consumption.

On the other hand, board-to-board and chip-to-chip communications in integrated circuits are mainly achieved by electronic signals with copper interconnects. The maximum speed at which integrated circuits operate depends on how fast electronic signals can be transmitted within the copper interconnects. It is anticipated that microprocessors will clock at more than 12 GHz in a decade and it appears unlikely that copper (Cu) lines would be able to handle these large bandwidth requirement. In Cu, frequency dependent losses above 1 GHz lead to significant signal attenuation and timing errors. Furthermore, the density and length of Cu lines being laid out on a chip is increase in each successive generation of microprocessor technology. The close proximity of Cu lines is leading to signal interference issues that will worsen over the years. There is a growing consensus that the only way to surmount these issues is by replacing copper interconnects with optical interconnection. Communicating with photons instead of electrons will permanently solve many issues such as signal attenuation, signal interference, heat dissipation and provide bandwidths that are presently unforeseeable.

Although technologies for optical communication are available, the challenge lies in integrating them with microelectronic platforms. To a limited extent, so far, the major avenue

toward optical interconnects on a chip has been achieved within the confines of the technology of III-V materials and their hybridization with Si chips. However, III-V semiconductor materials are expensive to manufacture and difficult to integrate with current Si-based CMOS semiconductor industry. If efficient light sources make use of Si are demonstrated, a major hurdle in integrating photonics with microelectronics can be overcome. However, due to its indirect band gap, Si was always considered an inefficient light emitter and was never a serious contender for light emitting applications. In 1991, Canham discovered a strong light emission in Si nanocrystals, introducing a new concept to solve the physical inability of bulk Si to act as efficient light emitter[4, 5]. The strong light emission from Si nanostructure has open a new avenue toward optical interconnects on a chip where all the major components, e.g., light emitters, modulators, waveguides, and photodetectors, are monolithically integrated into the CMOS environment.

1.1 Motivation

As nc-Si has great roles to play in both non-volatile memory devices and Si-compatible light-emitting devices, it is indispensable that the structural, electrical and optoelectronic properties are thoroughly investigated. The most popular Si nanostructure is the nanocomposite films of nc-Si embedded SiO_2 and they can be synthesized by implantation of silicon ions into a SiO_2 matrix followed by thermal induced Ostwald ripening of silicon clusters and their crystallization; by deposition of sub-stoichiometric Si-rich oxide (SiO_x) films using chemical vapor deposition (CVD), sputtering processes or reactive evaporation followed by a thermally induced phase separation and crystallization of the nc-Si. However, so far, there still lack of systemic investigation on the microstructure of the as-deposited amorphous SiO_x films by reactive magnetron sputtering, especially for local bonding

structure in nanoscale, i.e. the bonding configuration, distribution of the silicon and phase separation. A model concerning the local bonding structure would help to interpret of the nc-Si growth mechanism, electrical and light emission properties of the nanocomposite films of nc-Si embedded SiO₂. On the other hand, Si nanocrystals are usually induced by high temperature annealing of the amorphous SiO_x films. During annealing, significant structural changes take place due to the lattice relaxation, defect annihilation and thermal decomposition of the Si suboxides. The structure changes during annealing strongly influence the electrical and optical performance of the nc-Si/SiO₂ nanocomposite films. Therefore, a systematic investigation on the growth mechanism of nc-Si and the chemical structure evolution during annealing is indispensable.

As both the charge storage and the light emission (i.e. electroluminescence) are caused by the charge injection into the nc-Si embedded in the SiO₂ film, a clear understanding of the charge transport behaviors and the charge storage mechanism in the films will help to have a better understanding of its electrical and the light emission properties. To achieve the long retention time of quantum dot memory, the charge storage behavior during charge retention mode should be well understood. The charge trapping and storage mechanism in the nanocomposite films are usually characterized by the electric characterization techniques, i.e., *I-V* and *C-V* measurement. However, these studies by the pure electric characterizations are seldom correlated to the microstructure of the films. On the other hand, electric field-induced resistive switching effect has drawn extensive research due to its potential applications in next generation non-volatile resistance random access memories (RRAM)[6, 7]. Recently, a resistive switching behavior also has been reported in the Si-rich oxide (SiO_x) films synthesized by e-gun evaporation[8]. However, it lacks favorable explanations for the sudden

increase/decrease in current conduction and Ohmic conduction behavior in low resistance state. A systematic investigation on the resistive switching is desired and a model concerning the physical origins of the resistive switching should be developed.

In most of the previous studies of the electroluminescence (EL) from the nanocomposite films of nc-Si embedded SiO₂, high temperature (higher than 1100°C) annealing of the deposited films is usually adopted to induce the crystallization of the excess Si. Amorphous Si nanoclusters, on the other hand, provide an attractive alternative for the development of Si-based light emitting devices, because of low annealing temperature or even no annealing, an easy optoelectronic integration. In this project, we demonstrate strong EL emission in our as-sputtered amorphous SiO_x films embedded with amorphous Si nanoclusters. A detail study concerning the light emission from as-deposited amorphous SiO_x is conducted by correlating the microstructure. It has been reported that charge trapping in nc-Si strongly suppresses carrier injection and transportation in the gate oxide layer [9, 10], thus having a strong impact on luminescence. Therefore, a systematic investigation on of charging/discharging of nc-Si will help elucidate mechanism behind the EL emission performance.

1.2 Objectives

This project deposits magnetron sputtered nanocomposite films of Si nanocrystals embedded in amorphous SiO₂, or (nc-Si/a-SiO₂), and studies the structural, electrical and optoelectronic properties. The main objectives are:

- (1) To elucidate the atomic structure of the as-deposited amorphous SiO_x films synthesized by reactive radio frequency magnetron sputtering techniques, and to study the chemical structure evolution and the growth mechanism of nc-Si;

- (2) To explore the current transport, charge trapping mechanism and the influence of charge trapping on the current transport behavior;
- (3) To investigate the optoelectronic performance of the nanocomposite films and light emission mechanism.

1.3 Scope

To achieve the above mentioned objectives, this project sets out to accomplish studies:

(1) Deposition of the nanocomposite films and structure investigation

Si-rich SiO_x films are deposited on silicon wafer using reactive radio frequency magnetron sputtering of a silicon target in a mixture gas of argon and oxygen. A wide range of silicon concentrations can be achieved by controlling the argon/oxygen flow rate ratio. Selected films undergo post deposition annealing to induce the formation of nc-Si via rapid thermal annealing (RTA). The atomic bonding configurations and surface characteristics are investigated with X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and transmission electron microscopy (TEM). The atomic structure of the as-sputtered amorphous SiO_x is elaborated and a model concerning the atomic structure is proposed. The chemical structure evolution of the SiO_x films under various annealing temperature is studied. The rapid growth mechanism of Si nanocrystal and phase segregation during thermal annealing are discussed. The obtained structural and chemical properties are used for the analysis of electrical and optoelectronic properties.

(2) Electrical properties

Metal oxide semiconductor (MOS) structures based on Al/SiO_x/p-substrate are fabricated. The current transport behaviors of the magnetron sputtered nanocomposite films of nc-Si

embedded SiO₂ are investigated using the current-voltage (*I-V*) and capacitance-voltage (*C-V*) measurements. The current conduction and charge transfer mechanisms are discussed by correlating with the microstructure. The influence of charge trapping on the current transport behaviors is characterized. The charge storage mechanism is studied by examining the core-level shift caused by photoemission-induced charging effect during XPS measurement. An electric field-induced bipolar resistive switching effect in the Si nanocomposite film is observed, and the physical origins of the resistive switching effect are interpreted.

(3) Optoelectronic properties

Light-emitting devices based on the indium tin oxide (ITO)/SiO_x/p-Si substrate are fabricated. Strong visible electroluminescence (EL) is observed from both the as-sputtered amorphous SiO_x films and the films after high temperatures annealing. The light emission mechanisms are studied by correlating with the microstructure and explained based on the current transport behaviors. The influence of nc-Si density and distribution on the light emission properties is explored. The influence of charge trapping/detrapping in the nc-Si on the light emission is investigated.

1.4 Major contributions of the thesis

The major contributions are listed as follows:

A. Structure of nanocomposite films of Si nanocrystals embedded SiO₂

1. Amorphous Si nanoclusters embedded in SiO₂ films are successfully fabricated in the as-sputtered films.

2. A new model concerning the atomic microstructure of the as-sputtered amorphous SiO_x films has been proposed to contain Si cluster core with suboxides shell domains, which themselves embedded in the SiO₂ matrix.
3. The chemical evolution of the SiO_x films during annealing was studied and a two-step decomposition process of Si suboxides was proposed.
4. A non-diffusion nanoclusters growth model responsible for the rapid growth of Si nanoclusters during annealing has been proposed and attributed to the thermal segregation of the Si suboxides.

B. Electrical properties of nanocomposite films of nanocrystals embedded SiO₂

1. The current transport behaviors in the nc-Si embedded SiO₂ nanocomposite films have been investigated, and three conduction mechanisms contributing to the current conduction in the Si nanocomposite film have been identified.
2. The charging effect on the current conduction was investigated and the influence of charging voltage and charging time on the charging effect were discussed.
3. The charge storage mechanism in the Si nanocomposite films was studied by X-ray photoelectron spectroscopy (XPS) technique by correlating with its microstructure.
4. Electric field-induced reversible bipolar resistive switching is observed from the Al/nc-Si:SiO₂/Si/Al device. The resistive switching mechanism is attributed to formation/rupture of conductive filament at the SiO_x/Si substrate interface.

C. Optical properties of nanocomposite films of Si nanocrystal embedded SiO₂

1. Visible EL from the as-sputtered Si-rich oxide films was demonstrated.

2. The EL behaviors have been explained in terms of the formation of tunneling paths of Si nanopartilces and the radiative recombination of the injected electrons and holes via the luminescence centers along the tunneling paths.
3. The influence of the charging/discharging of nc-Si on the EL performance has been studied. Charge trapping results in the reduction in the number of the injected carriers available for the radiative recombination due to the increase in resistance of the tunneling paths formed by the nc-Si.

1.5 Organization

This thesis is organized as follows:

- Chapter 1. Background, motivation, objective, scope and thesis organization are briefed.
- Chapter 2. Literature survey on nanocomposite films of Si nanocrystals embedded SiO₂. Various methods for synthesizing Si nanocrystals embedded SiO₂ nanocomposite films are described; knowledge concerning the microstructure of the as-deposited amorphous SiO_x films is illustrated; growth mechanisms of Si nanocrystals during thermal annealing are elaborated; finally the electrical and optical properties of the films characterized by various techniques are discussed.
- Chapter 3. Experimental setup and methodology are described; various characterization techniques are elaborated.
- Chapter 4. The atomic structure of the as-sputtered amorphous SiO_x films is elucidated; the rapid growth mechanism of the Si nanocrystals during the thermal annealing is discussed; the chemical structure evolution and thermal decomposition of the Si suboxides during the thermal annealing are elaborated.
- Chapter 5. Electrical characterization of the nanocomposite films of nc-Si embedded SiO₂.

The charge transport and charge trapping mechanism are studied; the influence of charge trapping on the current conduction is elaborated; the resistive switching effect is investigated.

Chapter 6. Optoelectronic characterization of the magnetron sputtered SiO_x nanocomposite films. The light emission mechanisms are discussed; the influence of charging trapping on the electroluminescence performance is investigated.

Chapter 7. Conclusions and recommendation.

Chapter 2 Literature Review

Nanocomposite thin films of Si nanocrystals (nc-Si) embedded in amorphous SiO₂ have attracted intense attention due to their potential applications in next generation quantum dot non-volatile memory and Si-based compatible light emission device. In this chapter a detail literature survey is conducted, and the methods for synthesizing Si nanocrystals are briefed. Knowledge concerning the structure of the nanocomposite films of nc-Si embedded SiO₂ is illustrated, including the local bonding configuration of the as-deposited films, the growth mechanism of nc-Si. The electrical and optical properties of the nanocomposite films characterized by various techniques are discussed.

2.1 Synthesis of the nanocomposite films

The promising applications of Si nanocrystals have stimulated great interest in development of various synthesis techniques that are fully compatible with conventional wafer-processing technologies. Many techniques have been demonstrated to successfully synthesize nc-Si. In general, synthesis of nc-Si can be realized by electrochemically etching single-crystalline silicon in hydrofluoric acid, resulting in a sponge-like structure called porous silicon; by implantation of silicon ions into a SiO₂ matrix followed by thermal induced Ostwald ripening of silicon clusters and their crystallization; by deposition of sub-stoichiometric Si-rich oxide (SiO_x) films using chemical vapor deposition (CVD), sputtering processes or reactive evaporation followed by a thermally induced phase separation and crystallization of the nc-Si. In this section, the common techniques used to synthesize nanocomposite films of nc-Si embedded SiO₂ are reviewed. First of all, magnetron sputtering technique which is employed to synthesize the samples in this thesis is discussed. Secondly, other common techniques,

including chemical vapor deposition, ion implantation and evaporation, are briefed. Finally, a comparison of the techniques discussed in this section is also given.

2.1.1 Magnetron sputtering

Sputtering is a physical vapor deposition technique that has been widely used to deposit thin films of various materials. In sputtering, atoms and molecules are removed from a source materials called “target” and deposited as a thin film on a chosen substrate. Removal of atoms from the target is accomplished by energetic ions that are formed by electrically ionizing desired gases. These ions are accelerated towards the target by an electric field, and bombard with the target. When the energy transferred by ions exceeds the binding energy of the target lattice, bonds in the target are broken and atoms are ejected out.

Co-sputtering

The simultaneous deposition of two or more different target materials as a mixture can be achieved by co-sputtering either two or more individual sputtering targets or one primary target attached with small pieces of secondary targets. During the last decade, Si-rich SiO_x films have been widely prepared by radio frequency (RF) magnetron co-sputtering from a SiO_2 glass plate target and a pure Si target[1, 2], or from a SiO_2 glass target on which some Si single-crystal chips were placed[3, 4]. The compositions of the films with different microstructures can be controlled by varying the RF power applied to the targets or by adjusting the number of silicon tips and their position on the SiO_2 .

Reactive sputtering

When a reactive gas is introduced into the vacuum chamber, chemical reaction occurs between the sputtered materials and the reactive gas, resulting in formation of a wide variety of useful compound thin films. The reactive gas may be in the molecular state or can be

activated by the Penning ionization/excitation process of Ar^+ ion to form of more chemically reactive or more easily adsorbed species. Typically, the reactive gases should have a low atomic masses ($\text{N}=14$, $\text{O}=16$) and are thus not effective in sputtering process. Oxide and nitride films are often fabricated using reactive sputtering. Deposition of SiO_x films by using reactive sputtering of a single silicon target in a gas mixture of Ar/O_2 has been demonstrated[5, 6]. Reactive sputtering is highly preferable approach to deposit SiO_x films as its allows high deposition rates and high purity compact films as a result of the kinetic energy input from the glow discharge[7]. Besides, a wide range ($0 < x < 2$) of SiO_x composition can be obtained easily by varying the oxygen partial pressure of gas mixture of Ar/O_2 . In this thesis, reactive magnetron sputtering technique was employed to synthesize all the samples.

2.1.2 Chemical vapor deposition

Chemical vapor deposition (CVD) is a chemical process used to produce high-purity, high-performance solid materials. The process is often used in the semiconductor industry to produce thin films. In a typical CVD process, the substrate is exposed to one or more volatile precursors which react and/or decompose on the substrate surface to produce the desired deposit. Both low pressure chemical vapor deposition (LPCVD)[25-28] and plasma enhanced chemical vapor deposition (PECVD)[29-32] have been frequently used in the fabrication of Si nanocomposite films. Si-rich SiO_x films can be synthesized by the reaction of high-purity precursors of SiH_4 and N_2O . The chemical reaction is oxidation of silane with N_2O [27]:

The Si concentration in this method can be controlled by the $\text{SiH}_4/\text{N}_2\text{O}$ partial pressure ratios. The SiO_x films synthesized by CVD have been shown a good control of the film composition, good adhesion to substrate, low deposition defects, and low compressive stress[30].

2.1.3 Ion implantation

Ion implantation is a process by which ions are accelerated to a target at energies high enough to bury them below the target's surface. High-energy ions, typically 10~200 KeV, are produced in an accelerator and directed as a beam onto the surface of the target. The ions impinge on the substrate with kinetic energies 4~5 orders of magnitude greater than the binding energy of the solid target, penetrating the surface of substrate films. The implanted ions can eventually lose their energy as a result of the collision with the target atoms. The stopping of ions is a controllable process, and the distance of ion stopping follows a Gaussian distribution. The ion implantation is usually carried out in a vacuum chamber at very low pressure (10^{-2} ~ 10^{-3} Pa) with an implant dose of 10^{15} ~ 10^{16} cm⁻². Si nanocrystals embedded SiO₂ films have been synthesized by ion implantation combined with a subsequent thermal annealing process[29, 33-36]. In a typical fabrication process, Si ions are implanted into the thermally grown SiO₂ film followed by a high-temperature annealing in N₂ or Ar ambient to induce the precipitation of nc-Si in SiO₂. The key advantage of such techniques is its precisely and reproducibly controlling the density and depth distribution of nc-Si in SiO₂ by the implant energy and dose.

2.1.4 Evaporation

Evaporation is physical vapor deposition method of thin film deposition. In evaporation the substrate is placed inside a vacuum chamber, in which the source material is evaporated. The source material is then heated to the point where it starts to boil and evaporate. The vacuum allows vapor particles to travel directly to the target object (substrate), where they condense back to a solid state. This principle is the same for all evaporation technologies, only the

method used to the heat (evaporate) the source material differs. There are two popular evaporation technologies, which are electron beam evaporation and resistive evaporation, each refereeing to the heating method. In electron beam evaporation, a high kinetic energy beam of electrons is directed at the material for evaporation. Up impact, the high kinetic energy is converted into thermal energy, heating up and evaporating the target material. In resistive evaporation, a tungsten boat, containing the source material, is heated electrically with a high current to make the material evaporate. In evaporation, SiO_x can be formed either by reactive evaporation of Si powder in oxygen atmosphere in vacuum chamber. The composition of the deposited films is controlled by the oxygen partial pressure.

2.1.5 A comparison of various synthesis techniques

There are still many other techniques that have been used to synthesize nanocomposite films of Si nanocrystals embedded SiO₂, such as pulse laser deposition (PLD)[37], Molecular beam epitaxy (MBE)[38]. Each of the fabrication techniques has its own advantages and disadvantages. For example, the ion implantation guarantees good reproducibility and masking flexibility, good extendibility to larger wafers and good process control for a mass production. But nc-Si synthesized by ion implantation are usually confined in a narrow layer in the SiO₂ with a large nanocrystal size distribution. Samples fabricated by ion implantation are often suffer serious Si/SiO₂ interface damage, high density of oxide defects and poor nanocrystal depth and shape control, which strongly degraded the performance of the Si nanocrystals devices. Si nanocrystals fabricated by CVD approaches show a good uniformity, low impurity and high density. However, individual nanocrystals can not be fabricated with monolayer precision, and the resulting nc-Si have a wide range of size distribution. A size fluctuation larger than 40% to 60% have been reported due to the nucleation dynamics[39].

Evaporation deposition entitles a fast deposition rate, but suffering from poor uniformity and low density. As compared to other film deposition techniques, the magnetron sputtering is preferred in terms of high deposition rate, high purity films, extremely high adhesion of films, and excellent uniformity on large-area substrates. In addition, the synthesis of nc-Si using magnetron sputtering technique is fully compatible to the mainstream CMOS technology, thus it can be easily integrated into the existing process follow. In this project, magnetron sputtering technique is employed for all the fabrications.

2.2 Structure of the nanocomposite films

The microstructures of nanocomposite films have been drawn intense attention due to its critical role in determining the electrical and optical properties of the devices. In this section, the microstructure and the local bonding configurations of the as-deposited amorphous SiO_x films are discussed. The growth mechanism of nc-Si during the post deposition annealing is detailed.

2.2.1 Bonding configuration of the as-deposited SiO_x films

As for the bonding configuration of the as-deposited SiO_x films, there are mainly two models proposed based on both theoretical calculation and experimental observation. The random-bonding model (RBM) was first proposed by Philipp [8] in which silicon and silicon-oxygen bonds are considered statistically and randomly distributed throughout a continuous random network. Temkin [9] et al. proposed a random-mixture model (RMM) based on theoretical calculation. The RMM model assumes small domains in which either silicon is bonded only to silicon or, only to oxygen, corresponding to a two-phase mixture.

Random-bonding model

The random-bonding model assumes that each Si atoms is tetrahedrally coordinated by n oxygen and (4-n) silicon atoms, with the probability of n (0, 1, 2, 3, or 4) being determined statistically based on the proportion of Si and O atoms present, that is, based on x . There is a statistical distribution of the five basic bonding units, $\text{Si}-(\text{Si}_{4-n}\text{O}_n)$, $n= 0, 1 \dots 4$. In these tetrahedral units, a Si atom is bonded to four other atoms of either Si or O, and the O atoms are each bonded to two Si atoms of different tetrahedral[8]. The five types bonding tetrahedral with (4-n) Si-Si bonds and n Si-O-Si bonds are schematically shown in **Figure 2.1** The relationship between the overall concentration x and the concentrations of the individual units in the RBM have been determined by Philipp [8] and also Temkin [9]. The individual concentrations can be derived from considerations based on the statistical replacement of Si-Si bonds in amorphous Si by Si-O-Si bonds while maintaining the fourfold coordination of Si and the twofold coordination of O. The detail concentration of the components Si-O_n ($n=0, 1, \dots, 4$) are given by [10]

$$I_n(x) = \frac{4!}{(4-n)!n!} \left(\frac{x}{2}\right)^n \left(1 - \frac{x}{2}\right)^{4-n} \quad (2.2)$$

Figure 2.1 The five possible tetrahedrons of Si-Si and Si-O-Si bonds in SiO_x . [11]

Random-mixture model

In Random-mixture model, the amorphous SiO_x is expected to be composed of randomly arranged clusters of Si and SiO₂ of varying sizes. In this model, the concentrations of the two species have simple linear relationships to the overall concentration x , for example the concentrations of Si and SiO₂ are simply:

$$I_0 = 1 - \frac{x}{2} \quad \text{and} \quad I_4 = \frac{x}{2} \quad (2.3)$$

However, physical and chemical properties of the material are quite different from the properties of a macroscopic mixture of phase, and therefore the size of the separated regions was assumed to be ~ 10 Å in reference [9]. Only a thin boundary layer between the domains of silicon and SiO₂ was postulated. Dupree *et al.* [12] successfully performed magic-angle spinning investigations on silicon monoxide and estimated that the domains are even larger than 20 Å. Very recently, on the basis of transmission electron microscopy, Klaus *et al.* used a series of electron spectroscopic images to investigate the configuration of the amorphous silicon monoxide powders as shown in Figure 2.2 [13]. The resulting Si (oxygen) map shown in Figure 2.2 clearly exhibits regions where silicon (oxygen) is enriched relative to the regions with lower silicon (oxygen) content. The regions which are silicon (oxygen)-rich appear well separated and are between 3 and 4 nm in diameter. In intensity profiles map of the silicon (or oxygen), the variation in chemical composition and the size of the separated regions is displayed. The distribution maps of the elements yield direct proof for the existence of a chemically inhomogeneous microstructure on the nanometer scale. There are oxygen-rich regions representing the SiO₂ phase and others containing elemental silicon.

Figure 2.2 (a) Distribution map of silicon in silicon monoxide, brightness correlates with Si content and profile of silicon distribution. (b) Distribution map of oxygen in silicon monoxide, brightness correlates with oxygen content and profile of oxygen distribution [13]

Other models

RBM and RMM are the ideal limits. Although the structural, electrical and optical properties of SiO_x materials have been extensively discussed within the frame of the RBM and RMM, some controversy has arisen about their general applicability. This controversy stems from experimental evidences showing that in SiO_x thin films with a given O/Si ratio, different distributions of oxidation states can be found according to the method of preparation. SiO_x thin films deposited by evaporation of silicon monoxide do not follow the distribution of Siⁿ⁺ states predicted by the RBM[14]. The experimental compositions of SiO_x films prepared with CVD or co-sputtering deposition techniques are intermediate between those of RMM and RBM[15]. Thus more realistic models are the nanometric scaled mixture model with different clusters sizes or the mixed phase model with different bond accumulation with one third pure Si. Also a cluster mixture model has been proposed which reported that the microstructure of SiO_x contains nanoscale amorphous clusters of Si and SiO₂, which themselves embedded in

the a-SiO_x matrix and separated by a thin layer of Si suboxides[16].

2.2.2 Growth mechanism of Si nanocrystals

Si nanocrystals usually form during high temperature annealing. The formation of nc-Si was thought to include nucleation, growth and ripening process. Two main models have been proposed for the growth mechanisms: the diffusion-controlled growth and the phase segregation growth. The diffusion-controlled growth theory believes that the nc-Si are grown by the classical nucleation, thermal diffusion of the excess Si atoms and ripen in the amorphous SiO_x matrix[17, 18]; while the phase segregation growth theory considers the rapid growth of nc-Si as a result of the segregation of Si suboxides[19].

Diffusion-controlled growth mechanism

The diffusion-controlled growth mechanism was proposed based on the observations that the average size of the nc-Si is dictated by the initial concentration of the Si in the SiO_x for a given annealing time and temperature: the higher the Si concentration, the larger the average size of the resulted nc-Si [17, 18]. In general, the nc-Si size decreases with increasing oxygen concentration. This implies that the nc-Si are formed in consumption of the excess Si due to the diffusion of the element Si atoms toward the nucleation center.

The diffusion-controlled growth mechanism of the nc-Si was detailed by Nesbit based on TEM studies of the diffusion behaviors of SiO_x films synthesized by CVD under various annealing temperature[20]. By assuming a spherical silicon cluster radius r , the silicon cluster growth rate in the SiO_x matrix at a given annealing temperature T_A can be expressed as

$$\left(\frac{dr}{dt}\right)_{r_i} = \frac{D}{C^b - C^a} \left(\frac{\partial C}{\partial r}\right)_{r_i} \quad (2.4)$$

Where r_i is the initial Si cluster radius, D is the diffusion coefficient of silicon in SiO_2 , C^a is the composition of stoichiometric SiO_2 , which is the assumed composition of the oxide matrix at the silicon cluster/oxide interface, and C^b is the composition of the silicon cluster, which is assumed to be 100% silicon. The composition in the oxide matrix near the silicon cluster, C , is assumed to be a linear function of distance into the matrix from the silicon cluster surface.

The $(\partial C / \partial r)$ can be approximated by the following expression:

$$\left(\frac{\partial C}{\partial r}\right)_{r_i} = \frac{(C^m - C^a)}{r_i} \quad (2.5)$$

Where, C^m is the average composition of the entire film. By integrating the above equations with respect to r and time t , the silicon diffusion coefficient as a function of temperature, T can be expressed:

$$D(T) = \frac{r_2^2 - r_1^2}{2t} \left(\frac{C^m - C^a}{C^b - C^a}\right) \quad (2.6)$$

Where r_1 is the radius of the as-deposited silicon cluster, and r_2 is the radius after annealing for a time t at temperature T . The calculated values of the diffusion coefficients are shown in the third column of Table 2.1. It is shown that the diffusion coefficient of Si in the SiO_x films is independent of composition, with an average of $1.1 \times 10^{-16} \text{ cm}^2/\text{s}$ at 1100°C . The diffusion coefficient values of Si in the SiO_x films at different temperatures are shown in the forth column in Table 2.2. With linear regression analysis of the data in Table 2.2, the diffusion coefficient can be expressed as

$$D(T) = D_0 \exp(-Q / RT) \quad (2.7)$$

Where Q is the activation energy and R is the universal gas constant. The activation energy is 180 kJ/mole or 1.9 eV/atom , and D_0 is equal to $1.2 \times 10^{-9} \text{ cm}^2/\text{s}$. The diffusion coefficient of Si

at the low temperatures (700 °C and 800 °C) is quite low, thus the Si nanocluster size is still very small after annealing for up to 72 h at 700 °C or for 18 h at 800 °C as shown in **Table 2.2**. Besides, Harstein *et al.* indicated that temperatures are required to be >1150 °C for complete crystallization of the excess silicon [20].

Table 2.1 Silicon cluster diameter and calculated diffusion coefficients as a function of composition. Annealing conditions: 1100 °C, 15 min in nitrogen [20].

O/Si ratio	Silicon cluster Diameter (nm)	Calculated diffusion Coefficient ($10^{-18}\text{cm}^2/\text{s}$)
1.4	2.5	110
1.3	4.0	130
0.95	4.5	100
0.72	5.0	92

Table 2.2 Si cluster diameter and calculated diffusion coefficients as a function of annealing time and temperature for O/Si = 0.82 [20]

Annealing conditions		Si clusters	Calculated diffusion Coefficient
Temperature (°C)	Time (h)	Diameter (nm)	($10^{-18}\text{cm}^2/\text{s}$)
1060	1.0	9.0	86
950	2.7	5.5	15
800	18	4.5	1.1
700	72	3.5	0.18

Segregation growth mechanism

The segregation mechanism of Si oxide is proposed based on the observation of the rapid growth of nc-Si during pulse annealing or rapid thermal annealing. Kachurin *et al.* [19] studied the formation of nc-Si in the ion-implanted SiO_x films by pulse annealing. The implanted SiO_x samples were subjected to either rapid thermal annealing at 900-1200°C for 1 s or flash-lamp annealing at 1050-1350°C for 20 ms. The formation of nc-Si could not be explained by the diffusion-limited growth or solid-phase crystallization of amorphous Si phase inclusions due to the short annealing time and the low diffusivity of Si in a-SiO_x matrix.

They proposed a new model considering the Si nanocrystal formation through segregation of

Si atoms from SiO_x, rapid percolation-like formation of Si chains or fractals and the final transformation to Si phase inclusions and nanocrystals. The a-SiO_x system is unstable and tends to segregate into Si and SiO₂ even at low temperatures[21]:

The segregation proceeds as a percolation via “weak points” in the form of “silicon cracks” or “silicon breakdowns” in a-SiO₂. It does not need long-range diffusion of Si atoms and the process could be fast.

2.2.3 Interface structure between Si nanocrystals and a-SiO₂

During thermal annealing, nc-Si are formed and embedded in the SiO₂ matrix with a thin Si suboxides interfacial layer between them. The Si suboxide transition regions occur at nc-Si/SiO₂ interfaces as a natural consequence of the oxidation processes. However, it is shown that there are high densities of various defects at the interface regions, such as the weak oxygen bond (O-O)[22], the neutral oxygen vacancy (O₃≡Si-Si≡O₃, where ≡ represents the bonds to three oxygen atoms)[22], E_δ' center (O₃≡Si•+Si≡O₃, where • represents an unpaired electron and + is an trapped hole)[23] and the non-bridging oxygen hole center (≡Si-O•)[24]. These oxygen-related defects may serve as radiative or nonradiative recombination centers for excitations, thus responsible for optical properties of the structure. Also when electron devices scaling down to certain level, quantum effect become dominant, and carriers transport by tunneling between adjacent nc-Si. The local atomic structure at the nc-Si/SiO₂ interfaces, including Si suboxides bonding arrangement also play an important role in the carriers transport.

At an ideal Si-SiO₂ interface with single Si dangling bond termination, the bonding arrangements can be characterized as Si-Si₄ in the Si, where the subscript indicates the number of Si atoms bonded to the reference Si atoms, Si-O₄ in the oxide, and Si-Si₃O at the metallurgical boundary as shown in **Figure 2.3**[25, 26]. However, most of the interface between nc-Si and SiO₂ matrix are not perfectly, there are additional Si suboxide bonding arrangements, which form a Si suboxide interface transition layer[27, 28]. It is shown that the structures of the interfacial regions are strongly depending on the synthesis techniques, annealing temperature and annealing time. Si nanocomposite films fabricated by CVD methods are usually have a thin and abrupt interface[29], while samples by sputtering[30, 31], ion implantation[32] are usually results in a thick and rough interface. On the other hand, high temperature and long time annealing lead to more Si suboxides decompose into Si and SiO₂, resulting in an abrupt interfacial layer[33].

Figure 2.3 Schematic representation of nc-Si/SiO₂ interface: (a) abrupt interface and (b) rough interface with excess suboxides bonding in an interfacial transition region[34].

2.3 Electrical properties

While the investigation of structural properties of SiO_2 films containing nc-Si with various techniques, the electrical properties of such structures are increasing interest with applications of nano-memory devices and single electron devices utilizing nanocrystals as charge storage elements[35]. In this section, a comparison between the conventional FG memory and quantum dot memory has been conducted. The charge storage mechanisms in the nanocomposite films of nc-Si embedded SiO_2 are discussed. An electric field-induced resistive switching effect is introduced and elaborated.

2.3.1 Conventional floating-gate memory structure

A conventional floating gate (FG) non-volatile memory cell consisting of a source, drain, channel and floating gate is schematically illustrated in Figure 2.4. The floating gate is a continuous poly-Si layer that acts as the storage layer in the form of charge. The stored charge is isolated from the channel by an insulating a- SiO_2 layer that is make thick enough to prevent charge leakage from the floating gate. The cell is programmed during a “write’ operation in which electrons are drawn from the source and injected across the channel oxide into the poly-Si floating gate, and erased by pushing back the electrons to the source. The voltage required for the programming as well as the programming speed are strongly depend on the thickness of the channel oxide, i.e., thinner tunneling oxide enables lower operation voltage and faster speed.

Figure 2.4 Schematic cross-section of a floating gate memory device, in which the tunneling oxide must be thicker than 8 nm to maintain 10 years of retention time [36]

Rapid advance in silicon circuit design and fabrication results in aggressive scaling of semiconductor memory cells and dramatic increase in the density of memory array. According to the 2008 International Technology Roadmap for Semiconductor (ITRS), the FG-based flash technology has reached the 40 nm technology and will become as small as 10 nm by 2020 and the speed will increase more than several times. Although scaling down of conventional nonvolatile flash memory can be achieved by continuously thinning the control and tunneling oxide [37], it has its own limited potential. The limitation mainly results from the extreme requirements on the tunnel oxide separating the FG and the Si substrate. When the thickness of the tunnel oxide reduces to a certain levels, defects in the tunneling oxide can lead to a huge leakage current, which greatly reduces the retention time. The presence of a single such path will drain the entire charge stored in the continuous poly-Si, leading to the failure of the device. Therefore, the floating gate memory requires a thick tunneling oxide to reduce the defect-related charge loss. This limits the further scaling down of the floating-gate flash memory device. Currently, commercial flash memory devices use a tunneling oxide thicker than 8 nm to guarantee long retention time, which results in high programming voltage and slow operation speed [38].

2.3.2 Nanocrystal-based non-volatile memory devices

The utilization of discrete-trap storage nodes in flash memory devices offers a solution for the continuous scaling of existing flash memory technology. The basic idea of the “discrete traps” mechanism is to replace the continuous floating gate in nonvolatile memory devices by a layer of discrete charge trapping centers [39, 40], such as the quantum dots, as shown in Figure 2.5. In a quantum dot flash memory device, charges are stored in individual nanocrystals, a single leakage path due to a defect in the tunneling oxide can only discharge the charges stored in the particular dot near the defect. Nanocrystals further away from this defect will remain unaffected and the overall memory cell will still remain in a charged state. Hence the tunneling oxide thickness in the quantum dot memory can be reduced. The reduction in thickness enables direct tunneling hence faster program/erase operation compared to conventional flash memory devices (mainly the Fowler-Nordheim tunneling). The thinner tunneling oxide also allows lower voltage operation and less power consumption.

Figure 2.5 Schematic of a quantum dot nonvolatile memory device.

2.3.3 Coulomb blockade effect in quantum dots

In quantum dot nanostructures, when the mean-free-path of electrons exceeds the dimensions of the device structure, quantum natures may dictate the physical properties of devices. In

quantum devices, charge transport properties are governed by tunneling. Due to the discrete tunneling of electrical charge, current flow through a quantum dot is a series of events in which exactly one electron passes through the quantum dot. The quantum dot is charged with one elementary charge by the tunneling electron, causing a self charging energy E_c given by [41]

$$E_c = \frac{e^2}{2C_{dot}} \quad (2.9)$$

where e is the elementary charge of 1.6×10^{-19} Coulomb, and C_{dot} is the self capacitance of the quantum dot given by

$$C_{dot} = 4\pi\epsilon_0\epsilon_{SiO_2}r \quad (2.10)$$

where r is the radius of nc-Si, ϵ_0 is the vacuum permittivity and ϵ_{SiO_2} is the dielectric constant of SiO₂. The self charging energy of the quantum dot causes a voltage buildup, $U=e/C_{dot}$, which prevents tunneling-in of a second electron. It needs to overcome the electric field induced by the previous injected electron to inject another electron into the quantum dot. Thus the current-voltage (I - V) characteristics of the quantum dot embedded dielectric films usually shown a staircase behavior. Typical I - V characteristic of the Si nanocomposite films showing Coulomb staircases is shown in Figure 2.6 [42]. Curve (c) is taken from a pure SiO₂ film. The curve shows an exponential dependence of the current on the bias voltage. However, remarkable features can be observed from the nc-Si embedded SiO₂ films' curve (a), measured at 30 K and curve (b), measured at 300 K, exhibiting threshold voltages and staircase on current.

Figure 2.6 Coulomb staircases in current-voltage characteristics (a) 4.7 nm nc-Si in diameter at 30 K, (b) 4.5 nm nc-Si at 300 K, and (c) 1.2 nm tunneling oxide without nc-Si [42].

2.3.4 Charge trapping mechanism

For the application of nonvolatile memory device, a long charge retention time is very critical and necessary. To achieve the long retention time of quantum dot memory, the charge storage behavior during charge retention mode should be well understood. There are mainly three charge trapping mechanism proposed, including charge storage at the conduction band of the nc-Si, the deep level defects in the nc-Si and the interfacial traps between the nc-Si and the SiO₂ matrix[43, 44].

Conduction band of the nc-Si

The observation of quantum confinement energy in nc-Si from high-frequency conductance characteristics[45] and the Coulomb blockade charging in the conductance-voltage measurements suggest that the charges are stored in the nc-Si[46, 47]. However, many researchers argued that the charges can not be trapped in the conduction band of the nc-Si

based on the following reasons[43, 48]. Firstly, the conduction band edge inside the nanocrystal is higher than that of substrate because of the band gap expansion due to the quantum confinement effect, which allows electrons to across the channel and tunnel back to the substrate very easily. Thus, long time retention can not be realized, which is inconsistent with the observed long retention time of the nc-Si based memory[44, 48]. Secondly, the experimental retention time measurement shows heavy temperature dependence. If the electrons are stored in the nanocrystal conduction band, the retention time should only show mild change between room temperature less than 100°C[44, 48].

Deep trap levels

A possible mechanism was proposed that an electron injected to the nanocrystal might fall into a deep trapping centers [44]. Such deep level traps have been reported to play a critical role in silicon nitride films used in metal-nitride-oxide-silicon (MNOS) memory structure, where excess charges are stored in deep traps at or near the nitride-oxide interface[49-51]. In the tunneling process under a positive voltage, the charges injected into a nc-Si will first fill the empty states, where the trap level is deeper, and then fill the states where the level is shallower. The number of trapped electron is closely related to the number of deep trapping centers. Thus a larger flat band shift is generally observed in the samples with more deep traps.

Interfacial defects

Besides the nc-Si, the interfacial defects adjacent to the amorphous SiO_x also are considered as the charge trapping sites. Actually, there are high density of interface defects that can act as effective charge trap centers because of the large surface-to-volume ratios, high surface

roughness and compositional disorders of nanocrystals. Such charging mechanism has been confirmed by Shi *et al.* [44, 48] who studied the effect of traps density on the long-term charge storage characteristics in the MOS memory based on nc-Si. To produce different defects and trap density, after high temperature annealing to induce the nc-Si, they annealed their samples in H_2 ambient at 430 °C and in vacuum at 700 °C. The annealing in H_2 ambient could effectively decrease interface traps by H-passivation, and the annealing in vacuum resulted in high density of interface traps. The C - V hysteresis of various annealed MOS diodes was shown in Figure 2.7[44]. The flat band voltage shift is attributed to the injection of holes or electrons. The maximum shift in the C - V measurement is observed in the vacuum annealed sample having the highest trap density, the minimum shift is observed in the H_2 annealed diode having the lowest trap density, and the middle is in the as-deposited sample. This indicates that more charges are stored in the vacuum annealed nanocrystals than in the H_2 annealed ones, indicating interface defects play an important role in charging trapping.

Figure 2.7 C - V hysteresis loops in various annealed MOS diodes [44].

2.3.5 Resistive switching memory

Resistive switching effect induced by electric field has drawn extensive research due to its potential applications in resistance random access memories (RRAM)[52, 53]. Resistive switching effect is characterized by an extreme change of resistance between the high resistance state (HRS) and the low resistance state (LRS) for logic signal (off and on states) in the current-voltage characteristics of the metal-insulator-metal structure as shown in **Figure 2.8**. Many metallic binary oxides such as TiO_2 [53-55], NiO [56, 57], ZnO [58], CuO [59] and perovskite oxides such as SrTiO_3 [60], SrZrO_3 [61] and PrCaMnO [62] have been demonstrated such resistive switching properties. Although the switching mechanism is still an open question, various switching models such as conducting filament model[53], Schottky barrier model[54] and trap-controlled space-charge-limited current (SCLC)[60, 63] have been proposed.

Figure 2.8 Bipolar resistive switching characteristics of the TiN/ZnO/Pt devices[64].

Although the Si nanocomposite films of nc-Si embedded SiO_2 has been demonstrated promising for the quantum dot flash memory applications. However, resistive switching

memory effect is seldom observed from such Si nanostructure. Until recently, Tsai et al reported a resistive switching behavior in their Si-rich oxide films (SiO_x) as shown in **Figure 2.9** [65]. The conduction mechanisms were dominated by Schottky emission or Poole-Frenkel emission in their films, and the resistive switching is result from the movement of carrier in the SiO_x band gap associating with the energy band twist[65]. The change in resistive is over 10^2 times and the retention time attains to 2×10^3 s. Although there is still lack of favorable explanations for the sudden increase/decrease in the current conduction, their discovery shows the promising to utilize Si, the most favorable material for modern microelectronics, as the potential candidature for the RRAM, thus allowing us to fabricate the devices with the mature Si-based mainstream complimentary metal-oxide-semiconductor (CMOS) technology at a reasonable cost. In this study, a reproducible bipolar resistive switching phenomenon from an $\text{Al}/\text{nc-Si}:\text{SiO}_2/\text{Si}$ MOS structure is demonstrated with a colossal resistive switching ratio of $\sim 10^5$ times. The resistive switching is explained by a combined model of conductive filament of oxygen vacancies and electronic barrier at the SiO_x/Si substrate interfaces.

Figure 2.9 resistive switching behavior of the SiO_x films[65].

2.4 Light emission from the Si nanocomposite films

As electronic device dimensions increasingly become smaller and smaller, the traditional electrical interconnects that were used for chip-to-chip communication becomes increasingly impractical due to the heat dissipation of the metal wires which threatens the reliability of both the device and the system. Fortunately, optical interconnects would probably provide us with a promising alternative strategy for overcoming these challenges. Since chip-to-chip communication via optical interconnects requires an on-chip emitter and detector, an important challenge on the materials and the integration of photonic devices into the main stream Si process has triggered a new research subject, i.e., Si photonics. However, unfortunately, because of the indirect-gap nature, bulk Si is a poor light emitter due to the low probability of radiative transition. Optoelectronic integration has only been achieved within the confinement of the technology of III-V materials and their hybridization with Si chips. It can be claimed that the inability of Si to emit light seriously compromises our ability to get true large-scale optoelectronic integration at reasonable cost.

In this section, the band structure of bulk Si are introduced, and the physical inability of Si as the light emitter are discussed. The methods to set the Si as efficient light emitter are introduced, and various physical origins of the light emission from the nanocomposite films of Si nanocrystals embedded SiO₂ films are elucidated.

2.4.1 Band structure of Si

The band structure of a material is intimately dependent on several factors, including crystal structure, lattice constant, chemical species, bonding and bond lengths, electronegativity,

stiffness, and elasticity[66]. Conventionally, the band structure of a semiconductor is represented by the dispersion relation $E(K)$, where E is the energy of an electron (or hole) at the band edge with a wave vector K in the first Brillouin Zone (BZ). Crystal symmetry requires that $E(k)$ have extrema at the zone center and the zone boundary. However, these are not the only points at which extrema can occur. In the case of the essentially covalent group IV elements and compounds (C, SiC, Si and Ge, for example), additional extrema occur in the lowest conduction band away from the zone center. The band structure of silicon is schematically shown in Figure 2.10[67], where the energy is plotted as a function of the wavevector k , along the main crystallographic directions in the crystal. As can be observed, the minimum energy in the conduction band is shifted by a k -vector relative to the valence band. Since the energy gap is the difference between the valence band at $k = 0$ and the lowest point in the conduction band. When this lowest point occurs at $k = 0$, the semiconductor has a direct gap because a transition can occur at the zone center with both the initial and final states having the same momentum vector $k = 0$. When the lowest point of conduction does not occur at $k = 0$, the semiconductor is an indirect gap material. Most of the semiconductors are direct band gap. However, the bulk silicon is an indirect band gap semiconductor, with a band gap of 1.12 eV at room temperature.

Figure 2.10 Energy band diagram of Silicon[67]

In a direct semiconductor, radiative transitions can occur quite easily as an electron excited into the conduction band minimum at $k = 0$ can spontaneously decay into the valence band state also at $k = 0$, yielding a photon of energy equal to the bandgap (in semiconductor parlance, this is referred to as an electron hole radiative recombination) as shown in Figure 2.11. The light emission process in a direct band gap material is a first-order process with a much shorter radiative lifetime (nanoseconds) and a much higher luminescence efficiency. In an indirect semiconductor, however, a change of the electron momentum or wave vector is also needed. This can be accomplished by the transfer of momentum to the crystal through the creation of a phonon with a wave vector equal to that of the initial conduction-band state. This three-body event (electron, hole, and phonon) is significantly less likely to occur than a direct electron hole recombination. A phonon of the right k -vector and energy must participate, the phonon availability being governed in part by the phonon dispersion relation. Thus the light emission from an indirect material need quite a long time (microseconds) with a much lower luminescence efficiency. This simply explains the inability

of indirect gap semiconductors to emit light efficiently.

Figure 2.11 Schematic band diagrams for the photoluminescence process in a direct band gap (left) material and an indirect band gap material (right).

2.4.2 Approach for Si light emission

Much effort has been devoted towards the research of different approaches that are able to solve the physical inability of Si to act as a light emitter. Luminescence is a result of significant overlap in the electron and hole wave functions, thus engineering solutions seeks to increase this overlap and increase luminescence efficiency.

Impurity-mediated luminescence

Impurity that has energy level in the gap of the semiconductor is used as an intermediary state through which the electron can recombine with the hole. Electron-hole pairs injected either electronically or optically can recombine through impurity centers with enhanced the recombination rates compared with those of the pure Si crystal, in which recombination is intrinsically very slow. The enhancement can be considered as the consequence of the relaxed

k -selection (momentum conservation) requirement that is caused by the localization of the electron hole pairs near impurity center, such as the symmetry of the impurity state with respect to that of the wave functions of the electrons and holes, the degree of localization, and so on. The energy from the recombination of an electron-hole pair can be released by the generation of a photon, a phonon or phonons, or through a variety of other channels.

Nanocomposite films of quantum wires and dots in dielectric matrix

Quantum confinement in thin (few nanometers) wires or dots provides another possible approach to the engineering of a direct transition. As one makes the physical structure of the semiconductor into a fine quantum dot, the values of the allowed energy levels increase. As a result, the bandgap of a semiconductor that is a quantum wire or dot increase. Qualitatively, the confinement of the carriers in real space causes their wave functions to spread out in momentum space, which increases the likelihood of strongly radiative transitions. In addition, scattering at the wire or dot boundaries can supply the needed momentum more readily in a confined structure. The quantum wire approach of Si received a sharp boost from the initial discovery that porous Si with very fine filaments, a few nanometers across, can luminescence intensely in the visible at room temperature. This remarkable discovery was made by Canham at the Royal Signal and Radar Establishment (UK)[68]. Porous Si is self fabricated by an anodic dissolution process that is usually done in a HF based electrolyte. The principal feature of porous Si is extremely fine structures, either wires or dots, which are small enough to exhibit some quantum confinement effects. It has been shown that the luminescence from porous Si can be tuned in a wide range and relatively high quantum efficiencies could be obtained.

The main problem of these high porosity layers is to present unstable photoluminescence characteristics. Because of their very large specific surface, porous silicon films are highly chemically reactive and they oxidize in air. Another problem of porous silicon is its fragile nature and incompatibility with conventional IC technology. An alternative promising way to set silicon as a light emitter is to embed silicon nanoparticles into the dielectric films. Among these, nc-Si dispersed in a SiO₂ matrix has recently attracted great interest because their band gap is enlarged with respect to bulk silicon due to quantum confinement effects. This provides a possible way to relax the momentum conservation requirement and allows Group IV semiconductors with indirect bandgap to possess of efficient light emission properties[69, 70].

2.4.3 Photoluminescence of Si nanocomposite films

Photoluminescence (PL) is a luminescence process in which a semiconductor absorbs photons and then re-radiates photons. In general, PL is excited by illumination of the semiconductor with light which has a photon energy above the band gap energy. Photo-excitation causes electrons in the initial ground state (in the valence band) to cross the band gap, moving to into permissible excited states (in the conduction band). When these electrons return to their ground states, the excess energy is released in the form of radiative recombination. PL then occurs for wavelengths around the bandgap wavelength. Energy of the emitted light depends on the energy level between the two electrons states, the ground states and the excited state. The quantity of the emitted light is related to the relative contribution of the radiative process. **Figure 2.12** shows the typical PL spectra from the nanocomposite films of nc-Si embedded SiO₂.

Figure 2.12 Size-dependent PL spectra from nc-Si embedded in SiO₂[71]

2.4.4 Electroluminescence of Si nanocomposite films

EL is an optical phenomenon and electrical phenomenon where a material emits light in response to an electric current passed through it, or to a strong electric field. Si nanocomposite films of nc-Si embedded SiO₂ shows intense electroluminescence (EL) under biases[72, 73]. Not long after the discovery of visible photoluminescence from porous Si by Canham, in 1992, Koshida et al. reported the observation of electroluminescence (EL) from porous Si[74]. Thereafter, EL has been reported from various nc-Si/SiO₂ system[75, 76]. The observation of electrical field-pumped light emission from nc-Si based light emitter represents a crucial step towards the application of Si nanostructure in optoelectronics. In order to study the EL properties, the nanocomposite films should be incorporated into the light emitting devices. One approach is to use the structure of the metal-oxide-semiconductor light-emitting devices (MOSLED) in which the gate oxide is embedded with nc-Si, and the “metal gate” is made of semitransparent and conductive materials such as indium tin oxide (ITO), highly doped polycrystalline Si or Au. **Figure 2.13** shows a typical MOSLED structure with the Si

nanocomposite films in the gate oxide. The bias voltage is applied to the “metal gate”, and the radiative recombination of the electron-hole pairs lead to intense light emission. **Figure 2.14** shows the typical EL spectra under various gate voltages. The inset shows the injected current density and EL intensity as a function of applied voltage. It can be seen that the EL intensity is proportional to the injected current. In fact, it has been reported that the EL property is mainly determined by the numbers of the injected electrons and holes available for radiative recombination, and the key parameter in determining the EL properties is the current density passing through the device[76].

Figure 2.13 Cross-sectional scheme of the devices for EL measurement[77]

Figure 2.14 Typical EL spectra under different gate voltages. The inset shows the injected current density and the integrated EL intensity as a function of the gate voltage[78].

2.4.5 Light emission mechanism from nanocomposite films

Although efficient room-temperature light emission from nanocomposite thin film of SiO_2 embedded with nc-Si has been reported by many research groups. The mechanism of the light emission from such nanostructures is still under debate. A few models have been put forth to elucidate the luminescent mechanism. Firstly, a simple quantum confinement model proposes that a quantum confinement[79-82] could raise the band gap and that the light emission is due to the transition between band edge states[79, 82]. Secondly, an interface model suggests that the carriers are excited within Si nanocrystals, but they are thermally relaxed into the surface states and then recombined radiatively there[83]. Thirdly, the PL comes from some defect states[78, 80, 84, 85] existing in the films[78, 84]. Figure 2.15 shows the schematic diagram of various light emission mechanisms from nc-Si embedded SiO_2 films.

Figure 2.15 Schematic diagram employed to interpret the light emission mechanism (vertical arrows represent electronic transition: red arrows represent the external excitation process and green arrows represent the recombination of an electron with a hole). (a) An electron in the conduction band recombines with a hole in the valence band so that $h\nu = E_g$. (b) An electron trapped in an interface state recombines with a hole in the valence band leading to $h\nu < E_g$ and (c) Electron in a defect level located in a wide band gap materials (i.e. SiO_2) recombines with a hole.

Quantum confinement effect

When the size of the quantum dots reduces to small enough less the Exciton Bohr Radius, physical and electrical properties of the materials will be no more the same as its bulk state due to the strongly quantum confinement effect. Exciton Bohr Radius is the average physical separation between the electron and hole. In bulk, the dimensions of the semiconductor crystals are much larger than the Exciton Bohr Radius, allowing the exciton to extend to its natural limit. However, for a quantum dot small enough whose size approaches that of the material's Exciton Bohr Radius, then the electron energy levels can no longer be treated as continuous. They must be treated as discrete, meaning that there is a small and finite separation between energy levels. Because quantum dot's electron energy levels are discrete rather than continuous, the addition or subtraction of just a few atoms to the quantum dot has the effect of altering the boundaries of the band gap. The size dependence of the energy band gap of Si quantum dot have been studied widely, both in theoretical and experimental researches. Most of the theoretical works reported were based on effective mass theory and tight-binding semi-empirical approaches[86-92]. The relationship between the band gap of the nc-Si and its size can be roughly calculated using [91]

$$E_g = E_g^0 + \frac{C}{d^n} \quad (2.11)$$

Where d is the diameter of the nanocrystal, E_g is the band gap of nc-Si, E_g^0 is the band gap of bulk silicon at room temperature, C is an appropriately dimensioned (energy $\times$ (length) ^{n}) constant and n is the exponent related to the material.

The quantum confinement theory has been explained in the framework of the PL peak energies are depended on the nanoparticle size[80-82]. This size-dependent band gap of

semiconductor nanoclusters has been observed by light emission studies of the Si nanocomposite films. **Figure 2.12** shows a size-depended PL spectra of the nc-Si synthesized by laser pyrolysis of silane with size ranging from 2 to 8 nm [71]. It can be observed that the Si nanocrystals with a smaller size have a bigger band gap, emitting high energy light around violet color, while nc-Si with a larger size have a smaller bang gap, emitting low energy light around red color. **Figure 2.16** shows the correlation between the PL peak energy and average diameter of the nc-Si. It is seen that the experimental data compares nicely with the theory, which is represented by the solid curve and calculated according to the quantum confinement theory.

Figure 2.16 A comparison between the experimental resulting band gap of nc-Si and that of theoretically calculated as a function of size[71]

Defects-related light emission

Although quantum confined effect is the most popular light emission mechanism, however, several researcher from different groups have observed that PL energy does not always shift

with extended oxidation and the resultant particle size reduction as shown in **Figure 2.17**. There are two PL bands in **Figure 2.17** and they are not shift with the nc-Si sizes. Since the peak positions of these PL bands do not change, they can not be attributed to the quantum confinement effect. One of the possible explanations is the light emission from defect luminescent centers. In fact, the interface between Si nanoparticles and the amorphous SiO₂ matrix can contain many defects due to the large latticemismatch (about 7% or more), surface roughness, and variation in surface stoichiometry (SiO_x). These defects include weak oxygen bond (O-O)[22], the neutral oxygen vacancy ($O_3 \equiv Si-Si \equiv O_3$, where $\equiv$ represents the bonds to three oxygen atoms)[22], E_δ' center ($O_3 \equiv Si \bullet + Si \equiv O_3$, where $\bullet$ represents an unpaired electron and + is an trapped hole)[23] and the non-bridging oxygen hole center $\equiv Si - O \bullet$ [24]. The radiative recombination of exctions in various defects may emit light with characteristic energy. For example, NOV and NBOHC can emit the photons with the energies of 2.7 eV and 1.9 eV. WOB and E_δ' center may emit the photos with the energies of 3.0 eV and 2.0~2.2 eV.

Figure 2.17 PL spectra for different Si concentration in the films[93]

Interface-related light emission

While Yohibiko et al proposed a model from oxidized Si nanometer-sized spheres, in which

these oxidized Si nanometer-sized spheres consist of three regions: the crystalline Si core, the amorphous SiO₂ surface layer, and an interfacial layer between the crystalline Si core and amorphous SiO₂ surface layer as shown in **Figure 2.18**[83]. They proposed that the interfacial region contains non-stoichiometric amount of oxygen atoms. In an incompletely oxidized Si layer, oxygen atoms play important roles in electronic structures. Their calculations indicate that oxygen atoms may reduce the bandgap energy to be smaller than that of the crystalline Si core. Photogenerated electrons, holes, and excitons are then confined in this thin interfacial core. Radiative recombination occurs in this thin interfacial region, and the light emission is due to the radiative recombination in the interface region.

Figure 2.18 Energy-gap diagram of the three-region model[83].

2.5 Summary

Nanocomposite films of Si nanocrystal embedded SiO₂ shown promising in the non-volatile memory device and Si-compatible light-emitting devices. The standard approaches of synthesizing nc-Si include ion implantation of silicon into an amorphous SiO₂ matrix or deposition of Si sub-stoichiometric oxide films using chemical vapor deposition, sputtering,

or reactive evaporation. A high temperature annealing step is usually adopted for crystallization of the excess Si. Some previous studies have demonstrated the microstructure of the as-deposited amorphous SiO_x films mainly falls to random-bonding model (RBM) in which each Si atoms is a statistical distribution of the five basic bonding units, Si-(Si_{4-n}O_n), n= 0, 1...4 or random-mixture model (RMM) in which the alloy is expected to be composed of randomly arranged clusters of Si and SiO₂ of varying sizes. For the nc-Si growth mechanism, two main models have been proposed: the diffusion-controlled growth and the phase segregation growth. The charges can be trapped at the conduction band of the nc-Si, the deep level defects in the nc-Si and the interfacial traps between the nc-Si and the SiO₂ matrix. The physical origins of the light emission from such nanostructures are still under debate. Several models, including quantum confinement effects in nc-Si, surface states of Si nanocrystals, suboxide defects in Si/SiO₂ and interface states between the nc-Si have been proposed.

Nanocomposite films of Si nanocrystals embedded SiO₂ synthesized by reactive magnetron sputtering exhibits some very desirable characteristics due to the the high kinetic energy of the sputtered atoms. However, many concerns are still unaddressed and the fundamental of the structural, electrical and optoelectronic properties are still unclear. In order to understand this Si nanostructure and for its successful application in non-volatile memory and Si-compatible light emission devices, the following issues need to be investigated:

- (1) The microstructure of the as-deposited amorphous SiO_x films by reactive magnetron sputtering is still unclear, especially for the local bonding structure in the nanoscale. A model concerning its atomic structure would greatly help the interpretation of the nc-Si growth mechanism, electrical and optoelectronic properties.

- (2) The structure changes during annealing strongly influence the electrical and optical performance of the nc-Si/SiO₂ nanocomposite films. A system investigation on the growth mechanism of nc-Si and the chemical structure evolution during annealing is indispensable.
- (3) As both the charge storage and the light emission (i.e. electroluminescence) are caused by the charge injection into the nc-Si in the SiO₂ film, a clear understanding of the charge transport behaviors and the charge storage mechanism in the films is indispensable to have a better understanding of its electrical properties as well as the light emission properties.
- (4) The understanding of the charge trapping and retention mechanism in such nanostructures is still unclear. Although, intense efforts have been dedicated to clarify the charge trapping mechanism, these studies by the pure electric characterizations are seldom correlated to the microstructure of the films.
- (5) A resistive switching behavior in their Si-rich oxide films has been observed. However, there is still lack of favorable explanations for the sudden increase/decrease in the current conduction and the Ohmic conduction behavior in low resistance state.
- (6) In most of the previous studies about the electroluminescence (EL) focused on the nc-Si embedded SiO₂ films after high temperature annealing. However, amorphous Si nanoclusters are attractive alternative to nc-Si for the development of Si-based light emitting devices. A detail study concerning the EL from amorphous Si nanoclusters SiO_x is still missing.
- (7) Charge trapping in nc-Si strongly suppresses carrier injection and transportation in the gate oxide layer. Thus charge trapping should also have a strong impact on luminescence. Therefore, a systematic investigation on the influence of charging/discharging of nc-Si on

the EL emission performance is necessary.

In this project, a systematic investigation on the structural, electrical and optoelectronic properties was conducted. The local bonding configuration of the as-sputtered SiO_x films was examined. The chemical structure evolution and the growth mechanism of Si nanocrystals during annealing were discussed. The charge transport mechanisms were studied and the influence of charge trapping on the current conduction was elaborated. The light emission mechanisms from both as-sputtered amorphous SiO_x film and the films after high temperature annealing were explored and the influence of charging trapping on the electroluminescence performance was investigated.

Chapter 3 Experimental Procedures

This chapter describes the details of the thin film deposition with different Si concentration and thermal treatment conditions. Various characterization techniques for microstructure such as X-ray photoelectron spectroscopy, Raman spectroscopy, Transmission electron microscopy are briefed. The measurements of electrical and optical properties are introduced.

3.1 Deposition of Si-rich SiO_x films

SiO_x films were fabricated using reactive radio-frequency (RF, 13.56 MHz) magnetron sputtering of a Si target (4 inch, 99.999% in purity) in a gas mixture of Ar/O₂ at a controllable flow rate. The system used was an *E303A Magnetron Sputtering System (Penta Vacuum)*. *P*-type Si (100) wafers were used as substrates. Prior to deposition, the wafers were chemically cleaned in a *piranha bath* (a mixture of 3:1 concentrated sulphuric acid to hydrogen peroxide solution) at 120 °C for 1 hour, and then rinsed several times with deionized water. Then, the wafers were ultrasonically cleaned in acetone for 20 min and were then followed by ultrasonic cleaning in ethanol for 20 min. Finally the ultrasonic cleaned wafers were rinsed several times with deionized water.

Before deposition, the chamber was pumped down to the base pressure of 3×10^{-5} Pa. After that, argon and oxygen gas mixtures were introduced into the sputtering chamber and the ratio of argon over oxygen was controlled with a mass flow controller. The process pressure was adjusted by a pressure controller. Then the substrates were plasma cleaned for 5 min at a radio frequency induced substrate bias of 300 V to remove the surface oxide. The sputtering target was then pre-sputtered for 10 min before open the shutter to commence the deposition. The

deposition parameters are listed in **Table 3.1**. The deposition times were varied accordingly to achieve various thicknesses. The thickness was determined by a *Dektak 3SJ Profilometer* that has a probe that scans across a step created by the deposited film. The step was created by covering a small part of the Si substrate with photoresist and stripped after the deposition.

Table 3.1 Magnetron sputtering parameters of SiO_x films.

Parameters	Conditions
Base pressure (Pa)	$< 3 \times 10^{-4}$
Process pressure (Pa)	0.2
Power density (W/cm ²)	2.5
Ar flow rate (sccm)	100
O ₂ flow rate (sccm)	0.1 ~ 3.0
Substrate bias (V)	Floating
Substrate rotation (rpm)	20

3.2 Thermal Treatment

The as-deposited Si-rich SiO_x films are amorphous. A post deposition annealing procedure is needed to induce the crystallization of the excess Si. The thermal treatment was carried out by rapid thermal annealing (RTA) in a *Jipelec Jetfirest100 Rapid Thermal Processor*. During the rapid thermal annealing, the samples were heated by radiative transfer of energy from incandescent tungsten-halogen lamps and its temperature was recorded by a thermocouple when the annealing temperature was below 500°C and by an optical pyrometer when the annealing temperature was above. The chamber was pumped by a rotary pump for 180 sec to ~ 1Pa and then purged with 2000 sccm flow of Ar gas for 120 sec. This process was repeated for five cycles to remove adsorbed oxygen and other adsorbed molecules in the chamber. The temperature ramping rate was fixed at 50 °C/sec, and the annealing time was 180 sec for all the samples. The RTA oven was rapidly cooled to below 100°C with cooling water (within 30 sec). The annealing was done in an Ar-protected atmosphere with an Ar flow rate of 2000 sccm. In order to investigate the Si nanocrystal growth mechanism and the chemical structure

evolution during thermal treatment, the annealing temperature is set from 200 °C to 1200°C with an interval of 200°C.

3.3 Chemical structure

The atomic concentration, chemical states and bonding configurations of the as-deposited SiO_x films as well as the samples after thermal annealing were characterized by X-ray photoelectron spectroscopy (XPS). XPS, also called ESCA (Electron Spectroscopy for Chemical Analysis), can be used to probe the electronic and chemical structure of an element, especially for the surface analysis. XPS is extremely sensitive to the surface properties due to the small escape depths (~5 nm) of photoelectrons. A *Kratos AXIS X-ray photoelectron Spectrometer* using monochromatic Al-K α (1486.71 eV) X-ray radiation, operating at a reduced power of 150 W (15 kV $\times$ 10 mA) was employed to characterize the SiO_x films. The core-level spectra were obtained at a photoelectron take-off angle of 90° respect to the sample surface. First, a survey scan from 0 to 1200 eV was done in 1 eV step with a passing energy of 160 eV to determine the elements present in the film, and then it was following by a narrow scan of step size 0.1 eV with a passing energy of 40 eV at the binding energy range covering the peak position of the detected elements. The core-level was recorded after etching off the surface contamination for 300 sec with the build in Ar⁺ ion gun. The Ar⁺ ion gun was accelerated by a high voltage of 4 kV with a filament current of 15 mA at a gas pressure of 6.65×10^{-6} Pa. The ion etching was performed at an incident angle of 45° to the surface normal with a differential pumping Ar⁺ ion gun (*Kratos Macro Beam*). The atomic concentrations of the elements were calculated based on the integrated peak area ratio in considering various sensitive factors.

Although XPS is very useful to characterize the very top surface of materials, it is difficult to analyze the measured XPS spectrum because the energy of photoelectron electrons is greatly influenced by the chemical state of atoms. In most cases, the spectrum generated by the XPS irradiation has a complex shape due to the complex chemical environment of the core electrons, and it is unable to obtain useful information about the specific chemical structure or bonding state concerned. By the deconvolution with the use of Gaussian function or the Lorentzian function, it is possible to isolate individual XPS peaks and perform the qualitative and quantitative analyses for every component accurately. Figure 3.1 shows the XPS Si 2p core level peaks for the as-deposited $\text{SiO}_{1.2}$ sample. The Si 2p core-level spectrum is constituted of two main peaks separated by a flat region where the intensity does not drop to zero. It is quite reasonable to argue that the two Gaussian lines corresponding to the Si-Si₄ and Si-SiO₄ tetrahedrons are not sufficient to take into account the intensity level of the intermediary region between the two main peaks. According to the random-bonding model of the atomic structure of amorphous Si-rich SiO_x thin films[1], where a continuous random network model in which the local bonding was statistical in nature, and characterized by five different local bonding environments, Si-Si_{4-w}O_w, where $w = 0, 1, 2, 3, 4$. Taking this into account, all the XPS curves were deconvoluted using a fitting procedure based on the summation of Gaussian functions after Shirley background subtraction. A fitting process was conducted and optimized as follows. Initially, the binding energy of Si was placed to that of Si reference sample (99.8 eV) and these five Gaussian lines are expected to be equally spaced from the binding energy of Si⁰ to that of Si⁴⁺. During the fitting process the peak energies were allowed to vary within 0.1 eV only, in order to take into account small different charging effects on the samples. Instead the full width at half maximum (2Γ), and relative weight (W) were allowed to vary without any limit. Based on the above fitting procedures the Si 2p

core-level spectra are fitted by a superposition of five Gaussian peaks (Si^0 , Si^{1+} , Si^{2+} , Si^{3+} , Si^{4+}), corresponding to Si atoms in which zero, one, two, three, or all four Si-Si bonds have been replaced by Si-O bonds.

Figure 3.1 Deconvonlution of the Si 2p XPS spectrum obtained from the as-deposited $\text{SiO}_{1.2}$ sample.

3.4 Crystallinity Characterization

Raman spectroscopy has been widely used for the characterization of mixed-phase Si films. It provides a fast and nondestructive method to determine whether silicon particles are amorphous or crystalline. A *Renishaw Raman Spectroscope RM1000* using a HeNe laser source with an excitation wavelength of 633 nm, and a scan area of $\sim 3.14 \mu\text{m}^2$ was used. The SiO_x samples used for Raman characterization are deposited on Si wafer with thickness of ~ 300 nm. The data acquisition region was from 50 to 700 cm^{-1} , and the laser power used was ~ 1 mW. **Figure 3.2** shows Raman spectra for a typical amorphous SiO_x films deposited on normal glass which has no Raman signal in the concerned range and the spectra of a single crystalline Si wafer.

Figure 3.2 Raman spectrum of the amorphous SiO_x and the Si wafer.

For the crystalline Si wafer, there is a sharp transverse optic (TO) phonon peak at $\sim 521\text{cm}^{-1}$, and a weak TO peak at $\sim 310\text{ cm}^{-1}$. These two TO peak, especially for the peak at $\sim 521\text{ cm}^{-1}$, are the characteristics of crystalline Si. While for the amorphous SiO_x films, the spectrum shows typical a-Si features. The transverse-acoustic (TA) band at $\sim 160\text{ cm}^{-1}$ and the TO band at $\sim 480\text{ cm}^{-1}$ are scattering from the amorphous Si in the SiO_x films. The 480 cm^{-1} optical-phonon-scattering band originates from the destruction of the short-range order of the silicon lattice, i.e., the bonding between nearest-neighbor atoms. The 160 cm^{-1} acoustic-phonon-scattering band originates from the destruction of long-or intermediate range order of the lattice, is a measure of the density of states of the acoustic phonons.

3.5 Image of Si nanocrystals by TEM

Transmission electron microscopy (TEM) is extensively used to identify nanocrystals embedded in dielectric films, and information about nanocrystal sizes, distribution, and lattice structures can be obtained from TEM images. The electron diffraction pattern which reflects the scattering of electrons by atoms offers additional information about the crystal structure of

nanocrystal. To prepare suitable cross-section TEM specimens, first the Si wafers with SiO_x films were stuck face to face with 3M M-bond 610 glue and then hand grinded and polished for both sizes to a thickness of 30 μm . Then, samples were stuck to a copper ring, and milled by argon plasma at 5 keV under a thinning angle of 4° at room temperature. Finally, the microstructures of the samples were characterized using a transmission electron microscope (*JEM 2010*) equipped with an energy dispersive X-ray spectroscopy.

3.6 Fabrication of MOS structures

To study the electrical and optical behaviors, metal-oxide-semiconductor (MOS) structure based on the nanocomposite films of nc-Si embedded SiO₂ were prepared. The films used for electrical and optical characterizations are ~50 nm in thickness. **Figure 3.3** shows the schematic diagram of the MOS structure with the Si nanocomposite thin films as the active layer. Al top electrodes were formed for the MOS structure used for electrical characterization, and semi-transparency yet conductive indium-tin-oxide (ITO) top electrodes were formed for the MOS structure used for EL measurement.

Figure 3.3 Schematic diagram of the MOS structure used for electrical and optical characterization.

The Al gate electrodes were synthesized by RF magnetron sputtering of an Al target (4 inch, 99.999% in purity) with a shadow metal mask. The deposition of Al gate electrodes is similar with that of SiO_x films. The samples were plasma cleaned for 5 min at a radio frequency induced substrate bias of 300 V to remove the surface oxide before commence the deposition. The detailed deposition parameters are summarized in **Table 3.2**. Finally Al back contacts (~300 nm) are sputtered after plasma etching off the possible surface oxide.

Table 3.2 Deposition parameters of the Al top electrode and Al back contact.

Parameters	Conditions
Base pressure (Pa)	$< 3 \times 10^{-4}$
Process pressure (Pa)	0.5
Power density (W/cm ²)	2.0
Ar flow rate (sccm)	80
Substrate bias (V)	Floating
Substrate rotation (rpm)	20
Substrate heating	No

The ITO top electrodes were synthesized by RF sputtering the (In₂O₃)_x(SnO₂)_{1-x} compound target (4 inch, 99.999% in purity) in a gas mixture of Ar and O₂ with an controlled flow rate. The samples were plasma cleaned for 5 min at a radio frequency induced substrate bias of 300 V to remove the surface oxide before commence the deposition. The detailed deposition parameters are summarized in **Table 3.3**. The fabricated ITO electrodes are 120 nm in thickness with a diameter of 1 mm. Finally Al back contacts (~300 nm) are sputtered after plasma etching off the possible surface oxide.

Table 3.3 Deposition parameters of the ITO top electrode.

Parameters	Conditions
Base pressure (Pa)	$< 3 \times 10^{-4}$
Process pressure (Pa)	0.5
Power density (W/cm ²)	2.5
Ar flow rate (sccm)	80
O ₂ flow rate (sccm)	0.5
Substrate bias (V)	-20
Substrate rotation (rpm)	20
Substrate heating	No

3.7 Electrical Characterization

Current-voltage (I - V) and high frequency (1 MHz) capacitance-voltage (C - V) measurements were employed to study the electrical properties of the nanocomposite films of nc-Si embedded SiO₂ films. The main hardware for the electrical measurements was Keithley 4200 Semiconductor Characterization system and the Karl Suss probe station. The C - V curve is usually measured with a C - V meter which applied a DC bias voltage and a small sinusoidal signal to the MOS capacitor and measures the capacitive current with the AC ammeter. The charging behaviors of the nc-Si are studied by examining the shifts in the C - V characteristics after the application of a constant charge voltage (V_{Gate}) to the gate electrode. Figure 3.4 shows the C - V characteristics of the MOS structures with nc-Si embedded in the gate oxide after the application of a positive voltage of 10 V and a negative voltage of -10 V for 5 sec, respectively. A clear ΔV_{FB} with respect to the virgin C - V curve indicates the memory effect of the device structures. As can be noticed that , a positive voltage results in a negative ΔV_{FB} of ~ 2.06 V, suggesting the buildup of positive charges (hole) in the thin films, while a negative voltage results in a positive ΔV_{FB} of ~ 2.60 V, indicating strong negative charges (electron) trapping in the device. Since no ΔV_{FB} can be observed for the pure SiO₂ control sample without the nc-Si, the ΔV_{FB} in the flat band voltage is attributed to the charge trapping in the

nc-Si associated trapping centers in the SiO₂ films.

Figure 3.4 C-V characteristics of the MOS structures containing nanocrystals in the gate oxide.

The MOS capacitor is also frequently studied by the current-voltage (I - V) measurement. **Figure 3.5** shows the typical I - V characteristics of the pure SiO₂ control sample and the SiO₂ films containing nc-Si. Both of the samples were fabricated by reactive magnetron sputtering with an identical thickness of ~ 50 nm. One can observe that there is an extremely low tunneling current at the level of $\sim 10^{-12}$ A for the pure SiO₂ control sample. The introduction of nc-Si in the SiO₂ films significantly enhances its current conduction. The tunneling current increase about several orders for the SiO₂ films containing nc-Si. The significant increase in gate current is due to the formation of nc-Si in the SiO₂ matrix. The injected electrons can be transported along the tunneling paths formed by the high density nc-Si from the substrate to the gate electrode[2].

Figure 3.5 Typical I - V characteristics of the pure SiO_2 control samples and the Si nanocrystal embedded SiO_2 films.

3.8 Electroluminescence Characterization

To study the optoelectronic (EL) properties of the light emitting devices based on the Si nanocomposite thin films, an EL characterization system that is capable of applying constant voltage/current onto the gate electrode and collecting the light emission from the same gate electrode is required. Figure 3.6 illustrates the set up of such EL characterization system. During the EL measurement, a Keithley 2400 source measurement unit (SMU) was used to apply voltage/current to the ITO gate of the light-emitting device via the probe arm of a probe station. On top of the light-emitting device, a light probe connected to the low-loss fiber was used to collect the emitted light from the ITO gate. The spectrum of the light emission was then analyzed by a computer-controlled Dongwoo Optron DM150i monochromator (wavelength range: 185-1600 nm; resolution: 0.2 nm) equipped with a Dongwoo Optron PDS-1 photomultiplier tube (PMT) detector. The whole system was placed in a light-tight enclosure to avoid the influence of the ambient light.

Figure 3.6 Schematic diagram for the setup of an EL characterization system.

Chapter 4 Structure of the Nanocomposite Films of Si nanocrystals embedded SiO₂

This chapter reports a systematic investigation on the nanoscale microstructure of magnetron sputtered amorphous SiO_x films, and proposes a bonding configuration model concerning its local atomic microstructure. The annealing effect on the structure of the SiO_x films, i.e., the chemical structure evolution, crystallinity of the excess Si is also studied in detail. The growth mechanism of the nc-Si during high temperature annealing is discussed.

4.1 Structure of the as-sputtered SiO_x films

Some information concerning the structure of SiO_x films can be obtained from the literatures based on the study of Si monoxide. As discussed in Chapter 2, two main models have been suggested for the structure of the amorphous SiO_x based on fourfold-bonded Si and twofold-bonded O. The first is the random-bonding model (RBM) or continuous-random-network model[1] and the second model for the network is the random-mixture model (RMM)[2]. On the other hand, it has been reported that amorphous SiO_x films fabricated by magnetron sputtering shows a unique microstructure and local bonding configuration due to the high kinetic energy of the sputtered atoms and high surface diffusivity[3-5]. Thus a systematic study concerning its microstructure and local bonding configuration is desirable.

4.1.1 Chemical structure of the as-sputtered SiO_x film

X-ray photoelectron spectroscopy (XPS) is employed to examine the chemical structure of the

SiO_x films. For the study of the core level shift, Si 2p core-level spectra, C 1s spectra and O 1s spectra were recorded under the surface-scanning mode by XPS. Figure 4.1 shows the Si 2p XPS spectra for the as-deposited samples with a wide range Si concentration. The broadening and continuous variation in the shape of the Si 2p core-level provides a means for excluding the random mixture model (RMM) as the basic network structure. If the RMM were appropriated, the Si 2p core-levels for all concentrations would be characterized by two peaks of roughly 2 eV width separated by 4 eV in binding energy. Thus the asymmetrical broadening of the Si 2p core-level is attributed to the existence of Si suboxides (Si₂O, SiO and Si₂O₃) in the SiO_x. According to the deconvolution procedures described in Chapter 3, the Si 2p XPS spectrum was fitted by a superposition of five Gaussian peaks (Si⁰, Si¹⁺, Si²⁺, Si³⁺ and Si⁴⁺), corresponding to no Si-Si bond, one Si-Si bond, two Si-Si bonds, three Si-Si bonds, or all four Si-Si bonds had been replaced by Si-O bonds [6]. Figure 4.1 shows the results of the fitting by plotting the resulting line shape and the individual components under the corresponding spectra. Beginning at $x = 0.15$, a majority of Si remains Si⁰ and only small amount of Si phase is oxidized. With increasing x , the concentrations of the various Si chemical states change, and more and more Si phase react with the reactant oxygen. A majority of the Si phase has been oxidized into Si⁴⁺ at $x = 1.95$. On the other, there are sufficient Si suboxides in the as-deposited samples besides the Si and SiO₂ species regardless their Si concentrations, which shows a chemical feature predicted by RBM.

Figure 4.1 High resolution XPS Si 2p spectra of the as-deposited SiO_x films with a wide range of Si concentrations. Dot line is the measured data and the solid line is the result of Gaussian fitting (a) SiO_{0.15}, (b) SiO_{0.6}, (c) SiO_{1.0}, (d) SiO_{1.4}, (e) SiO_{1.7} and (f) SiO_{1.95}.

To check the validity of the RBM for our as-sputtered SiO_x samples, the intensities of the individual components yielded by XPS were compared with those predicted by the RBM and the RMM. Figure 4.2 (a) shows the component intensities as calculated according to the RBM and the RMM, and Figure 4.2 (b) shows the component intensities as obtained from the fitting of XPS spectra. By comparison the two plots, it can be seen that the experimental spectra differ significantly from those predicted by both models. In particular, despite of the fact that the amorphous samples contain five Si chemical structures, there is still no complete

agreement with the idealized random bonding statistics. This means that the formation of the various tetrahedral during film deposition cannot be treated as a purely statistical problem, but chemical factors must take into account. A further comparison reveals that the Si and SiO₂ concentrations obtained from our XPS analysis are too high comparing with those predicted by the RBM, which is an appreciable mixture characteristic of a composite material consisting of two distinct Si and SiO₂ phases. This is a feature of RMM in which the microstructure of the SiO_x consists of nanoclusters of Si and SiO₂. Therefore, it can be concluded that there are Si-rich or O-rich regions which should be used to compensate the high Si and SiO₂ concentration in our as-sputtered SiO_x films. Thus, it can be speculated that there are amorphous Si nanoclusters formed during the sputtering deposition. These amorphous Si nanoclusters are embedded in the O-rich SiO₂ matrix, and they are separated by a Si suboxides transition layer. Since the amorphous Si nanoclusters are formed in the sputtering deposition process, their size could be strongly determined by the availability of the excess Si (Si concentration), i.e., the higher the Si⁰ concentration, the larger of the Si nanoclusters. The formation of the amorphous Si nanoclusters in the as-sputtered SiO_x films, and the local atomic structure of the amorphous SiO_x films will be discussed in detail below.

Figure 4.2 (a) Dashed lines are relative concentrations of the basic bonding units in the random-bonding model (RBM) and solid lines are relative concentrations of the Si and SiO₂ components in the random-mixture model (RMM). (b) Relative concentrations of the five chemical states vs oxygen concentration, as obtained from the Gaussian fits.

RBM and RMM are the ideal cases. In fact, during the reactive sputtering deposition, the relative weight of chemistry and statistics of chemical structures are strongly depended on the ratio between surface diffusivity of the reacting species and the deposition rate. For a low deposition rates and high surface diffusivities, the formation of Si-Si₄ and Si-O₄ tetrahedra predicted by the RMM is more favoured than the formation of intermediate tetrahedral. On the other hand, at high deposition rates and low surface diffusivities, the atoms cannot jump on the surface for a long time and are rapidly quenched in their initial positions by the fast deposition of new layers. In this situation, the statistical approach of the RBM should be

dominated[7]. Even if a detailed analysis of the Si chemical structure in terms of the surface diffusivities is still missing. The influence of the deposition rate in determining the tetrahedral chemical structures has already been reported by many researchers in their XPS studies of SiO_x films. It has been demonstrated that the SiO_x films synthesized by LPCVD[8], evaporation[9] with a high deposition rate usually show chemical structure predicted by RBM, while the SiO_x films synthesized by co-sputtering with a low deposition usually show bonding configuration predicted by RMM[10]. In this project, it can be concluded that the reactive sputtering deposition at room temperature are in an intermediate regime of deposition rate/surface diffusivity which produces a SiO_x microstructure intermediate between those predicted by the RBM and the RMM.

4.1.2 Structure as revealed by valence band XPS spectra

Figure 4.3 shows the valence band XPS spectra for the as-deposited SiO_{0.6}, SiO_{1.0}, SiO_{1.4} samples. The valence band XPS spectra of a pure SiO₂ control sample fabricated with the same method is also presented for comparison. In the valence band of the SiO₂ control sample three groups of components can be distinguished. A feature labeled as A located at around 6-7 eV energy range, corresponding to the O 2P lone-pair band[11]. Two other components labeled with B and C, at higher binding energies, correspond to the strongly interaction of O 2p states with Si 3p and Si 3s level, respectively[11]. In the case of the films with excess Si, besides these three groups, an additional group D located at 1-4 eV above its valence-band edge is found. The additional group D is attributed to be the interaction between Si orbitals (i.e., Si 3p) which give states at these energies[12]. It is reported that for the SiO_x films with chemical structure following the RBM the signal of group D can not be observed when the Si concentration is low (i.e. x values is higher than 1.0). Moreover, theoretical calculation also

claimed that a minimum length of ~ 10 atoms in the Si-Si chains is required to observe this Si-Si bonding signals in the valence band[13]. However, the strong Si peaks intensity (Group D) in the valence band XPS spectrum of the magnetron sputtered SiO_{1.0} sample can be observed, and even is noticeable in the sample with very low Si concentration sample (SiO_{1.4}). Take these two assertions into account, the high intensity of group D strongly suggests the formation of Si-Si long chains (Si clusters) where the Si is bonded to another Si ion in the as-deposited films. In addition, the Group D in the valence band XPS spectrum has also been observed by other researchers in their XPS study of the nc-Si embedded SiO₂ films, and is attributed to the formation of Si nanoclusters[12, 13].

Figure 4.3 Valence band XPS spectra of the as-deposited SiO_x with various Si concentrations; the spectrum of the pure SiO₂ control sample is also presented for comparison.

A furthermore comparison among the valance spectra reveals that the intensity of the group D increases as the Si concentration increase. A down shift to the low binding energy of group D is also observed with the increasing Si concentration, i.e., the group D peaks located at 3.2 eV for SiO_{1.4}, 2.8 eV for SiO_{1.0} and 2.4 eV for SiO_{0.6}. The increased intensity and down shift of group D with Si concentration agrees well with that reported in literature[12]. The increase in intensity and down shift of position imply that the probability that a given Si is surrounded by other Si atoms has increased, so does the probability of interaction between silicon orbitals[11]. In another words, the size of the cluster increases with increasing Si concentration. These features depict an increase in Si nanocluster size with increasing Si concentration. This observation is also consistent with the fitting results from the Si 2p core-level spectra, which shows that the concentration of Si⁰ increases with increasing Si concentration.

4.1.3 Raman characterization of the SiO_x films

Raman signals origin from the lattice vibrations in solids and relate directly to the microstructure of the materials. And it has been extensively employed to characterize both crystalline and amorphous Si[14-16]. Figure 4.4 shows the Raman spectra of the as-deposited SiO_x samples with various Si concentrations. The Raman spectra of a pure SiO₂ films prepared by the same method is also presented for comparison purpose. The sharp peak located at ~520 cm⁻¹ and the weak peak at ~300 cm⁻¹ shown in Figure 4.4 are due to the phonon modes of crystalline Si. These two crystalline Si Raman peaks were also clearly visible from the crystalline Si substrate, whereas absent in the Raman spectrum of the SiO_x films deposited on normal glass substrate as shown in **Figure 3.2**. Thus, these crystalline Si peaks in the as-deposited SiO_x samples were attributed to the crystalline silicon substrate. For

pure SiO₂ films, the absence of other features except for the substrate peaks is because that the Raman efficiency of amorphous SiO₂ (a-SiO₂) is too low to give rise to detectable Raman signals, unless the a-SiO₂ film is sufficiently thick (thicker than several micrometers). In fact, for the as-deposited a-SiO₂ film with a thickness of about 300 nm in our study, Raman signals scattering from the a-SiO₂ were hardly detected. However, for samples containing excess Si atoms, besides the substrate peaks, other features (broad Raman peaks) are observed and the spectral features change depending on Si concentration.

Figure 4.4 Raman spectra of the as-deposited SiO_x films on Si wafer with various Si concentrations; the spectrum of the pure SiO₂ control sample is also presented for comparison.

For a slightly increase in Si concentration (i.e., SiO_{1.5}, SiO_{1.4} and SiO_{1.2}), although not strong, a transverse-acoustic (TA) band centered at low-frequency around 160 cm⁻¹ presents. With a

further increase in Si concentration (i.e., SiO_{1.1} and SiO_{0.9}), the intensity of the TA Raman peak at around 160 cm⁻¹ increases and another transverse-optical (TO) band located at high-frequency 480 cm⁻¹ appears and grows. For the high Si concentration samples (i.e., SiO_{0.7}, SiO_{0.6} and SiO_{0.4}), the TO band becomes distinguishable. These two broad TA and TO Raman bands are the characteristic peaks of amorphous Si, scattering from the excess amorphous Si in as-deposited SiO_x films.

Similar Raman spectral features have been observed by several other researchers from different research groups. These two broad amorphous Si features in their Raman research of SiO_x films were attributed to the formation of amorphous Si clusters[15, 16]. For example, Nesheva et al.[15] reported that these two amorphous Si Raman features are absent for their as-deposited SiO_x samples synthesized by evaporation when the annealing temperature is low than 250°C due to the absence of amorphous Si domains, and were clearly visible when the annealing temperature is higher (700°C), due to the formation of small Si domain as a result of phase separation. Kanzawa et al[17]. also claimed that the TA and TO amorphous Si (a-Si) Raman band origins from the a-Si nanoclusters by comparing their Raman spectra with the theoretically calculated vibrational density of state of the amorphous Si nanoclusters.

Besides, Kanzawa et al[17] demonstrated that small Si domains with a minimum size are required for the detectable of these amorphous Si Raman peaks in the SiO_x films. That is why there is no distinguishable amorphous Si Raman peaks in the Raman spectra of our as-sputtered SiO_x films with low Si concentrations (i.e., SiO_{1.2}, SiO_{1.4} and SiO_{1.5}). It is possible that the amorphous Si nanoclusters in these samples are too small to give out detectable Raman signals due to the low Si concentration. However, as-compared with the

pure SiO₂ sample, weak Si Raman intensity from 100-500 cm⁻¹, although not high, still can be observed, indicating the existence of amorphous Si phase in these samples. Note should be taken that the Si nanoclusters are formed in the sputtering deposition, thus its size may be strongly determined by the availability of the excess Si, i.e., the higher of the Si concentration, the larger of the a-Si nanoclusters. As can be observed from the XPS analysis that the concentration of Si⁰ increases with increasing Si concentration, thus, the size of the amorphous Si nanoclusters increases with increasing Si concentration, leading to the increasing in the intensities of TA and TO bands. Moreover, in the Raman spectrum of the as-deposited SiO_x films, quite different from SiO₂ films, a high-frequency shoulder at around 550 cm⁻¹ appears, extending up to 700 cm⁻¹. This high-frequency shoulder is also attributed to the Si nanoclusters as suggested by Kanzawa et al[17]. Therefore, based on the above interpretation, it is reasonable to assume that our as-sputtered SiO_x samples are chemically inhomogeneous, and there are amorphous Si nanoclusters formed during sputtering. The size of the amorphous Si nanoclusters depends on the Si concentration. These observations are consistent with our valence band XPS spectra.

Raman signals arise from the lattice vibrations in solids and related directly to the microstructure of the material. It has been concluded that the optical-phonon-like band in a-Si reflects the vibrational density of states (DOS) of the optical phonons. The optical phonons (TO band) are primarily related to the bonding between nearest-neighbor atoms, i.e., to short-range order, while the acoustic-phonon scattering (TA band) is related more to the intermediate or long-range order. Hence the relative intensity of the TA and TO Raman bands should reflect the vibrational density of states (DOS) of the optical and acoustic phonons of a-Si in the SiO_x films. It should be point out that the spectral features observed above

qualitatively agree well with those vibrational density of states (DOS) of amorphous Si clusters calculated by Feldman et al.[18]. The DOS spectra are calculated based on the magic-number clusters Si₃₃ (Si nanocluster composed with 33 Si atoms) and Si₄₅ (Si nanocluster composed with 45 Si atoms). Figure 4.5 shows rescaled DOS spectra of Si₃₃ and Si₃₅ clusters by Kanzawa et al. [17, 18], and the DOS spectra for amorphous Si is also present for comparison.

In the DOS spectra shown in Figure 4.5, both Si₃₃ and Si₄₅ clusters show a TA band at around 160 cm⁻¹ and a high-frequency TO band at around 480 cm⁻¹. But the spectral features of these two clusters are different. For the smaller Si₃₃ cluster, the intensity of the TA component is higher than that of TO band, whereas, with increasing clusters size, for the larger Si₄₅ cluster, the intensity of the TA band becomes slightly lower than that of the TO band. These changes in the DOS spectrum agree fairly well with these in the Raman spectrum observed by increasing the Si concentration. Although the Raman spectrum is determined by not only the DOS spectrum but also the matrix elements, the arguments based only on the DOS spectrum is not sufficient. Moreover, the calculations of Feldman et al.[18] were limited to only Si₃₃ and Si₄₅ clusters. However, a good qualitative agreement between theory and experimental allows us to conclude that a-Si nanoclusters have been already formed in the as-deposited films.

Figure 4.5 The total density of state (DOS) of the Si 33-atom cluster and Si 45-atom clusters as a function of frequency. DOS for a model of the pure amorphous Si structure is also included for comparison. [17, 18]

By comparison between the experimental results shown in **Figure 4.4** and theoretically calculated vibrational DOS spectrum shown in **Figure 4.5**, it can be observed that for the as-sputtered amorphous SiO_x with low Si concentrations (SiO_{1.2}, SiO_{1.4}, SiO_{1.5}), the intensity of the low-frequency TA bands at 160 cm⁻¹ is very weak, and the high-frequency amorphous Si components is even undetectable as shown in **Figure 4.4**. To the possible reason could be that the Si clusters are too small (smaller than Si₃₃) due to the low Si concentration in these samples. With the increasing of Si concentration, the intensities of TA bands at 160 cm⁻¹ strongly increase, and distinguishable TO band at 480 cm⁻¹ becomes visible. For a slightly increase in the Si concentration (Si_{1.1}, Si_{0.9}), the intensities of the TA bands at 160 cm⁻¹ is comparable with (even slightly higher than) that of the TO bands at 480 cm⁻¹, indicating that the amorphous Si nanoclusters with a size comparable to that of Si₃₃ have been formed in these as-sputtered samples. However, with a further increase in Si concentration (Si_{0.7}, Si_{0.6} and Si_{0.4}), the intensity of the TO bands at around 480 cm⁻¹ increases and becomes stronger

than that of the low-frequency TA bands at 160 cm⁻¹. It is quite possible that Si nanoclusters with a size larger than Si₄₅ have been formed in these samples. Based on the above discussion, one can deduce that the Si concentration can strongly determine the size of Si clusters, i.e., the higher of the Si concentration, the larger of the Si clusters.

4.1.4 TEM characterization

Transmission electron microscopy (TEM) is the most direct way to characterize the microstructure of the SiO_x films. However, due to the amorphous nature of the as-deposited SiO_x films and the extremely small size of the a-Si nanoclusters, it is quite difficult to characterize the microstructure of the amorphous SiO_x film with TEM. Even through, the amorphous Si nanoclusters can be observed from the high resolution transmission electron microscopy (HRTEM) due to the slight difference in lattice parameters between the Si and SiO_x films, which gives contrast. Figure 4.6 shows the HRTEM image of the as-deposited SiO_{0.6} sample. It can be observed that there are dark black amorphous Si contrasts in the dark brown SiO_x background. The amorphous Si nanoclusters are around 1~3 nm with a spherical shape. Here, the HRTEM provide a direct proof that amorphous Si nanoclusters are formed in the as-sputtered amorphous SiO_x films.

Figure 4.6 High resolution transmission electron microscopy of the as-deposited SiO_{0.6} film. The dark black amorphous Si nanoclusters are clearly visible, embedded in the dark brown SiO_x background.

4.1.5 Formation mechanism of Si nanoclusters

The formation of amorphous Si nanoclusters in the as-deposited SiO_x are seldom observed from these fabricated by CVD, evaporation or implantation techniques. Thus the physical origin of the formation of the amorphous Si clusters in the magnetron sputtered SiO_x films is speculated to relate to the high kinetic energy of the sputtered Si atoms. Figure 4.7 shows the schematic diagram of the formation mechanism of the a-Si nanoclusters during sputtering.

The mean free path of the sputtered particles can be estimated with **Equation 4.1**[4]

$$\lambda_a \approx \frac{1}{\pi(r_A + r_B)^2 n_B} \quad (4.1)$$

where r_A corresponds to the atomic radius of a sputtered particle and r_B corresponds to the atomic radius of Ar; n_B is the particle density ($=N/V=P/kT$) of Ar in the chamber. r_{Ar} is 0.191 nm, r_{Si} is 0.110 nm. Note that the chamber pressure is 0.2 Pa and the chamber temperature is 323K. For the non-oxidized Si atoms, the mean free paths are calculated to be 7 cm. At a target-to-substrate distance of 8 cm, this corresponds to that a probabilities of 50% sputtered silicon atoms reach the substrate without any collisions. During sputtering, the

high-kinetic-energy sputtered Si atoms fly toward to the Si substrate, part of the sputtered atom collide with oxygen atoms and are either full oxidized to form SiO₂ or partially oxidized to form Si suboxides. On the other hand, a large fraction of energetic sputtered silicon particles (1~2 eV) arrive at the substrate without any collision. The high kinetic energy enables the sputtered silicon atoms to migrate on the growing films surface in a 2-dimensional random walk manner on the film surface. It should be point out that the low deposition rate of reactive sputtering allows the energetic Si atoms diffuse for a long time on the film surface until running out of their kinetic energy. During the surface migration, part of them may be further oxidized by the residual oxygen atoms; however, a large amount of the Si atoms remain in Si⁰ state due to the oxygen deficient environment. These non-oxidized Si atoms may find an appreciated place where it can seriously bond to more than one other Si⁰ atoms, forming the amorphous Si nanoclusters. In addition, the surface migration energy of Si atoms on the SiO_x films can also be enhanced by the bombardment of the energetic particles on the growing films surface.

Figure 4.7 Schematic diagram of the formation mechanism of the a-Si nanocluster during sputtering deposition.

4.1.6 Microstructure of the as-deposited SiO_x films

For the nanoscale structures, the as-sputtered amorphous SiO_x films show features of both RBM (i.e., five chemical structures) and RMM (i.e., ultrahigh concentration of Si and SiO₂ species) due to complex chemical reaction process and the high kinetic energy of the sputtered particles. For the Si atoms reacting with oxygen, the Si atoms will bond to one or more (up to four) oxygen atoms once sputtered out of the Si target. On one hand, the introduction of Si-O bond will increase the size of the particles, i.e., the more Si-O bonds, the larger of the particle radius. Thus, the mean free paths significantly decrease, which means that the collision probabilities of the sputtered particles with the oxygen atom increase. Therefore, the kinetic energy of the oxidized Si atoms decreases significantly due to the collisions. Here, we define the sputtered Si atoms into three categories: (1) silicon in the forms of silica, (2) silicon in the suboxide states and (3) silicon in the forms of pure Si. For SiO₂ particles, they will reach the substrate almost without surface migration to form the matrix of the SiO_x films due to their low kinetic energy and low surface diffusivity. For the high energetic Si particles that reach to the substrate without any collision, they can form the a-Si nanoclusters due to their high surface diffusivity. As for the Si suboxides, since sufficient (almost half of the content) Si atoms are in the forms of Si suboxies, one should not take them to be the interface layer (usually with a thickness of several atomic layers) between Si clusters and SiO₂ matrix. However, they may form a transition layer between the Si clusters and the SiO₂ matrix to reduce the lattice distortion. This transition layer may form a shell of the Si clusters with increasing oxidation states far along from the Si clusters core. Based on the above discussion, we speculate that the microstructure of the as-deposited films as follows. The microstructure of amorphous SiO_x films contains Si cluster core with suboxides shell

domains, which themselves embedded in the SiO₂ matrix as shown in Figure 4.8. The Si cluster core can have a different size, thus the Si cluster core with suboxides shell domains.

Figure 4.8 Schematic diagram of the Si core with suboxides shell embedded in a SiO₂ matrix model for the microstructure of the magnetron sputtering SiO_x films.

4.1.7 Conclusions

The as-sputtered SiO_x films are amorphous, with a complex local bonding configuration and atomic microstructure due to the complex dynamic reactive sputtering process and the high kinetic energy of the sputtered Si atoms. X-ray photoelectron spectroscopy (XPS) analysis reveals that the as-deposited SiO_x films contain five Si chemical states (Siⁿ⁺, where n = 0, 1, 2, 3 and 4) in a wide composition range. It is found that amorphous Si nanoclusters are already formed in the as-deposited SiO_x films, and they are embedded in the O-rich SiO₂ matrix. Their size is strongly determined by the Si concentration in the SiO_x films. The physical origin of the formation of the amorphous Si clusters in the SiO_x films is related to the high kinetic energy of the sputtered Si atoms, and high surface diffusivity. The atomic microstructure of amorphous SiO_x films has been proposed to contain Si cluster core with suboxides shell domains, which themselves embed in the SiO₂ matrix.

4.2 Annealing effect on the microstructure

Si nanocrystals are usually induced by high temperature annealing of the amorphous SiO_x

films. During annealing, significant structural changes take place due to the lattice relaxation, defect annihilation and thermal decomposition of the Si suboxides. The structure changes during annealing strongly affect the electrical and optical performance of the Si nanocomposite films. Thus a system investigation on the structural changes during high temperature is essential. In this section, the chemical structure evolution and thermal decomposition of the Si suboxides during annealing are investigated in great details. The rapid growth mechanism of the Si nanocrystals is explored.

4.2.1 Chemical structure evolution

Figure 4.9 and **Figure 4.10** show the Si 2p XPS spectra of the SiO_{0.6} and SiO_{1.4} samples after annealing at various temperatures. The Si 2p core-levels of the as-deposited samples are also presented for comparison. The effect of annealing on the chemical structures can clearly observed by comparing with the as-deposited counterparts. The major effect of annealing on the chemical structures is to reduce the concentration of Si suboxides as well as to increase the content of Si and SiO₂ in terms of chemical structure. With increasing annealing temperatures, the concentrations of the various Si chemical states have been changed. The concentration of Si suboxides decreased, while the intensity of the Si⁰ and Si⁴⁺ peaks increased. Similar chemical structure evolution had also been found in reference [11]. The total Si concentration in the SiO_x films as a function of annealing temperature is shown in **Figure 4.11**. It can be observed that the total Si concentration in the SiO_x films almost keep constant in the wide range of annealing temperatures. This suggests that there is no oxidizing reaction of the SiO_x films during annealing. Thus, we can exclude the possible oxidizing-induced changes in the various Si chemical states during annealing. The changes in chemical structure are attributed to the fact that the Si suboxides were metastable and have a

potential to thermally decompose into more stable Si and stoichiometric SiO₂ to reduce the enthalpy of the system during annealing. This thermal annealing-induced decomposition of the Si suboxides has been reported by many researchers, and is widely accepted to the following reaction[19].

However, because the decomposition reaction need to overcome the energy barrier, thus to complete the decomposition reaction, long time and high temperature are needed. Therefore, there remain sufficient Si suboxides even after annealing at 1000°C for 300s. These Si suboxides may form a transition layer between the Si nanoparticles and the oxide matrix, which have been confirmed by several other researchers[6, 11, 20].

Figure 4.9 Si 2p core-levels of the SiO_{0.6} after annealing at 400°C (b), 700°C (c) and 1000°C (d); the Si 2p core-level of the as-deposited SiO_{0.6} are also presented for comparison. Dots lines are experimental data and the solid lines are the results based on Gaussian fits.

Figure 4.10 Si 2p core-levels of the SiO_{1.4} after annealing at 400°C (b), 700°C (c) and 1000°C (d); the Si 2p core-level of the as-deposited SiO_{1.4} are also presented for comparison. Dots lines are experimental data and the solid lines are the results based on Gaussian fits.

Figure 4.11 The total Si concentration vs annealing temperature of the SiO_{0.6} and SiO_{1.4} samples.

4.2.2 Thermal decomposition of the Si suboxides

In order to clarify the growth mechanism of the Si nanocrystals, the detailed thermal decomposition process of the Si suboxides should be fully understood. The dependence of the stability on Si oxidation numbers has been theoretically calculated by Barranco et al[19]. According to the stability of the Si-O-Si link, the thermal decomposition of the Si suboxides can be divided into the following two steps. The first reaction with reaction energy of -35kJ/mol is the partial decomposition:

The second decomposition reaction with reaction energy of -99kJ/mol is

Therefore, both of the decompositions are exothermic and can be viewed as oxygen exchanges between the reacting silicon atoms. These two reactions take place simultaneously but with different manner. Barranco et al [19] suggested that reaction (1) takes place by the ligand exchanging of oxygen atoms within the Si-(O₂,Si₂) tetrahedron with a energy barrier at least 54kJ/mol. Reaction (2) takes place by inserting oxygen into a Si³⁺-Si¹⁺ bond with an activation energy of 125kJ/mol. The first exothermic decomposition of Si²⁺+Si²⁺ into Si¹⁺+Si³⁺ occurs rapidly at relatively low thermal annealing temperatures. Since the reaction kinetic barrier of reaction (2) is much higher than that of reaction (1), the second decomposition although also exothermic, however, would be much slower and need higher annealing temperature due to the high activation energy. Therefore, reaction (1) should dominate at low annealing temperature, and reaction (2) is more pronounced at higher temperatures. This is consistent with our XPS results as shown in Figure 4.12 and Figure 4.13.

Figure 4.12 and Figure 4.13 show the changes in the concentration of the five oxidation states in the SiO_{0.6} and SiO_{1.4} samples with annealing temperature as calculated according to the Gaussian fitting of the XPS spectra. It can be observed that upon annealing, there is a continuously increase in the concentrations of Si⁰ and Si⁴⁺ species, while a continuous decrease in the concentration of the Si suboxides. However, a further observation revealed that, for the Si suboxides, only the concentration of the Si²⁺ shows a continuous decrease within the wide range of annealing temperatures, whereas both the concentrations of the Si¹⁺ and Si³⁺ show a slight increase first when the annealing temperature is lower than 400°C, then decreased with a further increase in the annealing temperature. The first increase in the concentrations of Si¹⁺ and Si³⁺ could be due to the rapidly thermal decomposition reaction (1) at low annealing temperature. The resulted Si¹⁺ and Si³⁺ species will be decomposed into Si⁰ and Si⁴⁺ species according to thermal decomposition reaction (2) with a further increase in the annealing temperature, leading to the decrease in the concentration of Si¹⁺ and Si³⁺.

Figure 4.12 The changes in concentration of the five Si chemical states in the SiO_{0.6} sample as a function of annealing temperature obtained from the XPS analysis.

Figure 4.13 The changes in concentration of the five Si chemical states in the SiO_{1.4} sample as a function of annealing temperature obtained from the XPS analysis.

4.2.3 Valence band XPS spectra

Figure 4.14 shows the valence band XPS spectra of the SiO_{0.6}, SiO_{1.4} samples after annealing at various temperatures, respectively. The valence band XPS spectra of the as-sputtered counterparts and pure SiO₂ control sample are also presented for comparison purpose. The intensity of group D, which is representative the formation of Si nanoparicles, is absent in the SiO₂ control sample. However, it is clearly visible in the SiO_{0.6} and SiO_{1.4} due to the formation of Si nanoclusters. The intensity of group D in the as-deposited SiO_{0.6} is higher than that of the as-deposited SiO_{1.4}. The larger intensity of group D imply that the probability that a given Si is surrounded by other Si atoms has increased, so does the probability of interaction between silicon orbitals[11], which indicates that a larger-sized Si nanoclusters are formed. By comparing with their as-deposited counterparts, it is shown that there is an increase in the intensity of group D and a down shift of its position to low binding energy with increasing annealing temperature for both samples. Other changes in the spectral feature

are the increase in the intensity of group B and group C, especially group B, with annealing temperature for both samples. The increase in the intensity of group D is due to the growth of the Si nanoclusters because of thermal annealing. During annealing, the amorphous Si nanoclusters grow in consumption of the ‘free’ Si atoms in the SiO_x matrix by the classical diffusion growth mechanism or other mechanisms. On the other hand, as discussed above, the thermal decomposition of the Si suboxides during annealing can produce large amount of Si⁰ species, providing extra ‘free’ Si atoms. This also can promote the growth of the Si nanoclusters. The increase in the size of Si nanoclusters can also enhance the interaction between the Si 3p and the O 2s orbitals, thus leading to the increase in the intensity of group B. However, as there is almost no oxidizing reaction of the SiO_x films during rapid thermal annealing, the total amount of oxygen in the SiO_x is constant. Therefore the intensity of group A (O 2p lone-pair band) keeps unchanged.

Figure 4.14 Valance band XPS spectra of the SiO_{0.6} (a) and the SiO_{1.4} (b) after annealing at various temperatures; the valance band XPS spectra of the as-deposited samples and the pure SiO₂ control sample are also shown for comparison.

4.2.4 Crystallization of the excess Si

Figure 4.15 shows Raman spectra of Si_{0.6} and SiO_{1.4} samples after annealing at various temperatures, respectively. The Raman spectra of the as-deposited SiO_x samples and the SiO₂ control sample are also presented for comparison. It is apparent that the annealing leads to two types of variations in the Raman spectra. The first variation occurs when the annealing temperature is lower than 700°C. There is a strong increase in the intensity of the amorphous Si Raman features. The second variation occurs when the annealing temperature is higher than 700°C, characterizing by a decrease in the intensity of the TA and TO amorphous Si Raman band. As discussed above (XPS results), the thermal annealing leads to the great increase in the concentration of Si phase due to the thermal decomposition of Si suboxides. The increase in the intensity of the amorphous Si Raman features is due to the increase in the amount of amorphous Si phase during annealing as a result of the thermal decomposition of Si suboxides. The decrease in the intensity at high temperature is due to the transition of amorphous Si to crystalline Si when the annealing temperature goes up to 700°C.

Figure 4.15 Raman spectra of the SiO_{0.6} sample (a) and SiO_{1.4} sample (b) after annealing at various temperatures; the Raman spectra of the as-deposited samples and the pure SiO₂ control sample are also shown for comparison.

For the high Si concentration SiO_{0.6} sample, Both distinguishable TO band located at ~480 cm⁻¹, and TA band centered at ~160 cm⁻¹ are clearly visible for the as-deposited sample but absent in the SiO₂ control sample. And the intensity of the TO band is slightly higher than that of TA band, indicating amorphous Si nanoclusters with an size larger than Si₄₅ are already formed in the as-deposited SiO_{0.6} sample as discussed above. The intensities of the TO and TA band first increase with annealing temperature when the annealing temperature below 700°C and reach maximum at 700°C. The increase in the intensities of the TA and TO band is due to the increase in the concentration of amorphous Si phase because of the thermal decomposition of Si suboxides during annealing as shown in the XPS results. On the other hand, it can be noted that the increase in the intensity of the TO band is much higher than that of TA band with increasing annealing temperature, indicating an increase in the size of the amorphous Si nanoclusters. These Raman spectral features are consistent with our valance band XPS

analysis. Both the intensity of the TO band and the TA band decrease significantly when the annealing temperature is goes up to 800 °C. Distinguishable TO Raman band even disappear, instead of a broadening shoulder extending to 400 cm⁻¹. Both the TO and TA band disappear after annealing at 1100°C. It has been reported that the TO band at ~470 cm⁻¹ originates from the destruction of the short-range order of the silicon lattice, i.e., from the bonding between nearest-neighbor atoms of the silicon lattice[14], while the TA band at ~160 cm⁻¹ originates from the destruction of long- /or intermediate-range order of the Si lattice[14]. Thus the decrease in the intensity of the TO and TA band indicates an annealing-induced lattice relaxation process, which reduce the average bond-angle distortion, and improve the long-range order of the Si lattice. During annealing at 800~900 °C, it is quite possible that short-range-ordered Si nanoparticles are formed due to the decrease in the local band-angle distortion, leading to the strong decrease in the intensity of TO band. However, long-range-ordered nc-Si are still not available at these stages, this is why the intensity of the TA band is still very high. When the annealing temperature is higher than 1100°C, all the amorphous Si phase transits into crystalline Si. Both TO and TA bands disappear, indicating nanocrystalline Si with well defined lattice is formed.

For the lower Si concentration SiO_{1.4} sample, distinguishable TA and TO amorphous Si bands at around 160 and 480 cm⁻¹ can not be observed when the annealing temperature was below 300°C. This might be due to the concentration of the amorphous Si was too low, or the size of the initial Si nanoclusters was too small, therefore separated amorphous Si peaks can not be detected at this stage[15]. When the annealing temperature goes up to 400°C, a broad peak at ~160 cm⁻¹ appears as shown in **Figure 4.15** (b). However, separated amorphous Si peak at ~480 cm⁻¹ still not presented. The Raman spectra features almost keep unchanged even if the

annealing temperature increases to as high as 700°C. The availability of the distinct amorphous features on the Raman spectrum when the annealing temperatures are higher than 400°C is because an increase in amorphous Si concentration resulted from the thermal decomposition (or phase separation) of the Si suboxides, and the growth of the initial amorphous Si nanoclusters. The first increasing intensity indicated a continuity of the thermal decomposition with increasing annealing temperatures. The decreasing intensity of the amorphous Si phase after annealing at 800°C indicated that the amorphous Si have been partially transformed into crystalline Si. The same as SiO_{0.6} sample, fully crystallization occurs when the annealing temperature is higher than 1100°C.

4.2.5 TEM image

The formation of nanoscale particles in a network of amorphous SiO₂ matrix are directly confirmed with TEM as shown in Figure 4.16. High density and homogeneously distributed Si nanoparticles with nearly spherical shape in the amorphous matrix of SiO₂ are clearly visible in the TEM micrograph. The corresponding HRTEM image shows that these Si nanoparticles have well defined atomic lattices, indicating the formation of nc-Si. Their size ranged from 4 to 7 nm resulting in a mean crystal size of 5 nm in diameter.

Figure 4.16 TEM image of the SiO_{1.4} samples after rapid thermal annealing at 1100°C for 180s. The inset shows the HRTEM image of an individual Si nanocrystal. Spherical Si nanocrystals with well defined lattice are formed.

4.2.6 Conclusions

The thermal annealing leads to significant structural changes due to the lattice relaxation, defect annihilation and thermal decomposition of the Si suboxides. There are continuous increase in the concentrations of Si and SiO₂, while continuous decrease in the content of Si suboxides (Si₂O, SiO and Si₂O₃) with increasing annealing temperature due to the thermal decomposition of the Si suboxides. The decomposition of the Si suboxides takes place by two consequence decomposition reactions, $\text{Si}^{2+} + \text{Si}^{2+} \rightarrow \text{Si}^{1+} + \text{Si}^{3+}$ (1) and $\text{Si}^{1+} + \text{Si}^{3+} \rightarrow \text{Si}^0 + \text{Si}^{4+}$ (2). Decomposition reaction (1) dominated at the annealing temperature of 400 °C or lower, and decomposition (2) are more pronounced at high temperature. The Si nanoparticles are amorphous when the annealing temperature is lower than 700°C. These Si nanoparticles are partially crystallized and become short-range-ordered due to the reduction in the bond-angle distortion when the annealing temperatures reach 800~900 °C. Fully crystallized Si nanocrystals with well defined lattice are formed when the annealing temperature goes up to 1000°C or above.

4.3 Growth mechanism of Si nanocrystals

The growth of nc-Si has been generally thought to following the classical nucleation and diffusion growth mechanism in the literature. Such model has suggested that the nanocrystal growth is simply controlled by the diffusion of the Si atoms in the amorphous SiO_x matrix at annealing temperatures between 900°C and 1100°C as shown in Figure 4.17.

Figure 4.17 Schematic diagram of the diffusion-controlled growth mechanism for Si nanocrystal in the SiO_x.

4.3.1 The rapid growth mechanism

Providing the grain growth in this study also follows the diffusion controlled mechanism. Assuming a spherical silicon cluster radius r , the silicon diffusion coefficient as a function of temperature, T can be calculated by **Equation 2.6**. Based on the TEM results, the diffusion coefficient is calculated to be 1×10^{-14} cm²/s for the SiO_{0.6} under the annealing temperature of 1000°C. The calculated diffusion coefficient of Si in the SiO_x films is ~100 times higher that reported in literature (an average of 1.1×10^{-16} cm²/s at 1100 °C). On the other hand, by following the classical diffusion-controlled growth mechanism, for the SiO_x films annealing at low temperature, i.e., 700 °C, the diffusivity of Si in SiO₂ is less than the order of 10^{-19} cm²/s[21], thus for a 300 second treatment the diffusion lengths are only in the order of Angstrom. Such a short diffusion is not sufficient for the growth up of Si nanoclusters. These conclusions are inconsistent with our valance band XPS spectra and the Raman spectra after annealing at various temperatures, which show that the Si nanoclusters growth rapidly even if the annealing temperature is as low as 700°C. Based on the above discussion, it can be concluded that diffusion-controlled growth should not be the dominated growth mechanism in our SiO_x films. Thus other growth mechanism responsible for the rapid growth of the Si

nanoclusters should be considered. It should be point out that there are two Si resources available for the growth of the Si nanoclusters during annealing: the first one is the ‘free’ Si atom initially exist in the SiO_x matrix, and the other ones are the Si⁰ species decomposed from the Si suboxides. The contribution of the these ‘free’ Si atoms resource can be ignored as the long-range diffusion-controlled mechanism does not dominated the growth of the Si nanoclusters. However, thermal segregation of Si suboxides could provide rapid growth of Si nanoclusters, thus is considered the responsible mechanism. The segregation proceeds as percolation via ‘weak points’ in the form of ‘Si creaks’ or ‘Si breakdowns’ in SiO₂. This does not need long-range diffusion and are very rapid[21]. Note that there are large amount of amorphous Si nanoclusters in the as-sputtered SiO_x films, these Si nanoclusters can act as the nuclei, and forming the diffusion sink. The segregation of the Si suboxides allows the Si atoms join the diffusion sink by short-order diffusion, leading to the rapid growth of the Si nanoclusters.

4.3.2 Three-stage growth mechanism

Recalling the XPS and Raman spectra after annealing at various temperatures and based on the above discussion, the growth of nc-Si can be divided into three stages. Stage I occurs at annealing temperature of 400°C or lower, where decomposition reaction (1) dominates. The thermal decomposition of the suboxides takes place very slowly at the low temperatures, and there are small amount of decomposed Si atoms. There is only slight change in the microstructure of the SiO_x films during annealing, and the growth of the nanoclusters is not significant at this stage. It can be observed that there is only a slight increase in the Si⁰ concentration in the XPS spectra, and a slight increase in the intensity of the TA and TO amorphous Si Raman bands.

Stages II occurs at annealing temperatures between 400 °C and 700 °C. In this stage, the thermal decomposition of the Si suboxides proceeds rapidly as decomposition reaction (2) becomes pronounced. A large amount of Si phase is segregated during annealing. The percolated segregation behavior allows many Si atoms to join the diffusion sink of the initial Si nanoclusters by short-range diffusion, leading to rapid growth of these nanoclusters. Even so, as the annealing temperature of 700°C is not sufficient to overcome the energy barrier for crystallization of Si clusters, the Si nanoclusters remain amorphous. This stage is characterized by the fast increase in the Si⁰ concentration as shown in the XPS analysis and the strong enhancement in the TA and TO amorphous Si Raman band.

Stage III occurs at annealing temperature of 800 °C or above. In this stage, the increasing annealing temperature provides enough diffusion energy and increases the atomic mobility of Si. Two types of diffusion take place in this stage. The short-range diffusion of the Si atoms towards the nanoparticles together with further decomposition of the Si suboxides contributed to the growth of them; the diffusion of Si atoms inside the clusters transformed them into more compact crystalline Si with well defined atomic lattices, which lead to the formation of nc-Si in a surrounding of amorphous SiO₂ net work. At relative low temperature of 800~900°C, local short-range-ordered clusters are formed by the decrease in the bond-angle distortion. However, long-range-ordered Si nanocrystals with well-defined lattice are still not available. These structure changes are characterized by the strong decrease in the intensity of the TO band in the Raman spectra. As the annealing goes up to 1000~1100°C, such high annealing temperature can provide sufficiently energy to self-organize the amorphous Si nanoparticles into more compact nc-Si with well defined atomic lattices. On the other hand, it

is quite possible that additional nucleation occurs through heterogeneous nucleation at the pre-existing defect sites where the threshold for nucleation is reduced by the energy released through the annihilation of the defect during annealing. However, once nucleation occurs with the formation of critically sized nuclei, the Si cluster growth is governed by the same phase segregation process as discussed above.

4.3.3 Conclusions

The growth mechanism of nc-Si is believed to be different from the classical nucleation and diffusion growth model. It is suggested that thermal segregation of the Si suboxides could provide rapid growth of Si nanoclusters, thus is considered the responsible mechanism. The segregation proceeds as percolation via ‘weak points’ in the form of ‘Si creaks’ or ‘Si breakdowns’ in SiO₂. This does not need long-range diffusion and are very rapid[21]. The growth of nc-Si is divided into three stages. Stage I occurs at annealing temperature of 400°C or lower; stages II occurs at annealing temperatures between 400 °C and 700 °C; stage III occurs at annealing temperature of 800 °C or above.

4.4 Summary

X-ray photoelectron spectroscopy (XPS) analysis reveals that the as-deposited SiO_x films contain five Si chemical states (Siⁿ⁺, where n = 0, 1, 2, 3 and 4) in a wide composition range. Amorphous Si nanoclusters are already formed in the as-deposited SiO_x films, and they are embedded in the O-rich SiO₂ matrix. Their size is strongly determined by the Si concentration in the SiO_x films, i.e., the higher of the Si concentration, the larger of the amorphous Si nanoclusters. The physical origins of the formation of the amorphous Si clusters in the SiO_x films are related to the high kinetic energy of the sputtered Si atoms, and high surface

diffusivity. The atomic microstructure of amorphous SiO_x films has been proposed to contain Si cluster core with suboxides shell domains, which themselves embedded in the SiO₂ matrix.

The thermal annealing leads to significant structural changes due to the lattice relaxation, defect annihilation and thermal decomposition of the Si suboxides. There are continuous increase in the concentrations of Si and SiO₂, while continuous decrease in the content of Si suboxides (Si₂O, SiO and Si₂O₃) with increasing annealing temperature due to the thermal decomposition of the Si suboxides. The decomposition of the Si suboxides takes place by two consequence decomposition reactions, $\text{Si}^{2+} + \text{Si}^{2+} \rightarrow \text{Si}^{1+} + \text{Si}^{3+}$ (1) and $\text{Si}^{1+} + \text{Si}^{3+} \rightarrow \text{Si}^0 + \text{Si}^{4+}$ (2). Decomposition reaction (1) dominates at the annealing temperature of 400 °C or lower, and decomposition (2) are more pronounced at high temperature.

The growth mechanism of nc-Si is believed to be different from the classical nucleation and diffusion growth model. As such model can not explain the rapid (~100 times faster than that predicted by classic diffusion model) growth of the Si nanoparticles in this study. Thus other growth mechanism responsible for the rapid growth of the Si nanoclusters should be considered. It is believed that thermal segregation of the Si suboxides could provide rapid growth of Si nanoclusters, thus is considered the responsible mechanism. The segregation proceeds as percolation via ‘weak points’ in the form of ‘Si creaks’ or ‘Si breakdowns’ in SiO₂. This does not need long-range diffusion and is very rapid.

Chapter 5 Electrical Properties of the nanocomposite Films of Si Nanocrystals embedded SiO₂

In this chapter, the metal oxide semiconductor (MOS) structures based on the nanocomposite films of nc-Si embedded SiO₂ were fabricated. The current injection and transport behaviors of the nanocomposite films are investigated. Various current conduction mechanisms dominating in the MOS structure are discussed. The influence of charging trapping and de-trapping in the nc-Si on the charge transport behaviors is examined. The charge trapping and storage mechanism is studied in detail. In addition, the electric field-induced resistive switching memory effect is observed and the physical origins of the resistive switching are examined.

5.1 Current transport

5.1.1 Models of current conducting

Various carrier injection mechanisms and current transfer mechanisms in the SiO_x-based films have been proposed. And the major relevant processes of charge injection and transport are schematically shown in **Figure 5.1**. In the case of high electric fields the electrons can be injected into the oxide layer via Fowler-Nordheim (FN) tunneling (1). Traps and nanoclusters can enhance the carrier injection and current flow by trap-assisted tunneling, or by direct tunneling from the conduction band of the Si substrate to the nanoclusters, as well as by direct tunneling of carriers among the clusters (3). The defects in the oxide layer appear as electron traps in the band gap of SiO₂ and the carrier also can transport via traps by Poole-Frenkel (PF)

conduction (3).

Figure 5.1 Energy-band diagram demonstrating electron injection and transport in ideal MOS structure with silicon oxide containing defects and Si nanoclusters.

These charge injection and transport mechanisms may occur concurrently, and they may dominate the current conduction in the film at different stages depending on the magnitude of the electric field. At low voltage, the SiO₂ matrix behaves as insulator, the direct tunneling of carriers via Si nanocrystals dominates the current conduction when the applied voltage less than the barrier height $(\phi_b - E_0)/q$. Where ϕ_b is the potential barrier height at the nanocrystal/insulator interface, E_0 is the ground state energy where the zero energy is taken at the minimum of the Si conduction band at the interface between the Si substrate and the dielectric layer. However, when the applied bias increases to certain level, i.e., when the applied voltage is higher than $(\phi_b - E_0)/q$. FN injection occurs and starts to dominate the current conduction. FN tunneling is a popular conduction process in thermal grown SiO₂ film. Under strong electric field, the strong band gap bending leads to the formation of the triangular barrier at the interface between the substrate and the dielectric layer. Thus electrons can easily tunnel through the triangular barrier into the conduction band of SiO₂ as shown in **Figure 5.1**, i.e., under the strong gate bias, the FN tunneling of electrons from the vicinity of the Si

conduction band (or the electrode Fermi level) to the SiO₂ conduction band occurs. The FN tunneling is characterized by the rapid increase in the I - V characteristics. On the other hand, as there are high density of various trap sites (i.e. defects, Si nanocrystals) in the films, PF emission may occur concurrently with the direct tunneling and FN tunneling in a wide electric bias range. PF emission describes the thermal emission of electrons from a localized trap to the conduction band of a dielectric layer under the application of an external electric field. Under an external electric field, the barrier height on one side of the trap is lowered due to the band gap bending and the trapped electrons can escape from the trap to the conduction band due to the thermal excitation, and moving towards to the electrode along the conduction band as shown in **Figure 5.1**.

5.1.2 Current injection and transport mechanisms

The I - V characteristics of the reactive magnetron sputtered nanocomposite films are shown in **Figure 5.2**. Comparing with the I - V curve of the pure SiO₂ control sample shown in **Figure 3.5**, the conduction of the SiO₂ films containing nc-Si are strongly enhanced, i.e., the gate current is at the order of 10^{-12} A for the pure SiO₂ control sample, and an increase by ~ 4 -5 orders of magnitude is observed for the SiO₂ films containing nc-Si. The strong increase in current conduction is attributed to the formation of tunneling paths of Si nanocrystals in the films. Note that there are high density of nc-Si in the gate oxide layer, thus carrier tunneling can take place between adjacent nanocrystals. A large number of such nanocrystals distributed throughout the oxide can form many tunneling paths that could drastically increase the conductance of the gate SiO₂. Therefore, under the strongly positive gate bias, electrons can easily tunneling from the Si substrate to the nc-Si in the gate oxide. The electrons injected from the substrate can be easily transported to the top Al gate by nc-Si assisted conduction.

Figure 5.2 The I - V characteristics of the SiO_{1.0} and SiO_{1.4} samples after annealing in Log-Log scale.

The I - V curve can be generally divided into three regions depending on the magnitude of the gate voltage, i.e., a low gate voltage region, a middle gate voltage region and a high gate voltage region as shown in **Figure 5.2**. In the low gate voltage region, the gate current increases slowly with the gate bias and the I - V curves show straight lines in the log-log scale plot. In the middle gate voltage region, there is a slightly increase in the slope of the I - V curve, indicating a slightly increase in the current conduction in the film. And in the high gate voltage region, a rapid increase in the gate current can be observed, indicating a sudden increase in the conductance of the films. Our observations show good agreement with the conduction behaviors of nc-Si embedded SiO₂ films reported in literature. For example, Wong et al[1] reported that the conduction mechanism in their SiO₂ films embedded with nc-Si synthesized with ion implantation technique follows the nanocrystal-assisted conduction (i.e. direct tunneling, Poole-Frenkel emission) and the nanocrystal-assisted Fowler-Nordheim tunneling depending on the magnitude of the gate bias. It is quite possible that the

mechanisms of carrier injection in our device may involve three contributions which are nc-Si-assisted direct tunneling in the low gate voltage region, nc-Si-assisted Pool-Frenkel emission in the middle gate voltage region and nc-Si-assisted Fowler-Nordheim tunneling in the high gate voltage region as shown in **Figure 5.3**.

Figure 5.3 Schematic diagram of the current conduction in the SiO₂ films embedded with Si nanocrystals under different gate bias.

At low voltage, there is a small band gap bending, and the current conduction is due to the direct tunneling between the nanocrystals that are separated from each other by SiO₂ as shown in **Figure 5.3**. This nc-Si-assisted direct tunneling conduction behavior can be characterized by a power-law behavior in the I - V characteristics

$$I = I_0 V^\zeta \quad 5.1$$

where I is the current, V is the voltage, ζ is the scaling exponent and I_0 is a coefficient[2]. The power-law behavior could be explained by a model similar to the one of collective charge transport in arrays of normal-metal quantum dots[2]. The values of the two parameters I_0 and ζ for the both I - V curves are presented in **Figure 5.4**. It can be seen that both samples agree well with power-law fitting in the I - V characteristics when the gate bias is lower than 10 V.

Both I_0 and ζ in Si_{1.0} sample is higher than that in SiO_{1.4} sample. As these two parameters reflect the conductance of the materials system, it should increase when more tunneling paths are formed with higher Si concentration. In other words, a larger I_0 and ζ means a large number of the percolative tunneling paths formed by the Si nanocrystals distributed in the SiO₂ matrix. As there is higher density nc-Si formed in the SiO_{1.0} sample than that in the SiO_{1.4} sample due to its higher Si concentration, so the conductance of the SiO_{1.0} sample is much higher than that in the SiO_{1.4} sample.

Figure 5.4 Power-law fitting of the I - V characteristics of the SiO_{1.0} and SiO_{1.4} samples; the dots are the experimental data and the solid lines are the power-law fitting results.

As the bias increases to the middle gate voltage region, the potential barrier of an electron in the conduction band of nc-Si can be modified by PF effect due to the large band bending of SiO₂ at high gate voltage, i.e., the barrier height on one side of the defect trap is lowered and the trapped electrons can escape from the trap to the conduction band of the SiO₂ matrix due to the thermal excitation, moving toward to the electrode along the conduction band. This process is considered as the nc-Si-assisted PF emission as illustrated in **Figure 5.3**. As the

energy barrier for the nc-Si-assisted PF emission is much lower than that nc-Si-assisted FN tunneling. Thus it is quite possible nc-Si assisted PF emission may dominate the current conduction at the middle range gate voltage.

As the gate voltage increases to a sufficiently high level, serious electric field-induced band gap bending occurs, and the electrons in nc-Si can tunneling through the triangle oxide barrier to the conduction band of the SiO₂ and finally reach the gate electrode. This process is considered as the nc-Si-assisted Fowler-Nordheim (FN) tunneling and is illustrate in **Figure 5.3(c)**. With this process the carrier conduction is rapidly enhanced as can be seen from **Figure 5.2** that there is a rapid increase in the gate current in the high gate voltage region until the breaking down of the device. Note that the nc-Si-assisted FN tunneling can occur concurrently with other nc-assisted conduction process (e.g. direct tunneling, Frenkel-Poole emission) at the high voltage.

5.1.3 Conclusion

The formation of nc-Si can strongly enhance the conductance of the nanocomposite films of nc-Si embedded SiO₂. It is shown that the nc-Si-assisted conduction (i.e. direct tunneling, Poole-Frenkel emission) and the nc-Si-assisted FN tunneling contribute to the current conduction depending on both the nc-Si concentration and magnitude of the gate bias. The direct tunneling via the nc-Si dominates the current conduction at low gate voltage, the nc-Si-assisted Frenkel-Poole emission dominates at the middle range gate voltage and the nc-Si-assisted FN tunneling dominates at high gate voltage.

5.2 Charging/discharging effect on the current transport

The memory effect is based on the charging and discharging of the nc-Si embedded in the gate oxide. Charging/discharging in nc-Si usually lead to the flat-band voltage shifts in the capacitance-voltage characteristics. However, the charging and discharging of the nc-Si will strongly influence the charge transport in the films[3, 4]. In this section, we report the influence of charging and discharging of nc-Si on the I - V characteristics of the MOS structures. It is shown that charge trapping in the nanocrystals can reduce the tunneling current dramatically, which can be explained in terms of the breaking of the nc-Si tunneling paths. On the other hand, the trapped charges can also tunnel out of the Si nanocrystals, leading to the recovery of the current.

5.2.1 Electric stress-induced changes in the conductance

Figure 5.5 shows the I - V characteristics of the MOS structure based the nanocomposite films before (i.e. the virgin sample) and after applying electric stress of -10 V and 10 V for 5s. Note that the maximum voltage of the I - V measurement was set to 5 V, which is low enough to avoid any charging/discharging effect caused by the electrical measurement itself. As can be seen in **Figure 5.5**, the repeated measurements did not cause a significant change in the I - V characteristic. This indicates that no significant charging or discharging in the nc-Si occurs during the I - V measurement and the conduction of the nanocomposite films was not affect by the measurement itself. However, after an application of electric stress of -10 V for 5s, the I - V characteristic is found to change drastically. As can be seen in **Figure 5.5**, the current is reduced by more than 10 times after the application of the negative electric stress. The reduction in the gate current indicates a large increase in the DC resistance (or decrease in the

conductance) of the Si nanocomposite film. However, the gate current is recovered back to the virgin case after an application of 10 V for 5s on the same pad, indicating a decrease in the DC resistance (or increase in the conductance).

Figure 5.5 *I-V* characteristics of the MOS structure before (i.e. the virgin case) and after applying electric stress of -10 V and +10 V to MOS structure for 5 s.

The increase in the DC resistance can be explained in terms of the breaking of some tunneling paths due to charging in the nc-Si caused by the electric stress. As-discussed previously, in the nc-Si distributed region, the electron conduction can take place between adjacent uncharged nc-Si via tunneling or other mechanism under external electric field as shown in **Figure 5.6**. Charge trapping occurs when the injected carriers are transported along the tunneling paths. The injected carriers could be trapped in the individual Si nanocrystals. On the other hand, as there exist a large amount of defects at the interfacial regions between the embedded nc-Si and the SiO₂ matrix[5], the carriers could also be trapped in these defects [6]. In either case, charge trapping is associated with the existence of the nc-Si.

Figure 5.6 Schematic diagram of the formation of the tunneling paths due to discharging (a) and breaking of the tunneling paths due to the charging.

The charge trapping, in turn, affects the carrier transport across the oxide layer in a number of ways: firstly, charge trapping in an nc-Si or a defect increases the resistance of the tunneling paths involving the nc-Si or the defect due to the electrostatic interaction of the transported carriers with the trapped carriers. Secondly, the tunneling paths related to the charged nc-Si could be broken due to Coulomb blockade [4]. Therefore, charge trapping will suppress the carrier transport across the oxide layer. Under the strong negative stress, holes from the p-type Si substrate and electrons from the Al gate are easily injected into the films. Some of the injected carriers could be trapped in the nc-Si associated trapping centers, leading to the reduction of the gate current. The recovery after the application of positive electric stress is

due to the release of some of the charges trapped. Under positive gate stress, electrons and holes are injected into the gate oxide, filling the trapping centers. On the other hand, some of the holes and electrons trapped under previous negative stress are now pushed back to the Si substrate and the Al gate, defilling the charge trapping centers. However, because of the low injection efficiency of holes from Al electrode and electrons from the electron minority p-type Si substrate, the defilling process overwhelms the filling process. Thus charged nc-Si associated trapping centers are released, leading to the recovery of the tunneling paths.

As discussed above, the negative electric stress allows charging up of trapping centers associated with nc-Si. Charge trapping of these centers has been confirmed by the C - V characteristics as shown in **Figure 5.7**. Application of a negative electrical stress of -10 V for 5s leads to a large positive flat band voltage shift in the C - V characteristic, indicating a large amount of electrons trapped in these centers. On the other hand, the flat band voltage shift can be recovered by applying of a positive electrical stress of +10 V for 5s.

Figure 5.7 Flat band voltage shift of the SiO₂ film embedded with nc-Si before (i.e. the virgin sample) and after application of opposite electric stress -10 V and +10 V for 5s.

5.2.2 Influence of the duration of the electric stress

To examine the influence of the duration of the electric stress on the charging/discharging effect, a sequence of electric stresses of -10 V were applied on a fresh new pad for 5s following a second electric stress of -10 V for 300s after the initial *I-V* measurement. **Figure 5.8** shows the *I-V* characteristics of the MOS structure before (i.e. the virgin sample) and after applying the electric stress of -10 V for 5s and a second electric stress of -10 V for 300s, respectively. The application of the first electric stress of -10 V on the pad for 5s leads to the gate current decrease from the order of $\sim 10^{-6}$ A for the virgin case to the order of $\sim 10^{-8}$ A. And the second application of -10 V on the same pad for 300s leads to a further decrease in the gate current to the order of $\sim 10^{-9}$ A. This indicates that an increase in the duration of electric stress can lead to a further charging up of the nc-Si, resulting in a further decrease in the gate current.

Figure 5.8 *I-V* characteristics of the MOS structure before (i.e. the virgin sample) and after applying electric stress of -10 V to the MOS structure for 5s and a second electric stress of -10 V for 300s.

5.2.3 Influence of magnitude of the electric stress

To examine the influence of the magnitude of the electric stress on the charging/discharging effect, a sequence of electric stresses of -15 V and 15 V were applied on a fresh new pad after the initial I-V measurement. **Figure 5.9** shows the *I-V* characteristics of the MOS structure based on the Si nanocomposite films before (i.e. the virgin sample) and after applying the electric stress of -15 V and 15 V for 5s. The *I-V* curve after the application of electrical stress of -10 V for 5s is also presented for comparison. The application of -15 V on the pad leads to a further decrease in the current comparing with the application of -10 V. It can be observed that the current is decreased from the order of 10^{-5} A for the virgin sample to the order of 10^{-7} A for the sample after applying the electric stress of -10 V for 5s, and the current is further decreased to the order of 10^{-9} A for the device after applying the electric stress of -15 V for 5s. This indicates that an increase in the magnitude of electrical stress can lead to a further charging up of the nc-Si, resulting in a further decrease in the gate current. However, a second application of electric stress of 15 V can release the charged nc-Si, recovering the conductance of the device.

Figure 5.9 *I-V* characteristics of the MOS structure before (i.e. the virgin sample) after applying electric stress of -10 V, -15 V and +15 V to the MOS structure for 5s.

5.2.4 Conclusion

In conclusion, a phenomenon of electric stress-induced changes in the current conduction from the nanocomposite films of nc-Si embedded SiO₂ synthesized by reactive magnetron sputtering is observed. The negative electric stress leads to the charge up of the nc-Si, while the positive electric stress lead to the release of the charges. The decrease in the conductance of the oxide is due to the strong charging up of the nc-Si associated trapping centers and the recovery of the conductance is due to the release of the charges under positive electric bias. An increase in the duration or magnitude of the electric stress can lead to a further increase in the charging/discharging effect. The phenomenon that the oxide resistance (or oxide conduction) can be changed by the external electric stress can be used in a new type two-terminal memory device application where information can be stored as a high- or low-resistance state. The memory could be programmed with a negative electric stress for a short duration and erased with a positive electric stress.

5.3 Charge trapping mechanism

For the application of nonvolatile memory device, a long charge retention time is critical and necessary. To achieve the long retention time, the charge storage behavior during charge retention mode should be well understood. However, to date, the understanding of the charge trapping and retention mechanism in Si nanostructures is still unclear. Several models for long-time charge trapping mechanism have been proposed, including the quantum size effect of nc-Si and interfacial oxygen-related defects traps between the nc-Si and the SiO₂ matrix[6-8].

5.3.1 Charging trapping in the XPS measurement

The charge trapping and storage mechanism in the nanocomposite films of nc-Si embedded SiO₂ are usually characterized by the electrical characterization techniques, i.e., *I-V* and *C-V* measurements. However, these studies by the pure electrical characterization are seldom correlated to the microstructure of the films. In this section, an alternative approach, X-ray photoelectron spectroscopy (XPS) technique was employed to study the charge storage mechanism in the Si nanocomposite films. XPS is a sensitive surface analysis technique to characterize the chemical structure of materials. During the XPS measurement, the samples are irradiated by monochromatic soft x-rays and characteristic kinetic and binding energies of emitted core electrons are measured. The kinetic energy of the photoelectron is the difference between the energy of final excited state and the initial ground state of the particular electron in the core-level. However, the knocking of a photoelectron from the sample surface will leave a hole with positive charge in the core-level as shown in **Figure 5.10**. As a result, the XPS spectra are taken for the system with positive charges rather than the neutral state. The

photoionization process can be expressed as

where $E(A)$ is the energy of isolated neutral atom at the initial ground state, $h\nu$ is the energy of X-ray photon, $E(A^+)$ is the energy of the positive charged ion in the final excited state and $E(e^-)$ is the kinetic energy of the photoelectron.

Figure 5.10 Schematic diagram of the X-ray radiation-induced charging during the XPS measurement.

It is essential to point out that the energy of the final state is taken from the charged ions rather than neutral atoms. With one photoelectron emission, the system is left a hole with a unit of positive charge. The net buildup of positive charges in deep core near the nucleus is energetically unfavorable. The positive charges will lead to the peak position shift to a higher binding as well as peak shape broadening. In fact, this charging effect on the XPS spectrum can be minimized by some charge compensation techniques, i.e. a low energy electron flood gun can be applied on the sample surface and act as charge neutralizer during the XPS measurement to compensate the positive charges as shown in **Figure 5.10**.

5.3.2 Charge trapping sites in nanocomposite films

It has been reported that the X-ray radiation will leave positive charges in the nc-Si/a-SiO₂ system due to photoemission[9, 10]. These charges may be trapped in the nc-Si, in the defects at the interfacial region between the nc-Si and SiO₂ matrix or the defects in the SiO₂ matrix. In all cases, the charging effect can cause the core-level to shift to a higher binding energy [11, 12]. As-discussed in Chapter 4, there are high concentrations of Si suboxides in the nc-Si embedded SiO₂ films even after high temperature annealing, and these Si suboxides mainly exist at the interfacial regions between the nc-Si and the SiO₂ matrix. The Si suboxides potentially contain high density of various oxygen-related defects. These defects were reported to be the weak oxygen bond (O-O)[13], the neutral oxygen vacancy ($\text{O}_3\equiv\text{Si}-\text{Si}\equiv\text{O}_3$, where $\equiv$ represents the bonds to three oxygen atoms)[13], E'_8 center ($\text{O}_3\equiv\text{Si}\cdot+\text{Si}\equiv\text{O}_3$, where $\cdot$ represents an unpaired electron and $+$ is a trapped hole)[14] and the non-bridging oxygen hole center ($\equiv\text{Si}-\text{O}\cdot$)[15]. On the other hand, the magnitude of the charging-induced core-level shift strongly depends on the concentration of the nc-Si and the oxygen-related defects. Thus, by examining changes in core-level shift caused by the photoemission-induced charging effect versus density of Si nanocrystals and the concentration of Si suboxides at the interfacial regions, the charge storage mechanism can be clarified. In addition, with this method, the charging mechanism can be interpreted by correlating with the microstructure. The variation in the density of Si nanocrystals and the concentration of Si suboxides can be mainly achieved by varying the Si concentrations in the SiO_x films.

5.3.3 Charge trapping mechanism characterization

In order to minimize the influence of experimental setup (i.e. the variation in sample focusing,

detection position or surface contamination of the different samples with various Si concentrations) on the charging effect during XPS measurement, a single sample containing various Si concentrations is preferred. In this study, a SiO_{1.5}/SiO_{0.3}/SiO_{1.5} sandwich structure was synthesized by reactive magnetron sputtering to deliberately achieve various concentrations of nc-Si and Si suboxides (potentially contain high density of oxygen-related defects). By XPS depth profiling of the sandwich structure with the Ar⁺ ions gun, we are able to obtain the XPS spectra with various Si concentration. By examining the changes of charging effect versus the depth distributions of nc-Si and Si suboxides, the charge trapping mechanism can be clarified. The above processes are performed with the charge neutralizer in off state.

The SiO_{1.5}/SiO_{0.3}/SiO_{1.5} sandwich structure was synthesized by reactive magnetron sputtering similar with that of single layer SiO_x films. During deposition, the radio frequency (13.6 MHz) target power was fixed at 150 W. The process pressure and the Ar flow rate were fixed at 0.5 Pa and 80 sccm, respectively. First, the oxygen flow rate was set at 1.5 sccm to deposit the 10 nm relatively low Si concentration bottom layer. Immediately after that, the shutter (between the substrate and the target) was closed and the oxygen flow rate was changed to 0.5 sccm. A waiting time of 10 minutes was respected to achieve the desired stable Ar/O₂ ambient before sputtering the 10 nm high Si concentration middle layer. Finally, the shutter was closed again and the oxygen flow rate was changed back to 1.5 sccm. The 10 nm low Si concentration top layer was deposited after another waiting time of 10 minutes. A pure a-SiO₂ control sample was also deposited by setting the oxygen flow rate at 3.0 sccm. Thermal annealing was carried out in Ar ambient at 1100 °C for 180 seconds.

Figure 5.11 shows the cross-sectional TEM micrograph of the sandwich structure. Nearly spherical-shaped nc-Si in the amorphous matrix of SiO₂ are clearly visible in the HRTEM micrograph. There are densely stacked nc-Si in the high Si middle layer and isolated nc-Si in the low Si top and bottom layer. The nc-Si size ranged from 3 to 5 nm resulting in a mean crystal size of 4 nm in diameter.

Figure 5.11 TEM micrograph of the SiO_{1.5}/SiO_{0.3}/SiO_{1.5} sandwich structure.

5.3.4 Charging trapping mechanism by XPS depth profiling

Figure 5.12 shows the Si 2p core-level spectra from the surface of the sandwich structure which was embedded with nc-Si and the pure SiO₂ control sample, respectively. The charging effect induced by the photoemission can be clearly observed by the Si⁴⁺ core-level shift. The Si⁴⁺ 2p core-levels shift to higher binding energy by 0.6 eV and 1.8 eV for the pure SiO₂ sample and the sandwich structure, respectively. Since Si⁴⁺ is the host material in the nc-Si/SiO₂ system under study, therefore, the Si⁴⁺ shift is used for monitoring the charging effect in the system during depth profiling. The introduction of the nc-Si into the SiO₂ can

shift the core-level to higher binding energy by 1.2 eV, which indicates that the charging capability of the nanocomposite film of nc-Si embedded SiO₂ is greatly enhanced comparing with that of the pure SiO₂. However, it is reported that for the nc-Si/a-SiO₂ system, the charges can be trapped either inside the nc-Si or the defects in the suboxides. As at the same time that the nc-Si is introduced into the SiO₂, a large amount of Si suboxides (Si₂O, SiO, Si₂O₃) which potential contain high density of oxygen related-defects were also produced. By depth profiling of the SiO_{1.5}/SiO_{0.3}/SiO_{1.5} sandwich structure, we are able to obtain the distribution of the nc-Si and Si suboxides. By monitoring the changes of the charging effects versus the concentration of nc-Si and Si suboxides, one may be able figure out the charge trapping mechanisms of the nc-Si embedded SiO₂ systems.

Figure 5.12 Si 2p core-level spectra obtained from the surface of the SiO_{1.5}/SiO_{0.3}/SiO_{1.5} sandwich structure and the pure SiO₂ control sample.

Figure 5.13 shows the Si 2p XPS spectra of the sandwich structure at different depths. The Si 2p XPS spectra are deconvoluted into five Gaussian peaks according to the deconvolution procedures described in Chapter 3. **Figure 5.13** (a), (b), (c) and (d) show the Si 2p core-levels

at the depths of 2 nm, 8 nm, 12 nm and 22 nm, respectively. The total Si concentration is calculated to be ~40at.% in both the low Si top and bottom layer, and increase to ~76at.% in the high Si middle layer. The Si 2p spectrum shown in **Figure 5.13** (b) (at the depth of 8 nm) is speculated to be obtained at the interface between the top layer and the middle layer. The XPS analysis indicates that various nc-Si and Si suboxides concentrations are achieved by the SiO_{1.5}/SiO_{0.4}/SiO_{1.5} sandwich structure.

Figure 5.13 Si 2p core-level spectra of the sandwich structure obtained at the depth of 2 nm (a), at the depth of 8 nm (b), at the depth of 12 nm (c) and at the depth of 22 nm (d)

As can be observed from **Figure 5.13**, not only the total Si concentration changes with the depth, but the peak areas of the five oxidation states also change, showing that the concentrations of the five oxidation states vary with the depth. The depth distribution of the relative concentration of each oxidation state can be obtained by calculating the ratio of $I_{Si^{n+}}/I_{total}$ ($n = 0, 1, 2, 3$ and 4) at various depths, where $I_{Si^{n+}}$ is the peak area of the oxidation state Si^{n+} and I_{total} is the total area of the Si 2p peaks. The sum of the relative concentrations of

Si suboxides (Si₂O, SiO and Si₂O₃) and nc-Si (Si⁰) versus the depth are shown in **Figure 5.14**. From the depth distribution of the Si suboxides and the nc-Si, one can observe that different concentrations of nc-Si and Si suboxides along depth have been achieved in our SiO_{1.5}/SiO_{0.3}/SiO_{1.5} sandwich structure. The majority Si atoms in the low Si top and bottom layer have been oxidized into SiO₂, leaving only small amount of Si suboxides and low density of nc-Si, while there are high concentration of Si suboxides and high density of nc-Si in the high Si middle layer. For example, the concentrations of the nc-Si are ~9at.% in the low Si top and bottom layer, ~51at.% in the high Si middle layer, and the concentrations of the Si suboxides are ~16at.% in the top and bottom layer, ~36at.% in the middle layer.

Figure 5.14 Binding energy shifts of Si⁴⁺ and Si⁰ species relative to the references at various depths, the squares and circles represent the Si⁴⁺ shift and Si⁰ shift, respectively. The depth profiling of the Si suboxides and nc-Si concentrations is included for comparison, the triangles and stars represent the nc-Si concentration and Si suboxides concentration, respectively.

Besides the concentrations of the five oxidation states, the binding energy of each oxidation state can also be obtained from the peak deconvolution. The core-level shift of Si⁴⁺ relative to the reference[12] (Si 2p in pure SiO₂) as a function of the depth is shown in **Figure 5.14**. To

clarify the charging mechanism in the system, the binding energy shift of nc-Si (Si^0) relative to reference (bulk Si) is also included in **Figure 5.14**. For the binding energy shift of the nc-Si, besides the charging effect, the quantum confinement effect of charges in the nc-Si can also shift its core-level to higher binding energy as discussed later. The binding energy shifts of both Si^{4+} and nc-Si demonstrate the same trend in **Figure 5.14**. The Si^{4+} and the nc-Si shifts are ~ 1.9 eV and ~ 1.3 eV, respectively, in the low Si top layer, but both decrease almost to zero in the high Si middle layer, and then increase again in the low Si bottom layer, returning to the same level as in the top layer. However, an increase in the concentrations of the Si suboxides in the middle layer can be observed in **Figure 5.14**. One may expect that there should be also an increase in the binding energy shift in the middle layer if the charges are trapped in the Si suboxides. The opposite trend of the binding energy shift with depth distribution of Si suboxides enables us to exclude the defects-related trapping mechanism in our films. Therefore it is speculated that the enhanced charging capability of our films is due to the formation of nc-Si.

But, one also should note that there is also no always consistent between the binding energy shift and the nc-Si concentration. A nc-Si concentration depended binding energy shift has been observed in **Figure 5.14**. As can be observed, there is strong charging effect in the low Si top and bottom layers which contain low density of nc-Si. While both the Si^{4+} and Si^0 shift decrease with increasing nc-Si concentration, and almost vanished when a densely stacked nc-Si layers are formed in the high Si middle layer. It is suggested that the charging effect is reduced with increasing nc-Si concentration. The effect of the nc-Si distribution on the charging effect can be explained in terms of the charges diffusion as illustrated in **Figure 5.15**. Charging diffusion can take place due to the charge transfer from the charged nc-Si to the

adjacent uncharged nc-Si by tunneling or other transport mechanisms[16]. In the high Si middle layer densely stacked nc-Si layers may be formed. The charge induced by the photoemission can easily diffuse out to the nc-Si that are not under the X-ray illumination, and thus the charge can be dissipated quickly, leading to a drastic reduction in the charging effect in this region.

Figure 5.15 Illustration of charge diffusion from the charged nc-Si to the adjacent uncharged nc-Si.

Assuming the photoemission-induced charges are trapped in the nc-Si. This charging effect will shift the Si 2p core-levels of all Si species to higher binding energy by the same amount. However, for the nc-Si, charge trapping in the quantum dot will cause a self charging energy (because of quantum confinement effect) which lead to an extra shift of the Si⁰ core-level to higher binding energy besides the charging effect. It is well known that the charging of quantum dot with one elementary charge will cause a self-charging energy $E_c = e^2/2C_{\text{dot}}$ where e is the elementary charge of 1.6×10^{-19} coulomb, and C_{dot} is the self-capacitance of the nc-Si[11]. This self-charging energy will shift the Si⁰ core-level to higher binding energy by E_c . The self-charging energy is calculated to be 0.12 eV for a 3 nm nc-Si, and decreases to 0.08 eV for a 5 nm nc-Si[11]. As the photoemission-induced charging effect and the self-charging energy (because of quantum confinement effect) of the nc-Si both

could shift the Si⁰ core-level to a higher binding energy independently, the Si⁰ shift would be larger than that of Si⁴⁺. That is why the nc-Si shift is slightly larger than that of Si⁴⁺ in the high Si middle layer. This phenomenon also confirms our assumption that the charge trapping in the nc-Si is dominant in our film. For these nc-Si distributed in the low Si top and bottom layer, they are separated from each other with a larger spacing due to the low concentration, thus the charge diffusion is much more difficult to take place. Therefore, the charging effect is much more significant in these two regions.

As discussed above, for Si⁰, besides the charging effect, the quantum size effect of nc-Si will increase the Si⁰ shift, one may also expected a higher binding energy shift of Si⁰ than that of Si⁴⁺ in the low Si top and bottom layer. However, quite contrarily, a smaller binding energy shift of Si⁰ than that of Si⁴⁺ is always observed in these two regions as shown in **Figure 5.14**. This can be interpreted by the differential charging (electrostatic charging) effect between the nc-Si and the oxide matrix[9, 12]. Differential charging always occur when the sample is partial (semi)conducting and partial insulating under X-ray radiation. This differential charging usually leads to the variation in Si⁴⁺-Si⁰ shift with different Si concentration[9, 10, 12]. Note that the kinetic energy of the photoelectrons under X-ray radiation can be simply written as

$$E_K = h\nu - E_B - \phi_S - q\phi \quad 5.3$$

where $h\nu$ is the x-ray energy, E_B is the binding energy, ϕ_S is the work function of the electron spectrometer, q is the electronic charge, and ϕ is the surface potential.

Since the experiments were performed using the same spectrometer, thus the effect of the spectrometer work function (ϕ_S) on the Si⁴⁺-Si⁰ shift should be negligible. Therefore, it can

only be differences in the material surface potential that can contribute to Si^{4+} - Si^0 shift. When characterizing nc-Si/SiO₂ system, one usually assumes that the surface potential is the same for Si^0 and Si^{4+} . However, the differential charging lead to the surface potential differences between Si^0 and Si^{4+} , thus the Si^{4+} - Si^0 shift in the nc-Si/SiO₂ system not only determined by the their chemical shift, but also their surface potential differences. The positive charges lead to the reduction in Si^0 surface potential, while the increase in Si^{4+} surface potential, equivalent to a reduction in Si^0 binding energy and an increase in Si^{4+} binding energy. It has been reported by many researchers that the Si^{4+} - Si^0 shift may vary from 3.5 -5.0 eV, depending on the nc-Si concentration in the films [9, 10, 12]. The Si^{4+} - Si^0 shift decrease with increase nc-Si concentration, and will be the same as that of bulk reference samples when densely stacked nc-Si are formed. The changes of Si^{4+} - Si^0 shift with nc-Si concentration can be employed to interpret why there is no always consistency between the binding energy shift of Si^0 and Si^{4+} along the depth.

Figure 5.16 shows the Si^{4+} - Si^0 chemical shift versus depth of the sandwich structure, and the depth distribution of nc-Si also included for comparison. The Si^{4+} - Si^0 shift is ~4.4 eV, in the low Si top and bottom layer which contain low density of nc-Si. However, densely stacked nc-Si are formed in the high Si middle layer, and the Si^{4+} - Si^0 shift is almost the same as the bulk references. The charging effect cause almost the same core-level shift of both Si^0 and Si^{4+} , while the quantum size effect of nc-Si lead to the core-level shift slightly larger than that of Si^{4+} .

Figure 5.16 Si⁴⁺-Si⁰ shift versus depth. The depth distribution of nc-Si is included for comparison.

5.3.5 Conclusion

In conclusion, the charge storage mechanism in the nanocomposite films of nc-Si embedded SiO₂ is studied by X-ray photoelectron spectroscopy (XPS) technique by correlating with its microstructure. Various concentrations of Si suboxides and Si nanocrystals (nc-Si) have been realized by sputtering deposition of SiO_{1.5}/SiO_{0.3}/SiO_{1.5} sandwich structure. The X-ray radiation shifts the Si 2p core-levels to higher binding energy due to the photoemission-induced charging effect. The nc-Si concentration dependent charging effect and the quantum charging effect were observed, which demonstrates that the nc-Si plays a dominant role in the charge trapping mechanism in the nc-Si/a-SiO₂ system.

5.4 Resistive switching effect in the nanocomposite films

Electric field-induced resistive switching effect has drawn extensive research due to its potential applications in next generation non-volatile resistance random access memories

(RRAM)[17, 18]. The resistive switching behavior is characterized by extreme change of resistance between the high resistance state (HRS) and the low resistance state (LRS) in the current-voltage (I - V) characteristics, corresponding to the ON and OFF states for logic signals. There are two kinds of resistance switching modes in which the devices are switched ON (set) or OFF (reset) by applying two voltages either with the same polarity or with the opposite polarity. Two main switching schemes can be distinguished as shown in **Figure 5.17**: unipolar and bipolar switching. In case of unipolar resistive switching, switching to the low resistance (on) state, i.e. writing the cell, occurs under the same voltage polarity as switching to the high resistance (off) state, i.e. erasing the cell. In case of bipolar switching, writing and erasing occur under different polarities. If V_{write} is positive, V_{erase} is negative and vice versa.

Figure 5.17 Typical unipolar switching (a) and bipolar switching behavior (b) [19].

Although the physical origin of the resistive switching is still an open question, various switching models have been proposed, in which the most popular one is the conducting filament model[17, 18] as shown in **Figure 5.18**. In the regime of conducting filament model, the devices need a so-called forming process, which makes an initial resistance lower by means of an electric stress. Under the strong electric stress, the defects/metallic ions align to form conductive filaments in HRS, leading to the transition to the LRS. The conduction in the LRS exhibits Ohmic behavior as the current can be transported via the metallic filaments.

After reset switching, the conducting filaments could be ruptured by Joule heating effect, and the devices turn back to the HRS. Besides, other models included Schottky barrier model[20] and trap-controlled space-charge-limited current (SCLC)[21] are also proposed to interpret the bipolar switching effect.

Figure 5.18 Schematic diagram of filamentary conduction; (a) Vertical stack configuration; (b) lateral, planar configuration. The red tube indicates the filament responsible for the ON state[19].

Recently, a resistive switching behavior in the Si-rich oxide (SiO_x) films synthesized by e-gun evaporation has been observed by Tsai et al[22]. The resistive switching was attributed to the charge trapping induced band bending, which significantly influenced the carriers transport in the SiO_x films. However, their models can not explain the sudden increase/decrease in the current conduction. Therefore, a more detail study concerning the physical origins is desirable. In this section, a reproducible bipolar resistive switching phenomenon from an Al/nc-Si:SiO₂/Si MOS structure is demonstrated with a colossal resistive switching ratio of $\sim 10^5$ times. The resistive switching is explained by a combined model of conductive filament of oxygen vacancies and electronic barrier at the SiO_x/Si substrate interface.

5.4.1 Resistive switching effect

Figure 5.19 shows the bi-stable switching characteristics of the Al/nc-Si:SiO₂/Si/Al structure at room temperature. By sweeping the voltage ($0\text{ V} \rightarrow +V_{\text{max}} \rightarrow 0\text{ V} \rightarrow -V_{\text{max}} \rightarrow 0\text{ V}$, indicated by arrows), a conspicuous I - V hysteresis is observed. No electroforming process is required for the device[23]. The device is in HRS during the first sweep of bias voltage from 0 to $+V_{\text{max}}$. There is a sudden increase in the current at V_{set} ($\sim 9\text{ V}$ for the first cycle) and the device switches from the OFF state to the ON state. Then, the device holds at the LRS during voltage sweeping from $+V_{\text{max}}$ back to 0 V. In the negative sweep direction from 0 to $-V_{\text{max}}$, the device remains at LRS, and the current increases with increasing voltage. However, an abrupt drop is observed as the voltage goes up to V_{reset} (-10 V for the first cycle). The device switches from ON state to OFF state. Then the sample holds at the HRS as the bias voltage sweeps from $-V_{\text{max}}$ to 0 V. This resistive switching effect is repeatable in the further hundreds of cycles measurements as shown in **Figure 5.19**. The HRS/LRS ratio of the device is about 5 orders of magnitude, which is far higher than that of observed in reference ([22]). It is also very interesting that only the positive set and the negative reset operations occur in the device. If a negative bias is applied for the initial transition, the device can not be switched to LRS. If the positive bias is applied for the set following the positive reset process, the switching is not stable, even comes to a failure state. This is the definition of bipolar resistive switching.

Figure 5.19 Bipolar resistive switching characteristics of the SiO₂ film embedded with Si nanocrystals of the switching operations for 1, 20, 40 and 60 cycles; the arrows indicate the voltage sweep direction; the inset shows the schematic diagram of a MOS structure.

5.4.2 Conduction mechanism at both LRS and HRS

To clarify the physical origins of the resistive switching, the current conduction mechanism in the HRS and LRS should be clarified. The I - V curves for the first resistive switching cycle were replotted in a Log-log scale as shown in **Figure 5.20**. Note that there are high density of nc-Si in the gate oxide layer, thus carrier tunneling can take place between adjacent nanocrystals as shown in **Figure 5.3**[4]. As discussed above, for the positive scan at HRS state, the electrons injected from the substrate can be easily transported to the gate by nc-Si assisted conduction (i.e., tunneling, Poole-Frenkel emission and nc-Si assisted Fowler-Nordheim tunneling). In the voltage-decreasing scan at LRS, the slope in the I - V curve is quite close to 1. The conduction mechanism is believed to be an Ohmic conduction. However, it should be pointed out that the nc-Si-assisted tunneling may also occur concurrently with the Ohmic conduction in the whole sweeping range of the LRS. The current conduction of the negative scan is analogous to that of positive scan except for that the electrons tunneling from Al

electrode to the Si substrate.

Figure 5.20 The I-V characteristics in log-log scale of the first resistive switching cycle. (a) the positive scan (b) the negative scan. Dots are the measured data and the solid lines are the results of power-law fitting.

5.4.3 Microstructure of the SiO_x film

The Ohmic conduction is a conduction behavior of metallic conductive filaments, which are very popular in the interpretation of unipolar resistive switching behavior in the metallic binary oxide. It is quite possible that metallic conductive filaments may be also formed in our current films, and responsible for the LRS. Although a charge trapping-induced band bending model is proposed for the resistive switching in SiO_x films in reference [22]. It is unsuitable to explain the tremendous increase and decrease in current density at V_{set} and V_{reset} in the I - V characteristics and the Ohmic conduction behavior at LRS. Thus other mechanisms which are

responsible for the colossal resistive switching ratio and the Ohmic conduction behavior should be considered. To interpret the physical origin of the resistive switching, the microstructure of the nc-Si embedded SiO₂ film should be clearly understood, and correlated to the conduction behavior of the film. The bonding configurations and chemical structures of the film were investigated by X-ray photoelectron spectroscopy (XPS). **Figure 5.21** (a) shown the Si 2p core-level of the annealed sample after etching off the surface contamination layer (~5 nm) with the build in Ar⁺ ions gun. It can be observed that there are high concentration of Si¹⁺, Si²⁺ and Si³⁺ (Si suboxides) besides elemental Si and amorphous SiO₂ in the film. The presence of Si suboxides in the film is quite natural because it is synthesized via reactive sputtering method where not all the Si atoms are fully oxidized due to the oxygen deficient ambient during deposition. It is well know that these suboxides potential contains high density of various oxygen-related vacancies[24], such as neutral oxygen vacancy [13] and non-bridging oxygen hole center [15]. On the other hand, it has been reported that the rough surface of nc-Si (as revealed by TEM image) also potentially contains various oxygen vacancies. These oxygen vacancies are positive charged in order to maintain the total charge balance and can act as holes[17]. Under strong electric stress, these oxygen vacancies may align to form conductive filaments and switch the device to LRS. However, it is crucial to note that our device has a MOS structure, and the non-metallic SiO_x/Si substrate interface will strongly influence the electric transport in the device. It is essential to point out that the SiO_x/Si substrate interface fabricated by magnetron sputtering is not prefect, and there is usually a rough Si suboxides interfacial transition layer (1~2 nm) between the SiO_x films and the Si substrate[25]. A 1~2 nm Si suboxides transition layer will not influence the nc-Si-assisted tunneling conduction behaviors; however, it can significant suppress the Ohmic conduction at LRS. **Figure 5.21** (b) shows the Si 2p core-level at the SiO_x/Si substrate interface.

It can be observed that the concentrations of Si suboxides in the SiO_x/Si substrate are much lower than that in the SiO_x film, so that the concentration of oxygen vacancies. It has been reported that the oxygen vacancies show a local conductivity a few orders of magnitude higher than the rest of the insulating materials[17]. Thus the SiO_x/Si substrate interface is less conductive than that of SiO_x, and can act as an electronic barrier, and dominating the Ohmic conduction behavior in the device.

Figure 5.21 Si 2p XPS spectra of the SiO₂ film embedded with Si nanocrystals. (a) Si 2p core-level in the SiO_x films; (b) Si 2p core-level at the SiO_x/Si substrate interface.

5.4.4 Resistive switching mechanism

Based on the above experimental results and discussion. We propose a combined model of

conductive filament of oxygen vacancies and SiO_x/Si interface electronic barrier to explain the switching behavior of the Al/nc-Si:SiO₂/Si MOS structure as shown in **Figure 5.22**. Initially, the device is in HRS, the first application of positive voltage to the top Al electrode push the oxygen vacancies move toward to the SiO_x/Si interface. The single crystal Si substrate is well known to have a low oxygen vacancies mobility in it, thus the permeation of oxygen vacancies through the Si substrate is almost impossible at room temperature. Therefore, the oxygen vacancies may accumulate at the SiO_x/Si interface, enhancing its conductivity. On the other hand, at a certain high voltage, the oxygen vacancies may also align to form tiny conducted filaments in the HRS and these tiny conduction filaments gather together to form stronger and more conducting filaments as shown in **Figure 5.22** (a). Once one or more conductance channels penetrate the electronic barrier at the SiO_x/Si substrate interface, the device is switched ON, leading to the transition to the LRS. The Ohmic conduction dominates the current conduction at the LRS as the current can be transported via the metallic filaments. However, as the nc-Si-assisted tunneling may also occurs concurrently with the Ohmic conduction at LRS, the slope in the *I-V* characteristics at LRS is not strictly equal to 1. Si nanocrystals play important roles in the formation of the conductive filaments. First of all, the introduction of nc-Si into the SiO₂ produces sufficient high concentration of oxygen vacancies in the gate oxide, providing the basic element of the conductive filaments. Secondly, in order to generate the filaments, the paths and mobility of the electromigration of these defects are essential. The extremely small size of the nc-Si results in large amount of nc-Si/SiO₂ interfaces. These interfaces may provide easy diffusion paths for oxygen vacancies. Finally, nc-Si-assisted tunneling at HRS results in a relative high current density. The High current density may generate locating heating, which accelerate the growth of the conduction paths.

Figure 5.22 Schematic diagram of the nc-Si-assisted tunneling, formation and rupture of the conductive filaments, (a) under positive voltage scan; (b) under negative voltage scan. The red dash lines in (b) indicate the SiO_x/Si interface.

In the negative scan at LRS, Ohmic conduction continually dominates the current conduction. However, under strong negative gate voltage, the oxygen vacancies in the conductive filaments are repelled away from the SiO_x/Si interface, reducing its conductivity. At a certain high voltage (V_{reset}), the conductive filaments may be ruptured at the SiO_x/Si interface when the concentration of the oxygen vacancies is reduced to a certain level in this region, and the device is switched OFF as shown in **Figure 5.22** (b). As stable positive reset process can't be observed, it is believed that the switching OFF is not the result of the rupture of the conductive filament by Joule heating, as proposed for the models of unipolar switching. The applied voltage bias may also alter the concentration of vacancies at the top interface, but this

variation is not significant enough to change the Ohmic contact property of that interface due to its high conductivity and its high concentration of oxygen vacancies. While the non-Ohmic SiO_x/Si substrate interface has a low concentration of oxygen vacancies, and is therefore sensitive to change, dominating the conductivity of the whole device. If applying negative electric stress on the initial device, the oxygen vacancies are attracted to the Al/SiO_x interface, leading to the decrease in concentration of the oxygen vacancies at the SiO_x/Si substrate interface, so the conductivity at this region. In this case, even nc-Si assisted tunneling still can take place, the conductive filament can not be formed, and thus the negative set process can not occur. This is why the negative set process can't take place.

5.4.5 Retention and endurance of the resistive switching effect

Figure 5.23 (a) shows the retention characteristics of the Al/nc-Si:SiO₂/Si MOS device. The current values are read out at 2 V at room temperature after the device was switched ON or OFF by the voltage sweeping cycles. It can be observed that the LRS and HRS resistance are stable for more than 10⁴ sec, reflecting satisfying retention characteristics of the device. **Figure 5.23** (b) shows the current of the HRS and LRS as a function of switching cycles. The current values are also read out at 2V at room temperature. The values of the HRS are somewhat fluctuant, and the values of LRS are almost the same in the cycle test. The resistance ratio of HRS to LRS are in the range of 5~6 orders of magnitude with in the 200 cycles of test.

Figure 5.23 (a)Retention; (b)Endurance behaviors of the Al/nc-Si:SiO₂/Si/Al device at LRS and HRS at the reading voltage of 2 V.

5.4.6 Conclusion

Electric field-induced reversible bipolar resistive switching is observed from the Al/nc-Si:SiO₂/Si MOS nanostructure. The device shows a colossal resistance switching ratio between high resistance state and low resistance state around 5 orders of magnitude. The conduction follows nc-Si-assisted tunneling regime (direct tunneling, Poole-Frenkel emission and Fowler-Nordheim tunneling) at HRS, and Ohmic conduction at LRS. X-ray photoelectron spectroscopy analysis shows that there is a large amount of Si suboxides which potentially contain high density of oxygen vacancies in the films. The resistive switching behavior is

attributed to formation of conductive filament due to the migration of oxygen vacancies under positive bias and rupture at the SiO_x/Si substrate interface under negative bias.

5.5 Summary

The formation of nc-Si can strongly enhance the conductance of the nanocomposite films of nc-Si embedded SiO₂. The strong increase in current conduction is attributed to the formation of tunneling paths of Si nanocrystals in the films. It is shown that there are three conduction mechanisms contributing to the current conduction in the Si nanocomposite film, including direct tunneling via the tunneling paths formed by nc-Si, nc-Si-assisted Poole-Frenkel emission and the nc-Si-assisted Fowler-Nordheim tunneling. These three conduction mechanisms dominate the current conduction in different stage depending on both the nc-Si concentration and magnitude of the gate bias. The charging/discharging of the nc-Si strongly influence the current conduction in the Si nanocomposite films. A negative electric stress leads to the charge up of the nc-Si, while a positive electric stress leads to the release of the charges. The decrease in the conductance of the oxide is due to the strong charging up of the nc-Si and the recovery of the conductance is due to the release of the charges. The increase in the duration or magnitude of the electric stress can lead to a further increase in the charging/discharging effect.

The charge storage mechanism in the Si nanocomposite films is studied by X-ray photoelectron spectroscopy (XPS) technique by correlating with its microstructure. Various concentrations of Si suboxides and Si nanocrystals (nc-Si) have been realized by sputtering deposition of SiO_{1.5}/SiO_{0.3}/SiO_{1.5} sandwich structure. The X-ray radiation shifts the Si 2p core-levels to higher binding energy due to the photoemission-induced charging effect. The

nc-Si concentration dependent charging effect and the quantum charging effect were observed, which demonstrates that the nc-Si plays a dominant role in the charge trapping mechanism in the nc-Si/a-SiO₂ system.

Electric field-induced reversible bipolar resistive switching is observed from the Al/nc-Si:SiO₂/Si/Al nanostructure. The devices can be switched on under positive electric bias and off under negative electric bias. The device shows a colossal resistance switching ratio between high resistance state and low resistance state around 5 orders of magnitude. It is shown that the SiO_x/Si substrate interface is less conductive, and can act as an electronic barrier, dominating the Ohmic conduction behavior in the device. The device can be switched ON by the formation of conducting filaments of oxygen-related defects, and switched OFF by the rupture of the conductive filaments.

Chapter 6 Optoelectronic Properties of the Nanocomposite Films of Si Nanocrystals embedded SiO₂

The observations of light amplification[1, 2] in nc-Si as well as the demonstration of field-effect light-emitting device[3] based on nc-Si have greatly increased the interest towards the photonic of Si nanostructure. In most of the previous studies about the electroluminescence (EL) from the nc-Si embedded SiO₂ films, where high temperature (higher than 1100°C) post-deposition annealing is usually adopted to induce the crystallization of the excess Si. However, the CMOS compatible annealing temperature is less than 700°C, therefore, for practical EL application, a low annealing temperature or even no annealing is preferred. In this section, we demonstrate the strong EL emission from our as-sputtered amorphous SiO_x, and a detail discussion concerning the light emission from the as-sputtered SiO_x is also presented. In addition, a comparison study is conducted for the EL performance from the SiO_x films after high temperature annealing to induce the crystallization of the excess Si. Finally, a systematic investigation on the influence of charging/discharging of nc-Si on the EL emission performance is also conducted.

6.1 Light emission from the as-sputtered amorphous SiO_x films

The standard approaches of synthesizing nc-Si include ion implantation of silicon into an amorphous SiO₂ matrix[4] or deposition of Si sub-stoichiometric oxide films using chemical vapor deposition[5, 6], sputtering[7, 8] or, reactive evaporation[9, 10]. A high temperature (higher than 1050°C[5]) annealing is needed for crystallization of the excess Si into silicon nanocrystals to give rise to nc-Si/a-SiO₂. Visible electroluminescence (EL) from various nc-Si/a-SiO₂ films has been observed. On the other hand, amorphous Si nanoclusters are

attractive alternative to nc-Si for the development of Si-based light emitting devices, mainly because their formation requires a low annealing temperature or even no annealing, thus allowing us to remarkably decrease the thermal budget needed for the nanostructure formation and an easier integration of the optical source in an electronic devices. Indeed, amorphous Si nanoclusters have been already received considerable attention as light emitting materials, and some reports about their PL properties, as well as theoretical studies on their electronic properties, have been published recently[11]. However, if compared with the very large number of already available data about nc-Si, amorphous clusters are still a relatively unexplored material. In particular, although electroluminescence in absence of crystalline nanostructures has been reported at 77K[11], there are few studies that correlated the origin of the emitted light with the presence of its nanostructure. This section studies the EL emission from the as-sputtered amorphous SiO_x films synthesized by magnetron sputtering of Si. The influence of the amorphous Si nanocluster size, density on the EL emission is discussed, and the origin of the electroluminescence is explored.

6.1.1 Electroluminescence response of the as-sputtered films

Intense and visible yellow-colored EL spectra are observed from the as-sputtered SiO_x films when a negative gate voltage (V_{Gate}) is applied to the ITO gate. Figure 6.1 shows the EL spectra from an as-sputtered amorphous SiO_{1.0} film under constant voltage with different magnitudes. Generally a broad EL spectrum is observed spreading over a visible wavelength range of ~350 to ~850 nm. The EL emission is not measurable by the characterization system until the magnitude of the negative V_{Gate} is larger than -5V, and then the EL intensity increases with the increasing V_{Gate} . No EL was detected under a positive gate voltage regardless of the magnitude of V_{Gate} due to insufficient hole injection from the ITO gate.

Figure 6.1 EL spectra from the as-sputtered amorphous SiO_{1.0} film under constant gate voltage with different magnitude.

Figure 6.2 shows the gate current (I_{Gate}) as a function of the magnitude of the V_{Gate} of the as-sputtered amorphous SiO_{1.0} sample. The curve fitting suggested that the I_{Gate} and the V_{Gate} has a power-law relationship $I = I_0 V^\zeta$, where I_0 is a coefficient, and ζ is the scaling exponent. It is found that the scaling exponent $\zeta = 1.6$ from the curve fitting. The power-law behavior of the current transport has been reported for arrays of small metallic dots and metal nanocrystal arrays[12, 13]. The value of the scaling exponent (1.6) is within the range of 1.66 to 2.26 for the two-dimension (2-D) array of quantum dots[14]. Note that ζ is affected by the concentration and distribution of nanocrystals as well as the charge trapping in the nc-Si. In particular, ζ could be changed by the application of a voltage due to the change in the charging state[14]. Based on the discussions in chapter 4, we have concluded that there are high density of amorphous Si nanoclusters in the as-sputtered amorphous SiO_x films, and carrier tunneling can take place between adjacent nanoclusters [15, 16]. A large number of such nanoclusters distributed throughout the oxide can form many conductive tunneling paths which significantly increase the conductance of the gate oxide,

leading to the observed power-law conduction behavior. Under negative gate voltage, electrons and holes can be injected from the ITO gate and the p-type Si substrate, respectively. The injected electrons and holes can tunnel through the tunneling paths formed by the amorphous Si nanoclusters, and recombine at the luminescent centers.

The integrated EL intensity as a function of the magnitude of the V_{Gate} is also shown in **Figure 6.2**. The dependence of the EL intensity on the V_{Gate} also follows a power-law behavior which has the same trends as the current transport, showing a linear relationship between the current transport and the EL intensity. The result indicates that the light emission is directly related to the carrier transport in the thin film. Since both the injected electrons and holes move along the tunneling paths in the amorphous Si nanoclusters, radiative recombination of the injected electrons with the injected holes is likely to occur along the conduction paths via some luminescence centers. This explains why the current transport and the EL intensity have a similar power-law dependence on the applied V_{Gate} .

Figure 6.2 The Gate current and the integrated EL intensity as a function of the gate voltage of the as-sputtered amorphous SiO_{1.0} sample.

6.1.2 Influence of Si concentration on the EL intensity

Figure 6.3 shows EL spectra from as-sputtered amorphous SiO_{0.6}, SiO_{1.0} and SiO_{1.4} films under a constant gate voltage of -15 V. The EL spectrum from the pure SiO₂ control sample also presented for comparison. The EL intensity is increase with increasing Si concentration in the as-sputtered amorphous SiO_x films. As the EL property is mainly determined by the numbers of the injected electrons and holes available for the radiative recombination, the key parameter in determining the EL properties will be the current density passing through the device [17-19]. The increase in the EL intensity with increasing Si concentration can be interpreted as follows. In samples of higher Si concentration, a higher number of Si nanoclusters are formed, resulting in more tunneling paths and higher current conduction, which in turn, gives rise to more light emission: with increase in the current conduction, more electrons from the ITO gate and more holes from the p-type Si substrate are injected into the amorphous Si nanostructure, leading to an increase in the radiative recombination of the injected electrons and holes and thus an increase in the EL intensity.

Figure 6.3 EL spectra from three as-sputtered amorphous SiO_{0.6}, SiO_{1.0}, SiO_{1.4} and SiO₂ films under constant gate voltage of -15 V.

6.1.3 Origins of Electroluminescence

The origin of the light emission was thought to be the quantum confinement effect of the Si clusters, which is thus associated with a size-dependent shift in the light emission energy [17, 19-21]. However, as shown in **Figure 6.3**, there is no obvious change in the EL position with Si concentration (i.e., size of the nanoclusters). Thus, the quantum confinement effect cannot explain the current results. Instead, an oxygen-deficient defect model, in which oxygen defect functions as a defect luminescent centre, seems to be a more suitable explanation for the current situation. According to this model, EL comes from the recombination of electron-hole pairs at the oxygen-deficient defects in the SiO_x films, and various oxygen-related defects may emit photons with energy in a range of 1.9 eV to 2.7 eV[17, 22-24].

The EL spectra can be deconvoluted into three Gaussian-shaped EL bands, as demonstrated in **Figure 6.4** for the SiO_{0.6} film under a constant gate voltage of -15 V, where the main peak locates at ~600nm (~2.0 eV) and two shoulder bands center at ~480 (~2.7 eV) and ~710 nm (~1.8 eV), respectively. Defects have been proposed as luminescent centres of SiO_x films [17, 22-24], such as the weak-oxygen-bond (WOB, O-O) defect, neutral oxygen vacancy (NOV, O₃≡Si-Si≡O₃, where≡ represents bonds to three oxygen atoms), non -bridging oxygen hole center (NBOHC, O₃≡Si-Si-O•, where • represents an unpaired hole), D centre and E' centre. Among these defects, the NOV and NBOHC are most widely observed in magnetron sputtered SiO_x films. The NOV[25] and NBOHC[26, 27] usually emit photons with energies of 2.7 and 2.0 eV, respectively. As discussed in chapter 4, there are high content of Si¹⁺, Si²⁺ and Si³⁺ (Si suboxides) besides elemental Si and Si⁴⁺ in the as-sputtered amorphous SiO_x films. Si suboxides contain high density of oxygen-related defects (i.e., the NOV and the

NBOHC [24]). Thus the ~480 nm and ~600 nm EL bands are ascribed to the NOV and the NBOHC, respectively. Amorphous Si quantum dots have been reported to generate luminescence bands at ~700 nm due to the quantum confinement effect of electron-hole pairs[28]. Thus the 710 nm band is believed to originate from the carrier radiative recombination in the amorphous Si nanoclusters. From the EL spectrum, it can be observed that a majority of the EL is contributed by the NBOHC. This result indicates that the NBOHC are the dominant luminescence centers during the EL emission. One possible reason is that the excitation energy for the NBOHC defects could be much lower than that of other luminescent centers, and the energy distribution of injected carrier can easily satisfy the requirement for the excitation of the NBOHC defects.

Figure 6.4 Deconvolution of the EL spectrum from the as-sputtered amorphous SiO_{0.6} into the following EL bands: ~480, ~600, and ~710 nm bands.

6.1.4 Light emission from the annealed SiO_x films

Figure 6.5 shows the typical EL spectra from the SiO_{1.0} after rapid thermal annealing at 1000°C for 180s under the constant voltage at different V_{Gate} . The spectral features are quite

similar with that of the as-sputtered amorphous SiO_x films. i.e., a visible broad yellow-colored peak centered at ~600 nm (~2.1 eV) extending from 400 to 850 nm can be observed when a negative gate voltage (V_{Gate}) is applied to the ITO gate electrode. These suggest that the physical origins of the EL from the annealed samples are the same as that from the as-sputtered amorphous SiO_x samples. i.e., the emission of light is believed to come from the Si nanocrystals and the oxygen-deficient defect centers such as the neutral oxygen vacancy ($O_3\equiv Si-Si\equiv O_3$) and non-bridging oxygen hole centres ($O_3\equiv Si-Si-O\bullet$).

Figure 6.5 Electroluminescence from the SiO_{1.0} after rapid thermal annealing at 1000°C under constant gate voltage with different magnitude.

6.1.5 Enhancement in luminescence intensity after annealing

However, a further comparison reveals that the EL intensities in the annealed samples are strong enhanced comparing to the as-sputtered SiO_x samples. I.e., the integrated EL intensity from the annealed samples is more than two times higher than that from the as-deposited amorphous SiO_x films as shown in **Figure 6.6** (a). As the EL intensity is mainly determined by the available number of injected electrons and holes, it is suspected that the increased EL

intensity in the annealed samples is due to the enhancement of the current conduction. **Figure 6.6 (b)** shows a comparison of the gate current between the as-sputtered samples and the samples after high temperature annealing.

Figure 6.6 Comparison the integrated EL intensity (a) and the gate current (b) between the as-sputtered amorphous SiO_{1.0} and the samples after annealing.

It can be observed that the gate current from the annealed samples also twice times higher than that in the as-sputtered samples. Figure 6.7 shows the gate current as a function of V_{Gate} of the annealed SiO_{1.0} sample. The curve fitting suggests that the I_{Gate} and V_{Gate} also have a power-law relationship with the scaling exponent $\zeta = 1.81$. The power-law behavior indicates that the current conduction in the annealed samples follows the nc-Si-assisted tunneling (i.e. direct tunneling, PF emission and FN tunneling) mechanism as discussed in Chapter 5. In

addition, the scaling exponent ζ in the power-law fitting reflects the conductance of the materials system, and it should increase when more tunneling paths are formed[14]. In other words, a larger ζ means a large number of the percolative tunneling paths formed by the Si nanocrystals distributed in the SiO₂ matrix. As the scaling exponent ζ in the annealed SiO_{1.0} sample (1.81) is higher than that in the as-deposited amorphous sample (1.60), it is suggested the annealed samples have higher conductance than the as-sputtered amorphous samples.

Figure 6.7 The gate current and the integrated EL intensity as a function of the gate voltage of the annealed SiO_{1.0}.

The increase in the conductance of the annealed samples can be mainly attributed to two contributions. The first one is the increase in the density of the nc-Si in the annealed samples. During the rapid thermal annealing, besides the growth of the initial Si nanocrystals, it is quite possible that additional nucleation occurs through heterogeneous nucleation at the pre-existing defect sites where the threshold for nucleation is reduced by the energy released through the annihilation of the defect, resulting in the increase in the density of the resultant nc-Si. This will produce more tunneling paths and enhance the conduction of the films. The

second contribution comes from the decrease in the average spacing (S) of the nc-Si in the SiO₂ films due to the growth in the size (D) of the nc-Si during annealing as shown in **Figure 6.8**. The decrease in the average spacing of nc-Si allows direct tunneling more easily to occurs, thus enhancing the tunneling conduction. The integrated EL intensity as a function of the magnitude of the V_{Gate} is also shown in **Figure 6.7**. As can be observed, the dependence of the EL intensity on the V_{Gate} also follows a power-law behavior which has the same trends as that of the current transport, showing a linear relationship between the current transport and the EL intensity.

Figure 6.8 Schematic diagram employed to depict the spacing between adjacent Si nanocrystals

Figure 6.9 shows the EL spectra of the SiO_{0.6}, SiO_{1.0} and SiO_{1.4} samples after rapid thermal annealing at 1000°C. The EL spectrum from the pure SiO₂ control sample which went through the same annealing condition also presented for comparison. It can be observed that the EL intensity is also increase with increasing Si concentration in the annealed samples. The increase in the EL intensity with increasing Si concentration can be interpreted as follows. In samples of higher Si concentration, a higher number of nc-Si are formed, resulting in more tunneling paths and higher current conduction, which in turn, gives rise to more light emission. This phenomenon is similar with that in the as-sputtered amorphous SiO_x films. However, the EL intensities are strongly enhanced in the annealed samples comparing with their

as-sputtered counterparts.

Figure 6.9 EL spectra from SiO_{0.6}, SiO_{1.0} and SiO_{1.4} after rapid thermal annealing at 1000°C for 300s under constant gate voltage of -15 V. The EL spectrum from the pure SiO₂ control sample which went through the same annealing condition also presented for comparison.

6.1.6 Conclusion

Intense visible broad electroluminescence spectrum with a dominant band at ~600 nm (2.1 eV) and two shoulder bands at ~480 nm (2.7 eV) and 760 nm (1.8 eV) has been obtained from both as-sputtered oxygen-deficient amorphous SiO_x films and the SiO_x films after high temperature annealing. A linear relationship between the EL intensity and the current transport has been observed, and both the current transport and the EL intensity have been found to exhibit a power-law dependence on the gate voltage. It is found that the physical origins of the light emission are the same for both the as-deposited amorphous SiO_x films and the SiO_x films after high temperature annealing. i.e., the emission of light is believed to come from the Si nanoparticles and the oxygen-deficient defect centers such as the neutral oxygen vacancy (O₃≡Si-Si≡O₃) and non-bridging oxygen hole centres (≡Si-Si-O•). The light emission increases with increasing Si concentration as a result of formation of more channeling paths

of chains of Si nanoclusters. However, it is found that the EL intensity in the annealed samples is strongly enhanced comparing with their as-sputtered counterparts. This enhancement in the EL intensity can be attributed to the increase the in the current conduction in the annealed samples. The increase in the current conduction is attributed to the increase in the nc-Si density and the decrease in the average spacing of the nc-Si after annealing.

6.2 Charging effect on the Electroluminescence

From the above discussed, it can be concluded that the EL property is mainly determined by the numbers of the injected electrons and holes available for radiative recombination, and the key parameter in determining the EL properties is the current density passing through the device [17]. And also in chapter 5, we concluded that charge trapping in nc-Si strongly suppresses carrier injection and transportation in the gate oxide layer [16, 29]. Thus charge trapping should also have a strong impact on luminescence. It is also reported that this charging effect can strongly reduce the EL efficiency in Si nanostructure[30, 31]. The reduction in EL efficiency was either attributed to Auger-type non-radiative recombination of excitons between the excited nc-Si and the charge carriers[30, 32] or to reduction in electric field in the gate/oxide and substrate/oxide interface because of the charge trapping in these two regions[33]. In this study, we observed a decrease in both EL intensity and gate current with increasing gate voltage in the Si nanocomposite films, which can not be explained by the previously proposed models. It is believed that the decrease in EL intensity with increasing gate voltage in this study is relate to the decrease in the number of the injected carriers for radiative recombination due to charging up of the nc-Si. The gate current and the EL intensity can be partially recovered by releasing part of the charges trapped.

6.2.1 Electroluminescence response

Visible EL is observed when a negative voltage is applied to the ITO gate as shown in **Figure 6.10** of the SiO_{1.4} after rapid annealing at 1000°C. However, No EL was detected under a positive gate voltage due to the low hole injection efficiency from the ITO gate[22]. The EL spectra obtained are quite broad, extending over the visible range from ~300 to 900 nm with the main peak located at ~600 nm. From the position and shape of the emission distribution, the emission is attributed to the Si nanocrystals and the oxygen-deficient defect centres such as the neutral oxygen vacancy ($O_3\equiv Si-Si\equiv O_3$) and non-bridging oxygen hole centres ($O_3\equiv Si-Si-O\bullet$).[24, 26].

Figure 6.10 Electroluminescence spectra under various gate voltage.

There are no obvious changes in the spectral position and shape under different gate voltage but the integrated EL intensities, as shown in **Figure 6.11(a)**. The EL intensity first increases then decreases with increasing gate voltage. This decrease in EL intensity with increasing gate voltage has been observed in literature[30-32]. The decrease in EL intensity was usually ascribed to the Auger-type non-radiative recombination of excitons at high gate

voltages[30-32]. However, in this study, besides the decrease in EL intensity, a reduction in gate current with increasing gate voltage is also observed as shown in **Figure 6.11(b)**. The gate current exhibits the same trend as that of the EL intensity: first increases as the applied gate voltage approaches 12 V, then decreases with a further increase in the gate voltage. This reduction in gate current with increasing gate voltage can not be explained by the previously proposed Auger-type non-radiative recombination of excitons mechanism, which always observed an increase in gate current with gate voltage[30, 31]. Thus, it is suspected that the decrease in EL intensity with increasing gate voltage in this study is relate to the decrease in the number of the injected carriers for radiative recombination, rather than the Auger-type non-radiative recombination of excitons.

Figure 6.11 Integrated electroluminescence intensity (a) and gate current (b) under increasing gate voltage for samples before (i.e. the virgin sample) and after applying electric stress of -30 V and +30 V for 5 s to the MOS structure.

6.2.2 Charging effect on luminescence intensity

This decrease in gate current and therefore the EL intensity can be explained by charging up of nc-Si associated trapping centers as discussed in Chapter 5. Note that there are high density of nc-Si in the gate layer, thus carrier tunneling takes place between adjacent uncharged nanocrystals [16]. Charge trapping occurs when the injected carriers are transported along the tunneling paths. The injected carriers could be trapped in the individual Si nanocrystals. On the other hand, as there exist a large amount of defects at the interfacial regions between the embedded nc-Si and the SiO₂ matrix[34], such as neutral oxygen vacancy [25] and non-bridging oxygen hole center[26], and the carriers could also be trapped in these defects [29]. In either case, charge trapping is associated with the existence of the nc-Si. The charge trapping, in turn, will suppress the carrier transport across the oxide layer. On the other hand, hole trapping reduces the electric field in the region of the oxide/Si interface while the electron trapping reduces the electron field in the region of the oxide/ITO interface respectively[33], resulting in the decrease in the hole injection from the substrate and the electron injection from the ITO gate during the luminescence. The above charging phenomenon leads to reduction in the gate current across the oxide layer, thus also the number of the carrier available for radiative recombination, and as a result, reduction of the EL intensity.

As there are nc-Si distributed throughout the dielectric oxide layer, holes from the p-type Si substrate and electrons from the ITO gate are easily injected into the films under the application of negative gate voltage during the measurement. Some of the injected carriers could be trapped in the nc-Si associated trapping centers, leading to the reduction of the gate

current as shown in **Figure 6.11(b)**, so that the EL intensity as shown in **Figure 6.11(a)**. It also can be observed in **Figure 6.11(b)**, the gate current decreases continuous with the increasing gate voltages when the gate voltage is higher than -12 V. This indicates that serious charge trapping phenomenon may already occur at the gate voltage as low as -12 V and the amount of charged nc-Si increases with applied gate voltages. However, it should be pointed out that there is no linear relationship between EL intensity and the gate current. The maximum of the gate current (5.06 mA) appears at the gate voltage of 12 V, while the maximum of the EL intensity occurs at the gate voltage of 18 V with a relative low gate current of 2.52 mA. It is likely that higher electric field activates more luminescence center to produce higher EL intensity even at a lower gate current.

6.2.3 Charging effect as revealed by C-V measurement

As discussed above, the negative electric stress allows charging up of trapping centers associated with nc-Si. Charge trapping of these centers has been confirmed by the C-V characteristics as shown in **Figure 6.12**. Application of a negative electric stress of -30 V for 1s leads to a large positive flat band voltage shift ($\Delta V_{FB} = +2.44$ V) in the C-V characteristic, indicating a large amount of electrons trapped in these centers. On the other hand, the flat band voltage shift can be partially recovered by applying of a positive electric stress of +30 V for 1s. The ΔV_{FB} returns from +2.44 V to +0.87 V by the positive electric stress. i.e., a +1.57 V has been recovered. The reduction in the flat band voltage shift demonstrates that part of the trapped electrons have been released by the application of the positive electric stress.

Figure 6.12 Flat band voltage shift of the Si nanocomposite films before (i.e. the virgin sample) and after applying electric stress of -30 V and +30 V for 1s.

6.2.4 Effect of electric stress on the luminescence

The light emission from the device was characterized after opposite electric stress plotted in **Figure 6.13**. Negative stress leads to a drastic decrease in EL intensity. The detailed integrated EL intensity and gate current versus applied gate voltage after -30 V for 1s are shown in **Figure 6.11** (a) and **Figure 6.11** (b), respectively. EL intensity and gate current both drop to a very low level. The negative stress leads to charging up of a majority of the nc-Si, breaking up most of the tunneling paths for carrier injections, resulting in the drastic reduction in the gate current. As the injection current drops, the number of the injected holes and electrons for the radiative recombination decreases, so does the EL intensity. Upon application of a positive electrical stress, however, the reduced EL intensity can be partially recovered (**Figure 6.12**). More details are shown in **Figure 6.11** (a) and **Figure 6.11** (b). The EL intensity and the gate current both show a great increase. The recovery is due to the release of some of the charges trapped in trapping centers associated with the nc-Si under positive electric stress. Under

positive gate stress, electrons and holes are injected into the gate oxide, filling the trapping centers. On the other hand, some of the holes and electrons trapped under previous negative stress are now pushed back to the Si substrate and the ITO gate, defilling the charge trapping centers. However, because of the low injection efficiency of holes from ITO electrode and electrons from the electron minority p-type Si substrate, the defiling process overwhelms the filling process. Thus charged nc-Si associated trapping centers are released, leading to the recovery of the tunneling paths. The fact that both EL intensity and gate current are still not yet recovered to their virgin state indicates that the charged nc-Si are not fully released. Full release of charges in the nc-Si can be done by low temperature annealing and Ultra Violet (UV) illumination [33].

Figure 6.13 Influence of the charge trapping/detrapping on the electroluminescence intensity after opposite electrical stress.

6.2.5 Conclusion

Electroluminescence (EL) from Si nanocrystals (nc-Si) distributed throughout the dielectric silicon oxide layer does not always increase with gate voltage: A decrease is observed after a

critical voltage. Charging up of the trapping centers associated with the Si nanocrystals is found responsible for the reduction in EL intensity and gate current. Charge trapping results in the reduction in the number of the injected carriers available for the radiative recombination due to the increase in resistance of the tunneling paths formed by the nc-Si. The reduced EL intensity can be partially recovered by application of a positive electrical stress to release of the trapped charges.

6.3 Summary

In this chapter, the light-emitting devices based on a structure of ITO/Si nanocomposite films /Si MOS structures have been fabricated. The EL performance of the SiO_x films before and after annealing has been investigated. Intense visible broad electroluminescence spectra with a dominant band at ~600 nm (2.1 eV) and two shoulder bands at ~480 nm (2.7 eV) and 760 nm (1.8 eV) have been obtained from both as-sputtered oxygen-deficient amorphous SiO_x films and the SiO_x films after high temperature annealing to induce the crystallization of the excess Si. The EL behaviors have been explained in terms of the formation of tunneling paths of Si nanopartilces and the radiative recombination of the injected electrons and holes via the luminescence centers along the tunneling paths. It is revealed that the light emission mechanisms are the same for both the SiO_x films before and after annealing. The physical origins for the light emission is believed to come from the Si nanoclusters and the oxygen-deficient defect centres such as the neutral oxygen vacancy ($\text{O}_3\equiv\text{Si}-\text{Si}\equiv\text{O}_3$) and non-bridging oxygen hole centres ($\text{O}_3\equiv\text{Si}-\text{Si}-\text{O}\bullet$).

The influence of the charging/discharging of nc-Si on the EL performance has been studied in great details. It is found that the EL intensity from Si nanocrystals (nc-Si) distributed

throughout the dielectric silicon oxide layer does not always increase with gate voltage: a decrease is observed after a critical voltage. Charging up of the trapping centers associated with the Si nanocrystals is found responsible for the reduction in EL intensity and gate current. Charge trapping results in the reduction in the number of the injected carriers available for the radiative recombination due to the increase in resistance of the tunneling paths formed by the nc-Si. The reduced EL intensity can be partially recovered by releasing of the trapped charges.

Chapter 7 Conclusions and Recommendation

7.1 Conclusions

In this thesis, nanocomposite films of Si nanocrystals (nc-Si) embedded SiO₂ have been prepared using radio frequency magnetron sputtering. The atomic structure and the chemical structure of the as-sputtered amorphous Si-rich oxides (SiO_x) films are studied in great detail. The rapid growth mechanism of the nc-Si and the chemical structure evolution during annealing is explored. For a better understanding of the electrical properties, the current conduction and charge transfer mechanism in the nanocomposite films have been studied. Moreover, the influence of charging trapping/detrapping in the nc-Si on the current conduction behavior has been investigated. In addition, a new resistive switching effect from the nanocomposite films is discovered and the physical origin of the resistive switching effect is discussed. Also, the electroluminescence (EL) properties from both the as-deposited SiO_x films and the samples after high temperature annealing are investigated. The light emission mechanisms are discussed. Furthermore, the influence of charging/discharging of nc-Si on the light emission performance is studied. Conclusions are drawn in the following aspects:

1. Structure of the as-sputtered amorphous SiO_x films

X-ray photoelectron spectroscopy (XPS) analysis reveals that the as-deposited SiO_x films contain five Si chemical states (Siⁿ⁺, where n = 0, 1, 2, 3 and 4) in a wide composition range. Various characterization techniques, including Raman spectroscopy, XPS valance band spectrum, and high resolution transmission electron microscopy, have revealed that amorphous Si nanoclusters are already formed in the as-deposited SiO_x films, and they are

embedded in the O-rich SiO₂ matrix. The physical origin of the formation of the amorphous Si clusters in the SiO_x films is related to the high kinetic energy of the sputtered Si atoms, and high surface diffusivity. The atomic microstructure of amorphous SiO_x films has been proposed to contain Si cluster core with suboxides shell domains, which themselves are embedded in the SiO₂ matrix.

2. Growth mechanism of the Si nanocrystals

Thermal annealing leads to significant structural changes due to the lattice relaxation, defect annihilation and thermal decomposition of the Si suboxides. There is a continuous increase in the concentrations of Si and SiO₂, while a continuous decrease in the content of Si suboxides (Si₂O, SiO and Si₂O₃) with increasing annealing temperature due to the thermal decomposition of the Si suboxides. The decomposition of the Si suboxides takes place by two consecutive decomposition reactions, $\text{Si}^{2+} + \text{Si}^{2+} \rightarrow \text{Si}^{1+} + \text{Si}^{3+}$ (1) and $\text{Si}^{1+} + \text{Si}^{3+} \rightarrow \text{Si}^0 + \text{Si}^{4+}$ (2). Decomposition reaction (1) is dominated at the annealing temperature of 400 °C or lower, and decomposition (2) is more pronounced at high temperature. The growth mechanism of nc-Si is believed to be different from the classical nucleation and diffusion growth model. It is believed that thermal segregation of the Si suboxides could provide rapid growth of Si nanoclusters, thus is considered the responsible mechanism.

3. Current conduction and charge transfer

The existence of nc-Si strongly enhances the conductance of the nanocomposite film. The strong increase in current conduction is attributed to the formation of tunneling paths of Si nanocrystals in the films. It is shown that there are three conduction mechanisms contributing to the current conduction in the nc-Si embedded SiO₂ film, including direct tunneling via the

tunneling paths formed by nc-Si, nc-Si-assisted Poole-Frenkel emission and the nc-Si-assisted Fowler-Nordheim tunneling. These three conduction mechanisms dominate the current conduction in different stage depending on both the nc-Si concentration and magnitude of the gate bias.

4. Influence charging/discharging on the current conduction

The charging/discharging of the nc-Si strongly affects the current conduction in the nanocomposite films. The negative electric stress leads to the charge up of the nc-Si, while the positive electric stress lead to the release of the charges. The strong charging up of the nc-Si associated trapping centers leads to the decrease in the conductance of the Si nanocomposite films and the release of the charges leads to the recovery of the conductance. An increase in the duration or magnitude of the electric stress can lead to an increase in the charging/discharging effect.

5. Charge storage mechanism

The charge storage mechanism in the nanocomposite films is studied using X-ray photoelectron spectroscopy (XPS) technique by correlating with its microstructure. Various concentrations of Si suboxides and Si nanocrystals (nc-Si) have been realized by sputtering deposition of $\text{SiO}_{1.5}/\text{SiO}_{0.3}/\text{SiO}_{1.5}$ sandwich structure. The X-ray radiation shifts the Si 2p core-levels to higher binding energy due to the photoemission-induced charging effect. The nc-Si concentration dependent charging effect and the quantum charging effect were observed, which demonstrates that the nc-Si plays a dominant role in the charge trapping mechanism in the nc-Si/a-SiO₂ system.

6. Resistive switching effect

Electric field-induced reversible bipolar resistive switching is observed from the Al/nc-Si:SiO₂/Si MOS nanostructure. The devices can be switched on under positive electric bias and off under negative electric bias. The device shows a colossal resistance switching ratio between high resistance state and low resistance state around 5 orders of magnitude. A conductive filament of oxygen-related defects and SiO_x/Si substrate electric barrier model is proposed for the resistive switching effect.

7. Electroluminescence performance

Intense visible broad electroluminescence spectrum with a dominant band at ~600 nm (2.1 eV) and two shoulder bands at ~480 nm (2.7 eV) and 760 nm (1.8 eV) has been obtained from both the as-sputtered oxygen-deficient amorphous SiO_x films and the SiO_x films after high temperature annealing to induce the crystallization of the excess Si. The light emission increases with increasing Si concentration as a result of formation of more channeling paths of chains of Si nanoclusters. It is shown that the physical origins of the light emission are the same for both the as-sputtered samples and the annealed samples, believing to come from the Si nanoparticles and the oxygen-deficient defect centers such as the neutral oxygen vacancy ($\text{O}_3\equiv\text{Si-Si}\equiv\text{O}_3$) and non-bridging oxygen hole centres ($\text{O}_3\equiv\text{Si-Si-O}\bullet$).

8. Charging/discharging effect on the electroluminescence

It is found that the EL intensity from Si nanocrystals (nc-Si) distributed throughout the dielectric silicon oxide layer does not always increase with gate voltage: a decrease is observed after a critical voltage. The charging up of the trapping centers associated with the Si nanocrystals is found responsible for the reduction in EL intensity and gate current. Charge

trapping results in the reduction in the number of the injected carriers available for the radiative recombination due to the increase in resistance of the tunneling paths formed by the nc-Si. The reduced EL intensity can be partially recovered by releasing of the trapped charges.

7.2 Recommendation

In this project, the nanocomposite films of Si nanocrystals (nc-Si) embedded SiO₂ are synthesized by reactive magnetron sputtering followed by rapid thermal annealing at high temperature. The microstructure of the as-sputtered amorphous SiO_x films is investigated. The growth mechanisms of the nc-Si and the chemical structure evolution during annealing are explored. The current transport and charge trapping mechanisms are examined and the resistive switching effect in the nc-Si embedded SiO₂ films is discussed. The optoelectronic response from both the as-sputtered SiO_x films and the films after annealing is studied, and the influence of charging/discharging of nc-Si on the electroluminescence performance is characterized. To make the research more complete, the following research could be done.

1. Reduction in crystallization temperature

Although nanocrystals formed by thermal crystallization are interesting, however, the crystallization temperature (higher than 1050°C) are too high, and thus is not compatible with the main CMOS industry processing temperature (below 700°C). Thus for a practical application, the fabrication temperature has to be substantially lowered. There are several methods that can be used to reduce the crystallization temperature of nc-Si, even without annealing. For example, doping the SiO_x films with low melting point elements like aluminum and nickel could lower crystallization temperature below 700°C[1], and applying certain specially treatment on the SiO_x surface such as plasma treatments, laser irradiation can

obtain the crystalline Si with out annealing[2, 3]. Thus, development of appreciate approaches to synthesize the nc-Si at low annealing or even no annealing is desirable and indispensable.

2. The interfacial structure

The microstructure of the Si suboxides interfacial layer between the nc-Si and SiO₂ matrix strongly influence the light emission properties and charge transport in the films. For example, the suboxides interfacial layer contains high densities of various oxygen-related defects. These oxygen-related defects may serve as radiative or nonradiative recombination centers for excitations, thus responsible for optical properties. On the other hand, when electron devices scaling down to certain level, quantum effect become dominant, and carriers transport by tunneling between adjust nc-Si. The local atomic structure at the nc-Si/SiO₂ interfaces, including Si suboxides bonding arrangement also can strongly influence the carriers transfer behavior. Therefore, a clear understanding concerning the microstructure of the Si suboxides interface layer may play an important role in interpreting the charge transport and trapping mechanism as well as the physical origins of the light emission. A further systematic study by using high resolution transmission electron microscopy or other methods will be great help to under the interface structure between the nc-Si and the SiO₂ matrix.

3. The current transport behavior

Due to the variation in the materials, fabrication process, film thickness, and trap density of the dielectric layer, there are many conduction mechanisms for the current transport in the nc-Si/SiO₂ system, including direct tunneling, Fowler-Nordheim (FN) tunneling, Schottky emission, Poole-Frenkel emission and Ohmic conduction. In most of the case (i.e. Schottky emission, Poole-Frenkel emission and Ohmic conduction), the conduction mechanism is

sensitive to the measurement temperature, and such temperature-dependence is useful to distinguish the current conduction mechanism with each other. For example, the current-voltage (I - V) curve can be reconstructed as a function of measurement temperature, and the dominated conduction mechanism follows a straight line in the reconstructed plot according to it. Thus for a better understanding of the carrier transport mechanism in the Si nanocomposite films, the electrical properties should be characterized and discussed as a function of measurement temperature.

4. The light emission mechanisms

To have a better understanding of the light emission behavior, a systematic photoluminescence (PL) measurement should be carried. To further confirm the physical origin of the light emission from the nanocomposite films, certain special heating treatment should be adopted to deliberately eliminate the concentration of the defects in the films. For example, the samples can be re-annealed at diluted oxygen or hydrogen atmospheres at relative low temperature to passivate the oxygen-related defects after high temperature annealing. A comparison study between the samples with different defects concentrations would be great help to reveal the light emission mechanism.

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