Characterization of silicon nanocrystals embedded in SiO₂ matrix

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**Characterization of Silicon Nanocrystals
Embedded in SiO₂ Matrix**

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School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
Doctor of Philosophy

2005

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Summary

Structures consisting of Si nanocrystals embedded in SiO₂ films are candidates for Si-based optical devices because of their light-emitting ability. In addition, there is renewed interest in their possible applications in nano-memory devices or single electron devices.

In this thesis, we have synthesized Si nanocrystals (nc-Si) embedded in SiO₂ films by implanting Si⁺ into SiO₂ films that are thermally grown on Si substrates. Various techniques, including spectroscopic ellipsometry (SE), x-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), x-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), Raman scattering, and photoluminescence (PL), have been used to characterize these films. Nanocrystal size information was obtained using TEM that correlated well with that obtained from XRD measurements. A very low evolution rate of nc-Si size on thermal annealing was found by TEM, XRD, and PL. We have developed a nondestructive and inexpensive approach for determining the depth distribution of Si nanocrystals in Si-doped SiO₂ films by spectroscopic ellipsometry. The results are in good agreement with SIMS analysis. One approach to determining optical constants and the dielectric function of Si nanocrystal embedded in SiO₂ matrix has been developed based on ellipsometric analysis. Dielectric suppression and band gap expansion of Si nanocrystals due to the quantum size effect were obtained, which are based on the effective medium approximation and models to simulate ellipsometric measurements on the material system. XPS has been employed to study

the evolution of chemical structures corresponding to the oxidation states as a function of annealing. We have demonstrated that thermal annealing does not necessarily convert all the implanted Si ions into Si nanocrystals; some Si suboxides still exist. In addition, by conducting an XPS study, it was found that the charging ability of nc-Si/SiO₂ is superior to that of pure SiO₂ film. The true Si 2p core level of Si nanocrystals embedded in SiO₂ matrix can be determined after subtracting the charging effect, which is found to be the same as that of bulk silicon.

Metal-oxide-semiconductor (MOS) capacitors have been synthesized with nc-Si embedded in the oxide. A flat-band voltage shift and single electron tunneling at room temperature can be observed, suggesting the possibility of realizing nano-memory devices and single electron devices. A new type of memory effect has been discovered with nanocrystals embedded throughout the gate oxide with the peak concentration of nc-Si being close to the oxide surface: The charge trapping in nc-Si can modify the capacitance of such MOS structures, while detrapping can lead to the recovery of the capacitance, suggesting the possibility of a new type of memory device. The two types of memory effects are based on different distributions of nc-Si within the oxide, and thus highlight the importance of nc-Si distribution in memory device applications. Studies on carrier transport via nanocrystals within the oxide have been conducted; a charge transport model is developed to explain the phenomena observed in current conduction characteristics.

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Chapter 1: Introduction

1.1 Motivation

SiO₂ films containing Si nanocrystals (nc-Si) have recently attracted much attention because of their light-emitting ability that makes them suitable for Si-based optoelectronic ICs. In addition, there is renewed interest in their possible applications in nano-memory devices or other single electron devices.

The photoluminescence (PL) of Si nanocrystals embedded in SiO₂ thin films with an intense and wide spectral emission peaking between 1.4 and 1.8 eV has been reported. Room temperature electroluminescence (EL) emission of nc-Si/SiO₂ thin films has also been recently reported. As the SiO₂ that contains Si nanocrystals can be synthesized by implanting Si⁺ into SiO₂ films that are thermally grown on Si substrates, the fabrication is compatible with standard CMOS processes.

In order to overcome the limitations of conventional nonvolatile and dynamic memory devices, it has recently been proposed that nanocrystals be used as charge storage elements embedded in the gate dielectric of a field transistor and located in close proximity (2-3 nm) to the transistor channel. The conditions for single electron memory device application, such as a large amount of charging energy for room temperature operation and an opaque tunneling barrier for suppressing co-tunneling or charge number fluctuation in the charge island, are usually met in the nc-Si/SiO₂ system. Despite the random distribution and size dispersion problems, nano-memory

devices with a gate oxide containing nanocrystals while operating at room temperature have been reported. The applications of single electron tunneling effects with nc-Si in electronic devices have the advantages of low-power consumption and high device density. For practical applications of single electron devices, Si-based processes are required for the device fabrication. For room temperature operation, the nc-Si used in single electron devices should be in nanometer scale (< 10 nm).

1.2 Objectives

In this work, SiO₂ containing Si nanocrystals is synthesized by implanting Si⁺ into SiO₂ films that are thermally grown on Si substrates. Studies related to optoelectronic and nano-electronic applications are carried out.

Optical and structural studies: Various characterization techniques including spectroscopic ellipsometry, XPS, FTIR, XRD, Raman scattering, and TEM are employed to investigate the optical and structural properties of the thin films, the relationships between the optical and structural properties, and the influence of the charge storage in the nanocrystals.

Electrical studies: C-V measurements are performed to determine the charge storage ability, and I-V is conducted to study the current transport in the dielectric films. The influence of nc-Si distribution on charge storage and carrier transport properties is also studied.

1.3 Major Contributions of the Thesis

The major contributions of the thesis are as follows:

1. Si nanocrystals embedded in SiO₂ dielectric films are successfully synthesized using the ion implantation technique.
2. A nondestructive and inexpensive technique for depth profiling of Si nanocrystals and optical constants in SiO₂ dielectric films is developed based on ellipsometry.
3. Optical constants and dielectric functions of Si nanocrystals embedded in SiO₂ matrix are determined by a technique developed in this study.
4. The band gap expansion of Si nanocrystals due to the quantum size effect is determined.
5. An XPS study on the evolution of chemical structures in nc-Si embedded SiO₂ films as a function of annealing is conducted.
6. Depth profiles of Si oxidation states corresponding to the chemical structures are determined by XPS.
7. A charging effect study for nc-Si embedded SiO₂ films is conducted by XPS.
8. Core levels of isolated nc-Si embedded in SiO₂ matrix are determined.
9. The memory effect based on charge trapping in Si nanocrystals is observed.
10. A charge storage characteristic study on the influence of nc-Si distribution in SiO₂ films is conducted. This study leads to the discovery of a new type of nano-memory effect.
11. Studies on the carrier transport in the nc-Si/SiO₂ system and the influence of nc-Si distribution on the carrier transport are conducted.

1.4 Organization of the Thesis

In **Chapter 1** of this thesis, we provide a brief introduction to the applications of nc-Si embedded in SiO₂ matrix and a description of the motivation behind this study.

In the following chapter, **Chapter 2**, a literature review is presented; the methods for synthesizing nanocrystals embedded in dielectric films are described; the physical properties of such films characterized by various techniques are discussed; and finally the applications of such structures based on their optical and electrical properties are introduced. In **Chapter 3**, we present some experimental results of optical and structural studies of nc-Si embedded in SiO₂ films using various techniques, as well as the electrical characterizations. Optical studies are presented in **Chapter 4**, in which we discuss a technique of depth profiling of nc-Si distribution and optical properties based on ellipsometry, and present the determination of the optical constants and dielectric functions of nc-Si. In **Chapter 5**, XPS is used to study the evolution of the five Si oxidation states in the nc-Si/SiO₂ system as functions of annealing temperature and annealing time. The depth profiles of the oxidation states are also determined. The charging effect in the material system and the core level shift have been investigated through XPS analysis. Detailed electrical studies on the nc-Si/SiO₂ system including charge trapping and carrier transport are presented in **Chapter 6**. These studies lead to the discovery of a new type of memory effect. A summary of the work carried out in this study as well as conclusions and recommendations for future research are presented in **Chapter 7**.

Chapter 2: Literature Review

2.1 Introduction

There are many technological problems affecting the design of future electronic circuits. These include the problems of implementing a device function with increased density on the chip, lower power consumption, and a simpler design. The design concepts used in conventional semiconductor technology cannot be scaled down indefinitely, and thus new concepts must be developed. In addition, Si has for a long time been considered unsuitable for optical IC due to its indirect band gap. Integrating optical IC with mainstream Si-related complementary metal-oxide-semiconductor (CMOS) technology is also a daunting problem that could considerably reduce the cost of optical IC fabrication. Recently, structures consisting of nanocrystals embedded in SiO₂ have emerged as candidates for a large number of optoelectronic, and ultra-dense and ultra-low power flash memory applications. The advantages of semiconductor nanocrystal/SiO₂ composites are their robustness and surface stability in comparison with porous materials and their full process compatibility with mainstream CMOS technology.

2.2 Synthesis of Nanocrystals Embedded in Dielectric Films

Dielectric films containing nanocrystals can be synthesized via various techniques, including sputtering, CVD, ion implantation, and laser ablation. SiO₂ has proven to be a robust matrix that provides good chemical and electrical passivation of nanocrystals.

In addition, the fabrication is fully compatible with mainstream CMOS processes, and thus allows the integration of optoelectronic devices into Si circuits. Therefore, SiO₂ films are commonly used as an embedding matrix.

(a) Co-sputtering Method

Semiconductor nanocrystals embedded in SiO₂ films can be prepared by co-sputtering from two electrodes, one with a semiconductor (Si, Ge, etc.) target and the other with a quartz target [1-8]. This method enables the production of alloyed materials with a controlled composition. An entire series of mixed compositions with different microstructures can be obtained by varying the RF power applied to the targets. By replacing the quartz target with other materials, nanocrystals can also be embedded in other dielectric films.

(b) PECVD Method

Plasma-enhanced chemical vapor deposition (PECVD) is one way to prepare Si nanocrystal/SiO₂ films. A Si-rich SiO₂ film can be formed using very high frequency (VHF) PECVD from an N₂O: SiH₄ mixture. The VHF and the right amount of pressure cause the gas to form plasma and then the Si ions will be doped in situ with SiO_x film formation [9].

(c) LPCVD Method

Low-pressure chemical vapor deposition (LPCVD) can be used to deposit a thin Si layer onto the SiO₂, which is thermally grown on a Si wafer [10, 33]. Such a deposition is normally carried out in a very high vacuum reactor at ~500°C with pure SiH₄. Then, SiO_x films can be formed by oxidation at ~900°C for various durations.

(d) Ion Implantation Method

One of the promising techniques used to elaborate nc-Si is the implantation of Si ions into SiO₂ films that are thermally grown on Si substrates [11, 13-15, 17-21, 23-

25, 67, 73, 74]. Si ions are implanted at the selected energy level (1-200 keV) with a dose ranging from 10^{16} to 10^{17} cm⁻². This method is attractive because it is easy to control the doping profile and the doping concentration by adjusting the implantation energy and dose, respectively.

(e) Laser Ablation Method

Laser ablation is carried out using laser pulses. The Si target can be ablated by a laser beam in an inert gas ambient. The ablated species will then accumulate on the substrate. Subsequent annealing in oxygen gas will lead to the formation of nc-Si embedded SiO₂ films [26, 27].

(f) Thermal Evaporation and Electron Beam Evaporation

In addition, nc-Si embedded SiO₂ films can be deposited by thermal evaporation of SiO powders onto rotating substrates [28]. In [29], it is also reported that Si nanocrystals can be embedded in Al₂O₃ matrix by co-evaporating Si and Al₂O₃ onto Si wafers.

2.3 Characterization of Nanocrystals Embedded in Dielectric Films

2.3.1 Size Images

Transmission Electron Microscopy (TEM) is an indispensable tool in materials research, and has been used in nano-scale investigations because of its ability to view the finest cell structures. This technique has the advantage of being able to identify nanocrystals and to provide information about size based on its resolving powers on the order of nanometer. Semiconductor nanocrystals embedded in SiO₂ films normally have a mean radius ranging from 1 to 10 nm characterized by TEM and other

techniques (XRD, PL, etc.) [1-30]. Fig.2.1 shows the cross-section images of nc-Si embedded in SiO_2 films from [30]. In graph (c), Si nanocrystals can be clearly observed with a mean size of about 2 nm.

Fig.2.1. Cross-section TEM images of an nc-Si embedded sample [30].

2.3.2 Photoluminescence

Much research has been conducted using photoluminescence (PL) to explore the physical and structural properties of semiconductor nanocrystals embedded in SiO_2 films [2, 4-8, 11, 13-15, 17, 19, 21, 23-25, 30-32, 67, 73, 74]. Both Si and Ge nanocrystals as luminescent sources have been found to yield characteristic luminescence bands corresponding to nanocrystal size, as shown in Fig.2.2 and Fig.2.3, respectively. Regarding Fig.2.2, a higher implantation dose was considered to lead to a bigger Si nanocrystal size, and thus a redshift due to the size effect could be observed with the increase of Si implantation fluence.

Fig.2.2. Photoluminescence spectra of Si-implanted silica glass with a fluence of $1 \times 10^{17} \text{ cm}^{-2}$ (a) at 77 K, (b) at room temperature, and (c) with a fluence of $2 \times 10^{17} \text{ cm}^{-2}$ at room temperature. [14]

Fig.2.3. PL spectra at room temperature of Ge nanocrystals in SiO_2 for (a) size $\approx 2.1 \text{ nm}$, (b) size $\approx 3.3 \text{ nm}$, (c) size $\approx 4.8 \text{ nm}$, and (d) size $\approx 6.0 \text{ nm}$. [2]

The luminescence mechanism in Si or Ge nanocrystals has previously been investigated [14, 15, 17, 23, 30, 67, 73]. There is still considerable debate over the

luminescence mechanism; that is, whether light emission occurs via a recombination of quantum-confined excitons within the nanocrystal or via interface-related defect states. K. S. Min *et al.* proposed that the visible PL in their samples was not due to the quantum-confined excitons in Ge nanocrystals but to the radiative defect centers in SiO₂ matrix. This was because, according to their theoretical calculations, the PL peak position should have correlated well with the size of the Ge nanocrystals, whereas in their samples of Ge embedded SiO₂ films, there appeared no significant PL emission changes associated with Ge nanocrystal size. Moreover, their Xe-implanted samples also showed visible photoluminescence at room temperature [67]. In [17, 73], a group of scientists also proposed that PL emission from Si nanocrystals embedded in SiO₂ should be related to the recombination at the nc-Si/SiO₂ interface, because the experimental Stokes shift between absorption and emission was independent of nanocrystal size and correlated well with Si-O vibration energy. On the other hand, M. L. Brongersma *et al.* believed that the PL emission should be attributed to the recombination of quantum-confined excitons in the nanocrystals, as they found that the temperature dependence of the radiative decay rate was in good agreement with a model that takes into account the exchange energy splitting corresponding to nanocrystal size [23]. S. Guha also attributed the PL emission to the excitonic recombination within Si nanocrystals. He proposed a model to simulate PL spectra with an average size of nc-Si and a size distribution that fitted well with his experimental results [15]. But he also suggested that additional experiments should be carried out to confirm his conclusions. Later, S. Guha *et al.* published their new result that the calculated size-dependent band gap energy agreed well with the quantum confinement model. However, regarding the origin of PL, a narrow size distribution of nanocrystals may be helpful for reaching conclusions [30]. It is reported in [14] that

two PL bands appeared: one centered around 2.0 eV and observed in as-implanted samples; the other located at 1.7 eV and observed in high-temperature annealed samples. The authors attributed the first band to the recombination in Si-related excess defects in SiO₂, while the 1.7 eV band was ascribed to the recombination at the nc-Si/SiO₂ interface.

The effect of nanocrystal size on PL was reported in [31]. The authors presented a simple and efficient method of synthesizing Si nanocrystals in a specific depth of SiO₂ films and with a specific density of nanocrystals. A size-dependent blueshift of the luminescence was observed, as shown in Fig.2.4. The blueshifts of the PL emission peak were attributed to the quantum confinement, taking oxygen passivation of the nanocrystals into account. There is also a report on the size effect on PL emission [74] in which results similar to those in [31] were obtained. The authors indicated that larger nanocrystals contained more nonradiative defects.

Fig.2.4. PL spectra showing a blueshift with the nc-Si size reduction. [31]

The dependence of PL on the annealing condition has been investigated in detail [23, 73]. In [23], the Si-implanted SiO_2 films were annealed in flowing O_2 at 1000°C for various durations up to 30 min, resulting in the oxidation of Si nanocrystals. As shown in Fig.2.5, a blueshift of 200 nm for the PL emission appears upon 30 min annealing. This shift was explained in terms of the quantum size effect whereby a reduction of the average nanocrystal size leads to emission at a shorter wavelength.

Fig.2.5. Room temperature PL spectra of 100 nm thick SiO_2 films containing Si nanocrystals that were oxidized for 0, 3, 10, 15, 20, 25, and 29 min at 1000°C . [23]

In [73], the Si-implanted films were annealed in N_2 atmosphere for a duration from 15 min to 16 hours at 1100°C . The evolution of the nanocrystal mean diameter is presented in Fig.2.6, characterized by TEM and high resolution electron microscopy (HREM), and shows a slight increase from 2.5 to 3 nm. Such a low evolution of nc-Si size is interpreted in terms of a low diffusion coefficient of Si in SiO_2 .

Fig.2.6. Annealing effect on the nanocrystal mean size as a function of the annealing time. The squares are obtained from TEM images and the circles are obtained from HREM images. [73]

Exponential PL decay from nc-Si has been studied [24]. Fig.2.7 shows the time-dependent decays from a Si nanocrystal sample and from a porous Si sample. For both samples, longer wavelengths generally decay at a slower rate than do shorter wavelengths. The time-resolved decays exhibit a “stretched exponential” decay line as

$$I(t) = I_0 \exp[-(t/\tau)^\beta], \quad (2.1)$$

where $I(t)$ and I_0 are the PL intensity during the decay and the initial value (i.e., $t = 0$), respectively. Decay time τ and dispersion factor β are characteristic wavelength-dependent constants of the decay. There are three models proposed by researchers to explain the physical origin of the “stretched exponential decay” for the photoluminescence in porous Si:

1. The “stretched exponential decay” may result from a variation of carrier localization. Carriers can escape from the porous Si nanocrystals with different

possibilities and recombine non-radiatively in the non-radiative recombination centers nearby. [239]

2. The “stretched exponential decay” can be explained in terms of migration/diffusion of excitons in a system with randomly distributed and interconnected nanocrystals. [240,241]

3. The “stretched exponential decay” may be a consequence of a distribution of nanocrystal shapes for a fixed volume. [242]

The study in [24] suggests that the decay results from the migration and trapping of excitons between nanocrystals of random size.

Fig.2.7. Time-dependent PL decays. The excitation wavelength is 355 nm. [24]

Recently, high-efficiency PL has been obtained by the deposition of luminescent SiO₂ film at room temperature using the PECVD technique [32]. The structural and optical properties were investigated for samples deposited at different temperatures by various techniques including PL, Raman, and FTIR. Up to a 12% improvement in PL efficiency was obtained when the deposition temperature was reduced from 250°C to room temperature.

Fig.2.8. Room temperature PL spectra of the SiO₂ films containing Si nanocrystals prepared at different deposition temperatures. [32]

Fig.2.8 illustrates the influence of the deposition temperature on PL intensity. A significant increase of PL emission intensity can be observed with a decrease of the deposition temperature. As the study in [32] suggested, a stoichiometric SiO₂ matrix and perfect Si/SiO₂ interfaces are very important to obtain high-efficiency PL. The SiO₂ films deposited at elevated temperatures are not completely stoichiometric, especially at the nc-Si/SiO₂ interfaces. There are many interface states existing and they become non-radiative recombination centers and frustrate the quantum confinement to a certain content. Secondly some lattice imperfections inside the nc-Si can degrade PL efficiency. There are two advantages for the low temperature

deposition. One is that the phase between nc-Si and SiO₂ is well-separated. Nearly stoichiometric SiO₂ could be formed. The other is that there is a large amount of hydrogen involved in the as-prepared films in low-temperature deposition, which is helpful in releasing the strains within nc-Si. Based on the two advantages, a higher PL efficiency can be obtained with the films prepared at low temperatures.

2.3.3 Electroluminescence

SiO₂ films containing Ge or Si nanocrystals show yellow or blue electroluminescence (EL) under biases [33-36, 38, 57]. Light-emitting diodes can be fabricated by the incorporation of Ge or Si into SiO₂ films with implantation or CVD. It is proposed that EL originated from the recombination of injected electrons and holes in nanocrystals near the nanocrystal/SiO₂ interface. The EL onset voltage normally ranges from 7 to 10 V. But in [36], it could be reduced to about 4 V, which is available for circuit operation. Fig.2.9 shows a typical EL spectrum from the nc-Si/SiO₂ nanostructured film, presented in [36]. Yellow light emission was obtained under a reverse bias of 5.0 V. The inset graph shows that the EL was only observed at the edge of the metal contact because of the thick Au contact.

Fig 2.9. Electroluminescence spectrum from the nc-Si embedded SiO₂ film. [36]

2.3.4 Second Harmonic Generation

Second harmonic generation (SHG) has been observed by Y. Jiang *et al.* [18]. They suggested that SHG originates from nc-Si/SiO₂ interface states depending on nanocrystal size, shape, and density. This technique has been proven to be a powerful tool for generating information about nonlinear optical properties of nanocrystals embedded in SiO₂ films. Fig.2.10 shows a time-domain SHG for the nc-Si embedded film, pure SiO₂ film on Si substrate, and Si substrate with native oxide. No time-domain SHG was observed in the pure 1.7- μm thick oxide. Photoinduced rise in SHG intensity in both native oxide and nc-Si embedded oxide are shown in Fig. 2.10. Following mechanism was introduced: electrons are photoinjected from the nc-Si's valence band to conduction band of SiO₂; they migrate to and accumulate in the traps at the oxide surface; thus a vertical electric field builds up, generating additional SHG signal.

Fig.2.10. Time-domain SHG from SiO₂ films containing nc-Si (filled circles), Si with native oxide (solid line), and the 1.7 μm SiO₂ on Si substrate without nc-Si (open circles). [18]

2.3.5 Electrical Issues

In a quantum sphere, when the electron mean-free-path exceeds the dimension of the device structure, quantum mechanisms will dominate the physical natures of the devices. Electron transport is governed by tunneling. Quantum confinement effects related to the electron's wave nature lead to redefinitions of capacitance and electrical forming. Tunneling time between quantum wells can be evaluated by solving the time-dependent Schrödinger equation as less than 0.25 ps [39], suggesting that an ideal quantum tunneling device works fast.

The Coulomb blockade effect is the electrostatic energy of the electron, e/C , occupying a given electronic state and preventing tunneling of other electrons to this state. To add one electron to a quantum state costs a charging energy of e^2/C . C is the capacitance of the quantum dot. Such an effect has been reported in the literature [48, 88, 91] from semiconductor nanocrystal embedded dielectric films. In such films, electron tunneling changes the electrostatic energy of the nano-sphere by a discrete value, while a voltage applied to the system changes the electrostatic energy in a continuous manner. Thus, if we sweep the voltage, the build up of the induced charge will be compensated in periodic intervals by the tunneling of discrete charges onto the nanocrystals. This competition between continuously induced charge and discrete compensation leads to so-called Coulomb oscillations in a measurement of the current [39, 44, 48, 88, 91, 96]. One typical I-V characteristic showing Coulomb staircases is presented in Fig.2.11.

Fig.2.11. An example of measurement of the Coulomb staircases in current-voltage characteristics. [39]

Data retention in Si nanocrystals has been modeled by S. Tiwari *et al.* [66] as a system of electrons trapping in electronic energy levels within quantum wells induced by nanocrystals. The energy level is defined as a discrete energy state inside a quantum well with finite potential barriers. The lifetime related to the decay of an electron from the energy level and through a potential barrier is referred to as the data retention time. Based on their model, S. Tiwari *et al.* predicted that electrons trapped in a quantum well in nano-memory devices with a tunneling oxide of 1.5 to 4.0 nm could last hundreds of days.

2.4 Applications of Nanocrystals Embedded in Dielectric Films

2.4.1 Waveguides and Si-based Lasers

Based on the doping profile of Si nanocrystals, Si nanocrystal waveguides in SiO₂ matrix have been proposed [42, 43]. Light confinement phenomena can be observed, suggesting the possibility of light transfer in Si-related circuits. The authors also concluded that with a proper doping concentration and profile of Si nanocrystals and Er, a net gain from a broadband source can be obtained [42]. Fig.2.12 is the schematic illustration of a waveguide structure based on Si-implanted SiO₂ films. The Si doping profile can be controlled by using ion implantation or PECVD. The structure illustrated in Fig.2.12 can easily be realized with middle layers containing much more Si atoms than the other regions. Light wave trapping may exist in the middle layers because light will be reflected within the layers with the high refractive index (n).

Fig.2.12 Schematic illustration of light trapping in the Si-implanted SiO₂ film on Si substrate.

Recently, optical gain has been reported in nc-Si synthesized by the implantation of Si into SiO₂ and annealing [52], leading to the hope that silicon laser can be fabricated. The gain spectra for both nc-Si embedded in quartz and thermally grown SiO₂ were observed, as shown in Fig.2.13. A wide band of light amplification was obtained by exploiting Si nanocrystals and nc-Si/SiO₂ interfaces. As the authors estimated, similar values to the III-V semiconductor for material gain can be reached with a higher density of Si quantum dots.

Fig.2.13. Optical gain as a function of wavelength. [52]

The origin of gain from this system is explain by a three-level model shown in Fig.2.14, which includes the top of the valence band of the nanocrystal, the bottom of the conduction band of the nanocrystal and the radiative interface state. Electrons are pumped from valence band to the conduction band and relax rapidly to the interface state. The rate of the depopulation of the initial state is much faster than its filling rate via the interface state. Population inversion between the top of the conduction band and the interface state is thus possible.

Fig.2.14. Schematic energy band diagram for a nanocrystal showing how population inversion can be reached. [52]

2.4.2 Si-based Optical Devices

Recently, studies on electroluminescence from nanocrystal embedded dielectric films have been conducted [33-36, 38, 57]. Potential applications include Si-based optical devices and low voltage active flat panel displays. The emission from the diode based on Si nanocrystal embedded film proceeds through successive steps: charge carriers injection from electrodes, their transport, and their recombination with light emission. However, the EL efficiency depends on the material properties: adjustment of electrodes' work functions to carriers' energy levels, balance between carriers' densities, and reduction of nonradiative recombination. Improving the low EL efficiency and reducing the onset voltage of the luminescent SiO_2 film are the current major research aims. Fig.2.15 shows a typical EL diode structure. Light emission will occur from the Pt gate when the onset voltage has been reached.

Fig.2.15. Cross-section scheme of the light-emitting device.

2.4.3 Nano-memory Device and Single Electron Device

(a) Nano-memory device

MOSFET devices with semiconductor nanocrystals embedded in the floating gate have been reported in the literature [44-48, 50, 96]. Fig.2.16 shows the cross-section scheme of a typical nano-memory transistor. For such a structure, electrons can be stored in the nanocrystals to screen the charge in the channel, thus leading to less channel charge for the same gate voltage. This can effectively change the threshold voltage. Given the nanocrystal density N_{nano} with the size t_{nano} , the tunneling oxide thickness of t_t , the control oxide thickness of t_c , and v_a , the average number of electrons per nanocrystal, the modified threshold voltage is approximately expressed as

$$\Delta V_T = \frac{eN_{\text{nano}}v_a}{\epsilon_{ox}} \left(t_c + \frac{1}{2} \frac{\epsilon_{ox}}{\epsilon_{\text{nano}}} t_{\text{nano}} \right) . \quad (2.2)$$

The speed of the device mainly depends on the thickness of the tunneling oxide and could be less than 100 ns for the write time. Charges stored in nanocrystals can be maintained for days or even weeks, showing good retention ability.

Fig.2.16. Cross-section scheme of the nano-memory device.

(b) Single Electron Device

The design concept used in single electron transistors is based on the Coulomb blockade of single charge tunneling. Such devices suggest the possibility of implementing electronics at the nano-scale. Single electron transistors may overcome the physical limitations of MOS transistors. The scale of MOS transistors is limited by the length of space of the charge layers, tunneling effects, and fluctuations of the doping concentrations. Single electron devices exploit the Coulomb blockade effect in very small capacitors, where single electron tunneling is dominant. Thus, these devices can be made to be much smaller than conventional MOS devices [53-56].

The typical structure of single electron transistors based on Si nanocrystals is shown in Fig.2.17 [53]. It was fabricated using nano-imprint lithography, consisting

of a narrow channel MOSFET with an Si quantum dot embedded between the channel and the gate.

Fig.2.17. Schematic illustration of a single electron transistor. [53]

Fig.2.18 shows the drain current as a function of the gate voltage. The device was characterized at room temperature. By applying a voltage of 7 V to the gate for 1 μ s, the charge trapping in the nanocrystal dot caused a shift in the threshold voltage. By applying 9 V for 1 μ s, the threshold voltage was increased more than it was by applying 7 V.

Fig.2.18. I_d vs. V_g for the single electron transistor at room temperature. [53]

Fig.2.19. Threshold voltage of the single electron memory as a function of the applied voltage pulse.

[53]

Fig.2.19 shows the discrete increase in the threshold voltage, which indicates that a electron charges into the Si quantum dot at 6 V and the second electron charges at 9 V. The result is attributed to the Coulomb blockade effect as a second electron needs a higher charging voltage to overcome the Coulomb energy arising from the first electron occupying the quantum state. Charge retention measurement was also conducted, as shown in Fig.2.20. The charge could be stored in the nanocrystal for days, showing good data retention ability. The authors indicated that a good SiO_2 quality is necessary for the improvement of retention charging.

Fig.2.20. The shift of threshold voltage as a function of waiting time. [53]

2.5 Summary

This chapter has presented the reader with a description of the methods of preparing dielectric films containing nanocrystals. The physical properties of such films have been characterized by other researchers using various techniques including TEM, PL, and EL. Tunneling and electrical forming between quanta dots in dielectric films have been reviewed. In single electron devices, the Coulomb blockade effect dictates the transport properties. Working with these films creates the possibility of realizing Si-based optical IC, nano-memory devices, and single electron devices.

Having looked at a number of studies by previous researchers, it is clear that there are still many areas to explore. How should nanocrystal distribution in dielectric films be determined? How does the band gap change with the reduction of nanocrystal size and how can it be determined? For waveguide applications, the depth profile of optical constants should be known. How can they be found? Have all the embedded semiconductor atoms been converted into nanocrystals after high temperature annealing? If the answer is no, then which ones have not been so converted? Does the distribution of nanocrystals affect the electrical properties? If yes, in what way? ...

We will discuss these issues in the following chapters.

Chapter 3: Synthesis and Characterization of Si Nanocrystals Embedded in SiO₂ Matrix

3.1 Introduction

Nanomaterial research, particularly into the synthesis and characterization of nanocrystalline Si embedded in SiO₂ films, has attracted much attention because such films exhibit light-emission properties and memory effects. Potential applications of these films are numerous, such as Si-based optical ICs, nano-memory devices, and single electron devices [57,46,59-61]. In order to realize some of the applications through modern CMOS processes, such films should be produced using a process that is fully compatible with Si technology.

This chapter describes the synthesis of Si nanocrystals embedded in SiO₂ films using the ion implantation technique. Processes for the fabrication of SiO₂ films containing Si nanocrystals and MOS structures with nc-Si embedded in the gate oxide have been developed that are fully compatible with modern CMOS technology. Various techniques, including XRD, TEM, SIMS, FTIR, Raman Scattering, and PL, are used to characterize the structural and physical properties of these films. Capacitance-voltage (C-V) measurements have been conducted to study the charge storage properties, while current-voltage (I-V) measurements have been carried out to study the charge transport properties of such films.

3.2 Synthesis

To synthesize Si nanocrystals embedded in SiO₂ matrix, it is essential to follow the conventional wafer-processing technologies. In this regard, the experimental design is based on the processes of CMOS fabrication, and the whole fabrication procedure was carried out in the cleanroom of the Micro-Fabrication Laboratory of the School of Electronic and Electrical Engineering at Nanyang Technology University.

To study the physical properties of Si nanocrystals, the experiment began with the p-type, 100-oriented Si wafers. 550 nm thick SiO₂ films were grown on the Si substrates by wet oxidation at 1000°C. The oxide was measured by ellipsometry to ensure that the thickness was within the specification of 550 nm $\pm$ 25 nm. Si ion implantation was conducted in a vacuum chamber at very low pressure (10⁻⁵ torr) at room temperature. SiF₄ was used as a source of Si ions, which is better than SiH₄ because of its easily ionized property. Large numbers of Si ions (10¹⁶-10¹⁷ atoms/cm²) were implanted into the SiO₂ films, and the implantation energies chosen ranged from 5 to 100 keV. Thermal annealing was carried out in N₂ ambient. For the annealing temperature experiment, the temperature varied from 500 to 1100°C, but the annealing time was fixed at 20 min. For the annealing time experiment, the time varied from 0 to 100 min, while the annealing temperature was kept at 1000°C.

To form a second sample, 30 nm SiO₂ thin films were grown on p-type Si wafers with (100) orientation by thermal oxidation in dry oxygen at 950°C. Then, Si ions were implanted into the SiO₂ films at energies of 1- 3 keV with a dose of 8 $\times$ 10¹⁶ cm⁻².

The annealing conditions for these thick oxide samples were the same as those described above.

Fig.3.1. Cross-section scheme of a SiO₂ film containing Si nanocrystals prepared with ion implantation.

A schematic cross section of a SiO₂ film containing Si nanocrystals is shown in Fig.3.1. As revealed later by SIMS measurement, ion implantation leads to a Gaussian-like distribution of Si nanocrystals in SiO₂ matrix. The method of forming the dielectric films consisting of Si nanocrystals is described below.

Step	Process	Description
0	Starting Wafer	P<100>, Boron doped, 9-12 Ω-cm
1	Oxide Growth	Spec = 550 ± 25 nm or 30 ± 2.5 nm
1a	Preclean	Clean Recipe 1. H ₂ SO ₄ /H ₂ O ₂ (4:1), 100 ± 5°C 10 min 2. Quick Dump Rinse 6 cycles 3. H ₂ O: HF = 20:1, RT 12 sec 4. Quick Dump Rinse 6 cycles 5. IPA Dry

Step	Process	Description
1b	Oxidation	<p>Wafer 1-8 # oxide thickness = 550 ± 25 nm, Wet oxidation at 1000°C 95 min. Pyrogenic steam, 1000°C 5 min. Dry oxidation, 1000°C 5 min. Annealing, 1000°C</p> <p>Wafer 9-11# oxide thickness = 30 ± 2.5 nm Dry oxidation at 950°C 5 min. Dry oxidation, 950°C 68 min. Dry oxidation, 950°C 1 min. Diluted dry oxidation, 950°C 20 min. Annealing, 950°C</p>
2	Si Ion Implantation – Varian® implanter	<p>Wafer 1# dose = $8 \times 10^{16} \text{ cm}^{-2}$ energy = 100 keV, Wafer 2# dose = $1 \times 10^{17} \text{ cm}^{-2}$ energy = 50 keV, Wafer 3# dose = $8 \times 10^{16} \text{ cm}^{-2}$ energy = 50 keV, Wafer 4# dose = $6 \times 10^{16} \text{ cm}^{-2}$ energy = 50 keV, Wafer 5# dose = $4 \times 10^{16} \text{ cm}^{-2}$ energy = 50 keV, Wafer 6# dose = $2 \times 10^{16} \text{ cm}^{-2}$ energy = 50 keV, Wafer 7# dose = $8 \times 10^{16} \text{ cm}^{-2}$ energy = 5 keV, Wafer 9# dose = $8 \times 10^{16} \text{ cm}^{-2}$ energy = 3 keV, Wafer 10# dose = $8 \times 10^{16} \text{ cm}^{-2}$ energy = 1 keV.</p>
3	Annealing	<p>Annealing wafers in nitrogen ambient</p> <p>a) For different temperatures 500°C, 600°C, 700°C, 800°C, 850°C, 900°C, 1000°C, 1100°C for 20 min</p> <p>b) For various durations 20 min, 30 min, 40 min, 60 min, 80 min, 100 min at 1000°C.</p>

Table 3.1 Process flow for the synthesis of Si-implanted SiO₂ films

3.3 Characterization of Structural and Physical Properties

3.3.1 SIMS Measurement and TRIM Simulation

With the samples prepared as described in **Section 3.2**, it is essential to ascertain the distribution of nanocrystals in the SiO₂ films. Secondary ion mass spectroscopy (SIMS) is widely used to trace elements in solid materials, especially semiconductors within thin films, and is noted for its exceptional sensitivity and depth profiling capability [63-65]. In our measurements, SIMS is used to determine the depth profiles of excess Si in SiO₂ films and Cs⁺ is used as the primary beam to sputter off atomic layers of the sample. Fig.3.2 shows a typical depth profile of excess Si in Si-implanted SiO₂ films. Implantation of Si at 50 keV with a dose of $2 \times 10^{16} \text{ cm}^{-2}$ leads to a Gaussian-like distribution from the surface to a depth of 160 nm.

Fig.3.2. Depth profile of excess Si in Si-implanted SiO₂ films. Implantation was conducted at 50 keV with a dose of $2 \times 10^{16} \text{ cm}^{-2}$.

TRIM code simulation is a group of programs that calculate the stopping and the range of ions into matter based on a quantum mechanical treatment of ion-atom collisions [62]. It is a theoretical and efficient method of forecasting the profile of implanted ions. Our calculations have been performed to obtain the ion distribution using the SRIM2003 code. Fig.3.3 shows the comparison of implanted Si profiles between TRIM simulation and SIMS measurement. Both TRIM simulation and SIMS measurement illustrate that 100 keV implantation of Si leads to a distribution from the surface to a depth of 250 nm with the peak being located at about 130 nm. The consistency between the two methods provides us with an opportunity to determine the profile of nanocrystals both theoretically and experimentally. The excess Si profiles in SiO₂ obtained from the two methods will be used as references to check the validity of a new depth profiling technique that is developed in this work based on ellipsometry. Details will be given in Chapter 4.

Fig.3.3. Depth profiles of the implantation of Si obtained from SIMS and TRIM code calculation.

3.3.2 Image of Si Nanocrystals Embedded in SiO₂ Matrix by TEM

TEM is extensively used to identify nanocrystals embedded in dielectric films [66-69], and information about nanocrystal sizes, distributions, and lattice structures can be obtained from TEM images. In order to prepare suitable TEM specimens, our wafers with Si/SiO₂ nanostructured films were cut into 5 mm discs. These discs were dimpled and polished for both sides. Then, samples were milled by argon plasma at 5 keV and a thinning angle of 14° at room temperature. Finally, microstructures of the sample were characterized using a transmission electron microscope equipped with an energy dispersive X-ray spectroscope.

Fig.3.4. TEM image of nc-Si embedded in SiO₂ matrix. The implantation was conducted at 1 keV into 30 nm SiO₂ film.

Fig.3.4 is a TEM micrograph showing the crystalline structure of nc-Si embedded in SiO₂ matrix. Throughout most of the image, only amorphous SiO₂ is visible and no lattice structures can be observed. The circled areas are the crystalline lattice

structures, which demonstrate the existence of nanocrystalline Si. The size of the nanocrystals ranges from 2 to 5 nm. From HRTEM images, the density of nc-Si is estimated to be at the level of $10^{11} / \text{cm}^2$. Equation 2.2 in Chapter 2 can be used to estimate the nc-Si density from flat-band voltage shifts. In the 30-nm samples, the density is about $3 \times 10^{11} / \text{cm}^2$. Results from the two approaches are consistent, and it is also reported in [45, 46] that the density of nc-Si is between $10^{11} / \text{cm}^2$ to $10^{12} / \text{cm}^2$.

3.3.3 Size Evaluation by XRD

Fig.3.5. XRD measurement of the nc-Si and the curve fitting.

XRD measurements were conducted with a Philips PW 3719 diffractometer. The mean grain size of the as-implanted samples and the samples annealed under different conditions were determined by X-ray diffraction analysis. Some studies have examined the grain size of semiconductors embedded in dielectric films [70, 71] from

the broadening of X-ray diffraction patterns. To obtain the size of nanocrystals, Scherrer's equation is generally used:

$$t = \frac{0.9\lambda}{\varepsilon \cos(\theta_B)} \quad (3.1)$$

where t is the size of the cluster, λ is the wavelength of the x-ray (0.154 nm), ε is the full width at half maximum (FWHM) of the Bragg peak in radians, and θ_B is the Bragg angle. However, ε should be corrected for instrumental broadening by using the following equation [72]:

$$\varepsilon^2 = \varepsilon_M^2 - \varepsilon_s^2 \quad (3.2)$$

where ε is the corrected FWHM, ε_M is the measured FWHM of the peak, and ε_s is the FWHM of polycrystalline Si standard (instrumental broadening).

Fig.3.6. Mean size of nc-Si vs. annealing temperature. The samples are prepared by 1 keV implantation into 30 nm oxide.

The XRD spectrum for the sample annealed at 700°C for 20 min is shown in Fig.3.5. The mean size could be determined from the FWHM of the Bragg peak after

correction for instrumental broadening, as described above. Using Scherrer's equation, the obtained mean size is about 2.7 nm, which is consistent with the TEM results. Furthermore, as can be seen in Fig.3.6 and Fig.3.7, the nc-Si size obtained is ~ 2.5 nm for the as-implanted sample and ~ 3 nm for the samples annealed at various temperatures for various durations. This result is similar to that of [73] in which it is reported that the nc-Si size increases slightly from 2.5 nm after 1 min annealing to 3 nm after 16 hours annealing at the temperature of 1100°C. This very slow evolution is due to the very low diffusion coefficient of Si in SiO₂. For the thick oxide samples with high-energy implantation, the mean size is about 4.5 nm, which will be discussed in Chapter 4.

Fig.3.7. Mean size of nc-Si vs. annealing time. The sample annealed for 0 min corresponds to the as-implanted sample. The samples were prepared by 1 keV implantation into 30 nm oxides.

3.3.4 Photoluminescence

To acquire the photoluminescence spectra, our samples were excited at various wavelengths ranging from 220 to 1100 nm with a Xe lamp as the excitation source.

Fig.3.8 shows the annealing effect on Si-implanted samples at 1 keV with $8 \times 10^{16} \text{ cm}^{-2}$ Si fluence. As can be seen in the figure, both the as-implanted and annealed samples emit light. There does not appear to be any significant modification of light emission intensity or any obvious shift in the emission peak position caused by annealing. These results are consistent with our XRD results. As discussed previously, annealing leads to a very small increase in the mean size of nc-Si (an increase of 0.5 nm) and such an increase does not seem enough to affect the light emission intensity. On the other hand, we do not observe any trend of redshift or blueshift as a result of annealing, as shown in Fig.3.9. The PL spectra of Si-implanted films annealed under various conditions all center around 751 nm with distortions within 1.5 nm. The results can be attributed to the fact that there is not enough modification of the nc-Si band gap because nc-Si only grows by $\sim 0.5 \text{ nm}$ through annealing. Band gap narrowing with such a small growth may not lead to significant emission distortion in PL spectra. Fig.3.10 shows the PL emission peak position as a function of annealing time. The sample annealed for 0 min represents the as-implanted film. The result is consistent with that of the annealing temperature study: no trend of redshift or blueshift was observed when the annealing duration was extended.

Fig.3.8. Room temperature PL spectra from Si implanted SiO_2 for the as-implanted sample and the sample annealed at 900°C in N_2 for 20 min.

Fig.3.9. PL peak position as a function of annealing temperature. The duration is fixed for 20 min.

Fig. 3.10. PL peak position as a function of annealing time. The temperature is fixed at 1000°C.

3.3.5 FTIR Characterization

Fourier transform infrared spectroscopy (FTIR) is an important technique in the characterization of the bonding and structural properties of thin SiO₂ films [75-80]. In this work, FTIR measurement was conducted to study the implantation and annealing effects on the Si-O bonding properties of Si-implanted SiO₂ films. The spectra of the films were obtained in the absorbance mode by subtracting the Si substrate spectrum from the total signal.

The FTIR spectrum of the pure SiO₂ film shows the characteristic Si-O stretching band, located at 1082 cm⁻¹, shown in Fig.3.11. After Si implantation, a shift of the stretching band to lower wavenumbers can be observed. This indicates that ion implantation causes a change in the Si-O bond structures, and the redshift could be interpreted as the narrowing of the O-Si-O bond angle as a result of the replacement of O atoms by the implanted Si atoms and the formation of Si-Si bonds [81, 82]

Fig.3.11. FTIR spectra of SiO₂ and Si-implanted SiO₂ films. The implantation energy is 100 keV with a dose of $8 \times 10^{16} \text{ cm}^{-2}$.

However, after annealing at 600°C, the frequency is increased back to the value of thermally grown SiO₂, indicating recovery of the Si-O networks from the as-implanted state. As can be seen in Fig.3.12, for a higher annealing temperature (>500°C), the stretching frequency is even higher than the value of thermally grown SiO₂, and the frequency increases with the annealing temperature. This situation is explained as follows. The thermal oxide primarily consists of a 144° bond angle of Si-O-Si (6-member rings). In addition, it contains a very small portion of bond angles of 120° (4-member rings) and of 160° or more (7-, 8-member rings) [83]. The annealing leads to an increase of the population of SiO₂ with larger bond angles corresponding to 7- or 8-member rings. Thus, the increase of the stretching frequency with the annealing temperature can be explained in terms of the increase of the apparent bond angle of the SiO₂ networks. Fig.3.13 also demonstrates this trend. With the annealing duration extended, the Si-O stretching frequency increases to a value that is even higher than that of the thermally grown SiO₂, which indicates the formation of a portion of 7- and 8-member rings.

Fig.3.12. Frequency of the Si-O stretching band as a function of the annealing temperature. The implantation energy is 100 keV and the dose is $8 \times 10^{16} \text{ cm}^{-2}$.

Fig.3.13. Frequency of the Si-O stretching band as a function of the annealing time. The implantation energy is 100 keV and the dose is $8 \times 10^{16} \text{ cm}^{-2}$.

3.3.6 Raman Characterization

Raman scattering has been demonstrated to be sensitive to the bonding of material and the order/disorder of crystalline structures [84-86]. Accordingly, this technique is suitable for examining the structural properties of our nanocrystal embedded films, providing complementary information about FTIR. Our samples were characterized by Raman scattering at room temperature using a Renishaw 1000 Ramascope system. The 514.5 nm line of an argon laser was used for excitation.

Raman spectra of Si-implanted films and pure SiO₂ films are shown in Fig.3.14. The narrow peak at 520 cm^{-1} can be observed in all spectra due to scattering by the silicon substrate. The as-implanted sample reveals a broadband centering at 520 cm^{-1} , which indicates the presence of disorder in the SiO₂ layer. Obviously, it is related to

the Si implantation, which introduces Si-Si bonds into the Si-O matrix (as presented in the FTIR study). Thus, the Raman spectra are modified with asymmetric broadening. As shown in Fig.3.14(b), high temperature annealing leads to the recovery of Si-O networks from the as-implanted state. It therefore reduces the disorder in Si-implanted films, resulting in the disappearance of the asymmetric broadening. This result agrees with that from the FTIR study as both implanted Si and the O-Si-O form their own networks as a result of annealing.

Fig.3.14(a). Raman spectrum of the as-implanted film. The implantation energy is 50 keV and the dose is $8 \times 10^{16} \text{ cm}^{-2}$.

Fig. 3.14(b). Raman spectrum for the Si-implanted SiO₂ films annealed at 1000°C for 20 min, and for the pure SiO₂ on Si substrate without nanocrystals (c). The implantation energy is 50 keV and the dose is $8 \times 10^{16} \text{ cm}^{-2}$.

3.4 Fabrication of MOS Structures with nc-Si Embedded in the Gate Oxide

MOS structures were fabricated using Si wafer-processing technology. 1 keV Si-implanted SiO₂ films prepared under different annealing conditions as described in section 3.2.1 were used to realize MOS capacitors. A 20 nm layer of aluminum was deposited on the oxide to form a gate electrode. The “lift-off” technique was used to remove unwanted metal areas. Ohmic contact on the backside of the wafer was formed by a standard aluminum alloy process in forming gas.

To study the influence of nc-Si distributions on electrical characteristics, MOS structures with nc-Si distributed throughout the gate oxide were also prepared. Silicon wafers were (100) oriented and boron-doped with a concentration of $2 \times 10^{15} \text{ cm}^{-3}$. Si⁺ ions were implanted at 14 keV with a dose of $3 \times 10^{16} \text{ cm}^{-2}$ into 30 nm SiO₂ films, which were thermally grown on Si wafers in dry oxygen at 950°C. The TRIM simulation shows that the Si ions were distributed throughout the gate oxide with the peak concentration occurring at a depth of about 20 nm below the SiO₂ surface, which is consistent with the Secondary Ion Mass Spectroscopy (SIMS) result. Thermal annealing was carried out at 1000°C in N₂ ambient for 1 hour to induce the nc-Si formation. Then, the oxide layer was thinned in a diluted HF solution and a 15 nm oxide was etched off so that the nc-Si concentration peak was located close to the surface. Finally, a 20 nm layer of aluminum was deposited on the oxide to form a gate electrode. Ohmic contact on the backside of the wafer was formed by a standard aluminum alloy process.

Fig.3.15 shows the schematic cross section of the MOS structure with nc-Si confined to a narrow region in the gate oxide prepared with 1 keV Si-implanted samples. Note that the nanocrystals are only distributed from the oxide surface to a depth of 15 nm. Fig.3.16 gives a schematic illustration of the MOS structure with nc-Si embedded throughout the oxide, with the peak concentration being located close to the metal gate. For such a structure, charging/ discharging in nc-Si leads to magnitude modulations in both MOS capacitance and gate current, which is very different from the situation of a conventional structure shown in Fig. 3.15, with which charging/discharging in nc-Si leads to flat-band voltage shifts. A detailed discussion on the effect of nc-Si distribution will be presented later in this chapter and in **Chapter 6**.

Fig.3.15. Schematic illustration of the MOS structure with nanocrystals confined to a narrow region in the gate oxide.

Fig.3.16. Schematic illustration of the MOS structure with nanocrystals distributed throughout the gate oxide. The peak concentration of nc-Si is at the oxide surface.

The process for fabricating the MOS structures is described below:

1. Synthesis of the MOS structures with nc-Si confined to a narrow layer in the gate oxide.

Step	Process	Description
0	Starting Wafer	P<100>, Boron doped, 9-12 Ω -cm
1	Oxide Growth	Spec = 30 ± 2.5 nm
1a	Preclean	Clean Recipe 1. $H_2SO_4/H_2O_2(4:1)$, $100 \pm 5^\circ C$ 10 min 2. Quick Dump Rinse 6 cycles 3. H_2O : HF = 20:1, RT 12 sec 4. Quick Dump Rinse 6 cycles 5. IPA Dry

Step	Process	Description
1b	Oxidation	Wafer A and B# oxide thickness = 30 ± 2.5 nm Dry oxidation at 950°C 5 min. Dry oxidation, 950°C 68 min. Dry oxidation, 950°C 1 min. Diluted dry oxidation, 950°C 20 min. Annealing, 950°C
2	Si Ion Implantation – Varian® implanter	Wafer A# dose = 8×10^{16} cm ⁻² energy = 1 keV.
3	Annealing	Annealing in N ₂ ambient a) For different temperatures 500°C, 600°C, 700°C, 800°C, 850°C, 900°C, 1000°C, 1100°C for 20 min b) For various durations 20 min, 30 min, 40 min, 60 min, 80 min, 100 min at 1000°C.
4	Patterning	Coating photo-resist Align and expose under UV Develop photo-resist and hard bake
5	Metal Deposition	Evaporation of aluminum for 20 nm
6	Photo-resist Strip	Dry techniques O ₂ ashing Nanostrip clean: 60°C for 10 min Drying process
7	Backside Metal Deposition	Aluminum = 1 μm Coating photo-resist onto front side (to protect nano-structured films) 50:1 HF dip for 30 sec Photo-resist strip Evaporation of Al
8	Metal Alloy	N ₂ 425°C for 20 min, load N ₂ +H ₂ 425°C for 25 min N ₂ 425°C for 2 min N ₂ for 20 min 425°C, unload

Table 3.2. Process for fabricating the MOS structures with nc-Si confined to a narrow region in the oxide.

2. Synthesis of the MOS structures with nc-Si embedded throughout the oxide.

Step	Process	Description
0	Starting Wafer	P<100>, Boron doped, 9-12 Ω -cm
1	Oxide Growth	Spec = 30 ± 2.5 nm
1a	Preclean	Clean Recipe 1. H ₂ SO ₄ /H ₂ O ₂ (4:1), 100 $\pm$ 5°C 10 min 2. Quick Dump Rinse 6 cycles 3. H ₂ O: HF = 20:1, RT 12 sec 4. Quick Dump Rinse 6 cycles 5. IPA Dry
1b	Oxidation	Wafer C and D Dry oxidation at 950°C 5 min. Dry oxidation, 950°C 68 min. Dry oxidation, 950°C 1 min. Diluted dry oxidation, 950°C 20 min. Annealing, 950°C
2	Si Ion Implantation – Varian [®] implanter	Wafer C# dose = 3×10^{16} cm ⁻² energy = 14 keV.
3	Annealing	Annealing in nitrogen ambient 1000°C for 1hour
4	Oxide Thinning	Wet etching 20:1 HF for 1.5 min (etching rate 10 nm/min) Drying process
5	Patterning	Coating photo-resist Align and expose under UV Develop photo-resist and hard bake
6	Metal Deposition	Evaporation of aluminum for 20 nm
7	Photo-resist Strip	Dry techniques O ₂ ashing Nanostrip clean: 60°C for 10 min Drying process
8	Backside Metal Deposition	Aluminum = 1 μ m Coating photo-resist onto front side (to protect nano-structured films) 50:1 HF dip for 30 sec Photo-resist strip Evaporation of Al
9	Metal Alloy	N ₂ 425°C for 20 min, load N ₂ +H ₂ 425°C for 25 min N ₂ 425°C for 2 min N ₂ for 20 min 425°C, unload

Table 3.3. Process for fabricating the MOS structures with nc-Si throughout the oxide.

For further device applications, the gate oxide thickness can shrink to less than 10nm via precise selection of the implantation energy and dose. For a conventional nonvolatile memory device based on nc-Si, it includes a substrate with source and drain regions, a 2-3 nm tunneling oxide above the substrate, and a control oxide embedded with nanocrystals above the tunneling oxide . Following processes can be used to fabricate the memory structure with an oxide thickness of less than 10nm: a oxide of 7-8 nm is grown firstly; Si ions are implanted at very low energy (less than 1keV) with a selected dose such that the implanted Si atoms distribute to a depth of 4-5 nm in the top oxide layer; thermal annealing is conducted to remove the damages induced by ion implantation. Total gate oxide thickness is 7-8 nm upon such a synthesis process.

For devices with high concentration of nanocrystals distributing throughout the oxide, the synthesis is much simpler: an oxide layer with expected thickness (such as 10 nm) is thermally grown on the substrate; Si ions are implanted with an acceleration energy set such that implanted Si atoms distribute throughout the oxide and exist to a depth of a few nanometers within the substrate; the dose and the energy are determined based on the thickness of the oxide layer required; thermal annealing in inert ambient to remove the oxide damages; the surface layer (say 5 nm) with a relatively low concentration of nanocrystals is removed by wet or dry etching. Thus , the oxide thickness can be reduced to 4-5 nm.

3.5 Electrical Characterization

The main hardware for the electrical measurements included the Keithley Model 4200 semiconductor characterization system, the HP 4284A precision LCR meter, and the Karl Suss probe station. The Keithley 4200 system is ideal for the DC device characterization and was mainly used for current-voltage measurements in this study. The HP 4284A LCR meter was used to measure the capacitance characteristics of devices at 1 M Hz. The experimental setup is illustrated in Fig.3.17.

Fig.3.17. Experimental setup for electrical measurements of MOS devices.

3.5.1 Capacitance-voltage Characterization

In addition to the light emission properties, SiO₂ films containing Si nanocrystals have attracted much attention as a promising candidate for nano-memory devices and single electron devices [46,59-61]. For these applications, C-V measurement is usually used to characterize charge storage, charging/discharging, and charge retention time properties.

Under identical measurement conditions, the control samples with pure SiO₂ (i.e., without nanocrystals) were also investigated, where no flat-band voltage shifts were found after application of -4V for 10 sec, as shown in Fig.3.18 (a). Fig.3.18 (b) shows C-V curves of MOS structures with nanocrystals embedded in the gate oxide after a negative voltage (-4V) was applied to the gate for 10 sec. A flat-band voltage shift for about 0.7 V can be noticed for the MOS capacitors. These results demonstrated that electron tunneling occurred from the gate towards the nanocrystals.

Fig.3.18. C-V characteristics of the MOS structures (a) without nanocrystals and (b) containing nanocrystals confined to a narrow region in the gate oxide.

Fig.3.19. The energy band diagram for electron trapping in nc-Si embedded in SiO_2 films.

The energy band diagram of the MOS memory is shown in Fig.3.19. When a negative voltage is applied to the gate, electrons will be injected from the metal gate and some of them will become trapped in the quantum wells induced by the nanocrystals. These “trapped charges” will lead to a flat-band voltage shift, as shown in Fig.3.18 (b).

Fig.3.20. Flat-band voltage shift (ΔV_{FB}) as a function of the gate voltage. Each negative voltage was applied to the gate for 1 sec.

The flat-band voltage shift (ΔV_{FB}) as a function of the gate voltage (V_g) is shown in Fig.3.20. Si ions were implanted into 30-nm oxide at 1keV and 2keV, resulting in different nc-Si distributions in the gate oxides. No ΔV_{FB} appears in the C-V curves at a negative gate bias lower than $-1V$. As can be seen in this figure, for 1keV and 2keV samples, a higher gate voltage leads to more electrons trapping in nc-Si, and thus a larger ΔV_{FB} . The 2keV-implanted sample shows a larger ΔV_{FB} at the same V_g than that of the 1keV-implanted sample. This can be attributed to the distribution of the nc-Si. The 2keV implantation leads to a deeper distribution of nc-Si near to the middle of oxide, and thus charge trapping in these devices are more effective to shift the flat-band voltage. The programming characteristics for different implantation energies are shown in Fig.3.21. The programming is performed with a negative 15V on the gate for various durations. For the 2keV-implanted samples, programming is possible even less than 1 ms duration, while programming is only applicable more than 1 s for 1keV-implanted samples. The difference between the two types of samples highlights the nc-Si distribution for memory device performance.

Fig.3.21. Programming characteristics of devices with different nc-Si distributions. The voltage applied to the gate is -15 V.

It is also possible for charges trapped in nc-Si to tunnel out. Measurements of the charge retention time at room temperature were conducted. The flat-band voltage after electron charging as a function of time is shown in Fig.3.22. The charging retention time for the structures is very long; that is, during the 10 hours ΔV_{FB} decreases only by 0.1 V. This means that few charges trapped in the nanocrystals tunneled out at room temperature, thus indicating very good data retention ability.

Fig.3.22. Flat-band voltage shift vs. time (sec).

As defects can lead to gate oxide charging, and thus a shift in flat-band voltage, a study on the evolution of flat-band voltage with annealing may be useful in understanding the effect of defects on the electrical characteristics of the devices. As shown in figure 3.23, the effect of annealing on the defects produced during ion implantation can be demonstrated by comparison of flat-band voltage for samples annealed under various temperatures and the V_{FB} for the SiO_2 with similar thickness. As can be seen in this figure for the as-implanted sample, the V_{FB} is around -40 V indicating that a large amount of defects were produced in ion implantation. For annealings conducted lower than 900°C, the flat-band voltage decreases with

temperature increasing, while for annealings conducted higher than 900 °C, there are no significant changes in flat-band voltage. Actually, V_{FB} for 900 °C, 1000 °C and 1100 °C are -1.7V, -1.4V, and -1.4V, respectively, almost the same as that of the pure SiO_2 sample. This means defects can be significantly reduced with a higher temperature annealing, and with an annealing higher than 900 °C, the defects can be reduced to the same level of the pure SiO_2 .

Fig.3.23 Changes in the flat-band voltage with annealing temperature. The annealing time is fixed at 20 min.

Such a conclusion is confirmed with the following experiments. We also measured flat-band voltage evolution with annealing time for an annealing temperature of 1000°C, and the result is shown in figure 3.24. As can be seen in this figure, the V_{FB} shows a very large decrease after the first 20 min but almost keeps constant after longer annealing. As a 20-minute annealing at 1000°C already reduces the defect level to that of the pure SiO_2 , there is no obvious modification in the flat-band voltages for longer annealing durations.

Fig. 3.24. Changes in the flat-band voltage as a function of annealing time. The annealing temperature is fixed at 1000°C.

In order to study the influence of nc-Si distribution on C-V characteristics, nc-Si was embedded in the gate oxide with the peak concentration close to the metal gate of MOS structures. For comparison, a MOS capacitor with a gate oxide thickness of 15 nm and a gate area of $100 \times 100 \mu\text{m}^2$ has a capacitance of ~ 23 pF under strong accumulation if there are no nanocrystals embedded in the gate oxide. However, as can be seen in Fig.3.25, when nanocrystals are embedded throughout the gate oxide, the capacitance is much larger than this value. A similar situation can be observed under inversion. This indicates that the nanocrystals make a major contribution to the capacitance when they are embedded in oxide with most of them located at the oxide surface.

Fig.3.25. C-V measurements of the MOS structures with Si nanocrystals embedded in the gate oxide close to the metal gate.

Fig.3.26 shows the situation of -5 V stress. As can be seen in this figure, the first 10 sec of stress reduces the capacitance at -3 V from the virgin value of 78.7 pF to a value of 2.5 pF, with a reduction factor of about 32, and the second 10 sec stress reduces the capacitance to a level that is close to the limit of our measurement system. The results of negative voltage stresses here indicate the influence of the nanocrystal distributions on the capacitance of the gate oxide. Details are discussed below. Another important observation from Figure 3.26, however, is that the flat-band voltage shift is not obvious. The reason for this is that, as most of the nanocrystals are located near the gate, the charge trapping in the nanocrystals will not have a large contribution to the flat-band voltage. A detailed discussion of the above phenomena is provided in **Chapter 6** where an equivalent capacitance model is proposed.

Fig.3.26. Influence of negative voltage stress on the C-V characteristics.

It should be noted that the influence of charge trapping in the nanocrystals on the C-V characteristics for the nc-Si distribution of this study is very different from that in nanocrystals confined to a narrow layer embedded in the gate oxide. In the latter case, the charge trapping in the nanocrystals leads to a shift of the C-V curve (i.e., a change in the flat-band voltage; see Fig.3.18), but it does not change the capacitance magnitude under accumulation or inversion. In contrast, in the former case, the charge trapping leads to a dramatic reduction in the capacitance magnitude, but no flat-band voltage shift can be seen as the MOS capacitance is reduced to an extremely low level. Of course, as most of the nanocrystals are located near the gate in this case, the charge trapping in the nanocrystals will not make a large contribution to the flat-band voltage. The difference between the two cases highlights the importance of the nc-Si distribution.

3.5.2 Current-voltage Characterization

The transport mechanisms and charge trapping of dielectric systems are generally studied using current-voltage characterization. Despite the large number of studies on electrical properties [61, 87-89, 91, 92, 94-98, 183], there are still many unanswered questions about the basic electrical characteristics of nano-memory devices. Our purpose is to improve understanding of the mechanism of electron tunneling via nanocrystals and of the influence of nc-Si distribution on carrier transport properties.

For all of the samples, I-V measurements were performed at room temperature. A typical tunneling current behavior of pure SiO_2 film with a thickness of 30 nm from 0 to 3.5 V is shown in Fig.3.27. One can observe an extremely low tunneling current within this range; that is, the current is at the level of $\sim 10^{-13}$ A.

Fig.3.27. I-V characteristics of pure SiO_2 films. The thickness of SiO_2 is 30 nm.

Fig.3.28. Coulomb staircases in I-V characteristics of the MOS structures with nc-Si embedded in the gate oxide.

Fig. 3.28 shows I-V characteristics of MOS structures with nanocrystals embedded in the gate oxide. As compared to the pure SiO_2 sample shown in Fig.3.27, the tunneling current increases about 1 decade with the introduction of nc-Si. This can be attributed to the fact that electrons can tunnel to the conduction band via the embedded nc-Si. Detailed discussions on tunneling via Si nanocrystals will be carried out in **Chapter 6**. In addition, several Coulomb staircases in the I-V curves can be observed with each step corresponding to one electron charging state. Single electron tunneling occurs via these electron states, leading to staircases in the gate current.

Nanocrystal distribution also plays an important role in carrier transport. Fig.3.29 shows the I-V characteristics of an MOS structure with nanocrystals embedded throughout the oxide. The curve is found to follow a power law, which is similar to a typical post-breakdown I-V characteristic [99-103] of pure SiO_2 thin films. The

current is over 6-7 orders higher than that for nc-Si confined to a narrow region in the gate oxide, and 7-8 orders higher than that for pure SiO₂ film with an identical oxide thickness, as shown in Fig.3.28 and Fig. 3.27, respectively. This indicates that the nc-Si plays a key role in the current transport. For the samples with nc-Si confined to the oxide, the embedded nanocrystals can assist electron tunneling, and thus a decade of increasing tunneling current can be observed as compared to the pure SiO₂ samples, while for the samples with nc-Si distributed throughout the oxide, the neutral (or uncharged) nc-Si can form tunneling paths connecting the Si substrate to the metal gate, and thus a large current can be expected. A detailed discussion will be carried out in **Chapter 6**.

Fig.3.29. I-V characteristics of an MOS structure with nc-Si distributed throughout the gate oxide.

3.6 Summary

In summary, SiO₂ films containing Si nanocrystals are synthesized using high-dose Si implantation at various energies into SiO₂ matrix thermally grown on Si substrates, followed by annealing. Depth profiles of nc-Si can be obtained by SIMS measurement, which is in good agreement with TRIM simulation. TEM and XRD measurements show a very slow evolution of nanocrystal size with annealing due to the low Si diffusion rate in SiO₂. In PL characteristics, there is no significant modification to the light emission intensity. Moreover, there is no obvious trend of a shift in the PL peak position under various annealing conditions. This can be interpreted in terms of the slow evolution of Si nanocrystals in SiO₂ matrix by annealing, as presented in the XRD and TEM studies. The Si-O stretching peak of the FTIR spectra is used to monitor the structural changes of the Si-implanted SiO₂ films with annealing. Thermal annealing results in Si-O matrix recovery, which is consistent with Raman characterization.

For the MOS structures with nc-Si confined to a narrow region in the gate oxide, the charge storage and charge retention time properties have been characterized by C-V measurements. The results show that such films could be used for nano-memory devices and single electron devices. Coulomb staircases due to single electron tunneling can be observed in I-V characteristics. The influence of nc-Si distribution on charge storage and charge transport has been described briefly. More detail will be provided in **Chapter 6**.

Chapter 4: Optical Studies of Si Nanocrystal Embedded in SiO₂ Films

4.1 Introduction

For Si nanocrystals embedded in SiO₂ matrix, it is generally believed that size effect leads to difference of their optical and dielectric properties from those of bulk crystalline Si, and as the Si nanocrystals are isolated by the SiO₂ matrix the situation should be also different from that of a continued Si-nanocrystal film. Therefore, it would be interesting to examine the properties of the isolated nanocrystals embedded in SiO₂ matrix, and knowing the dielectric function of the nanocrystals isolated in SiO₂ matrix is definitely important to both solid-state physics and the applications. In **Section 4.3**, it will be shown that we have successfully developed an approach to determination of dielectric function of Si nanocrystals embedded in SiO₂ matrix based on spectroscopic ellipsometry analysis. The energy gap expansion of the Si nanocrystals due to the nanocrystal size effect has been obtained by modeling the real part of the dielectric function. From the energy gap expansion, the nanocrystal size can be also evaluated with two independent models including the phenomenological model and the bond contraction model. The results are consistent with the nanocrystal size obtained from XRD and TEM measurements.

Optical data transmission is the most promising way to overcome the bottleneck of interchip and intrachip communication. As there is a huge investment in the silicon technology, it is desirable to use Si-based optical emission, modulation and detection

devices because they can be integrated onto Si chips by using the existing matured Si technology. Recently, optical gain has been reported in nc-Si synthesized by implantation of Si into SiO₂ and annealing [52], leading to a hope of the fabrication of silicon laser, and waveguiding effects have also been observed in the measurement of optical gain in a layer of nc-Si prepared by Si ion implantation into synthetic silica substrates [105]. For applications such as light-emitting structures, single electron memories, optical storage devices or waveguides, it is essential to have detailed information on the exact depth distribution of Si nanocrystals for the Si-doped SiO₂ films. In **Section 4.4**, we have developed a nondestructive and inexpensive method to determine depth profiles of nc-Si in SiO₂ films based on an appropriate multi-layer model with ellipsometry. The results are in good agreement with SIMS measurements and TRIM simulations. On the other hand, for optoelectronic and photonic applications of nc-Si embedded in SiO₂ matrix, the information of the profiles of optical constants of the material system is necessary. In **Section 4.5**, we report one approach to determination of the depth profile of optical constants of Si-implanted SiO₂ films based on spectroscopic ellipsometry (SE), which is to model the nc-Si depth distribution obtained from SIMS measurement.

4.2 Ellipsometry

In this section, the hardware of ellipsometry is presented as well as the fundamentals and measurement capability of ellipsometry and how to obtain the useful information from ellipsometric data.

4.2.1 Hardware

In a spectroscopic ellipsometer (J. A. Woolam Co. VASE[®]) there are several important optical components that should be addressed. Xe or Hg-Xe arc lamps are commonly used as the light sources for the ellipsometer, because they exhibit roughly constant intensity output both as a function of time and as a function of wavelength. UV and IR optical fibers are used for light transport in their specific transmission regions, coupling the light beam from the monochromator to the polarizer. Chopper used in the ellipsometric system is to modulate the light intensity for the subsequent synchronous detection. The calcite Glan-Taylor polarizer, which is nearly ideal, is used as the most important optical element to convert light with any polarization into linearly polarized light. The analyzer in the system is Si and InGaAs photo-detectors, which show insensitive to the polarization state and linear to the input light intensity. Fig. 4.1 shows the optical arrangement of the ellipsometric components, illustrating light starts from the light source and terminates with a detector.

1. Sample
2. Analyzer
3. Photo-detector
4. Polarizer
5. Modulator
6. Xe light source

Fig. 4.1. Cross section illustration of the arrangement of basic optical components used in ellipsometers.

4.2.2 Fundamentals

As ellipsometry employs polarized light for measurements [106,107], to understand nature of polarized light is necessary. The first step in understanding polarized light is to review the electromagnetic plane wave, which can be obtained via Maxwell's equations. And Maxwell's equations for a non-conducting and non-dispersive medium are well known as

$$\vec{\nabla} \cdot \vec{E} = 0 \quad (4.1)$$

$$\vec{\nabla} \cdot \vec{B} = 0 \quad (4.2)$$

$$\vec{\nabla} \times \vec{E} + \frac{1}{c} \frac{\partial \vec{B}}{\partial t} = 0 \quad (4.3)$$

$$\vec{\nabla} \times \vec{B} - \frac{\mu\epsilon}{c} \frac{\partial \vec{E}}{\partial t} = 0 \quad (4.4)$$

where E and B are the electric and magnetic fields, c is the speed of light, and μ and ϵ are the permeability and dielectric function, respectively. For electric field, following wave equation can be obtained by combining Eq.4.1-4.4

$$\vec{\nabla}^2 \vec{E} - \frac{1}{v^2} \frac{\partial^2 \vec{E}}{\partial t^2} = 0. \quad (4.5)$$

The optical impedance v is defined as

$$v = \frac{c}{\sqrt{\mu\epsilon}} \quad (4.6)$$

Solving Eq.4.5, the electromagnetic plane wave can be expressed as

$$\vec{E}(\vec{r}, t) = \vec{E}_0 \exp\left(\frac{i2\pi N}{\lambda} \vec{q} \cdot \vec{r}\right) \exp(-i\omega t) \quad (4.7)$$

where $\vec{E}_0$ is a complex vector constant specifying the amplitude and polarization state of the wave, N is the refractive index ($=n+jk$), q is a unit vector along the direction of wave propagation, ω is the angular frequency of the wave, λ is the wavelength of the light in vacuum.

In an ellipsometric system, it is commonly to use a so-called p- and s- coordinate system. A polarize beam of light can be written as Jones vector [106] with p- and s-components.

$$\vec{E} = \begin{bmatrix} E_p e^{i\theta_1} \\ E_s e^{i\theta_2} \end{bmatrix} \quad (4.8)$$

The matrix element with subscript p or s describes the amplitude and phase of the p component and s component, respectively. Further, for a linearly polarized light Jones vector can be written as

$$\vec{E} = \begin{bmatrix} E_p e^{i\theta} \\ E_s e^{i\theta} \end{bmatrix} \quad (4.9)$$

where θ is the phase angle identically for both p and s components.

Fig. 4.2. Schematic illustration of polarized light encountering a three-medium system.

Ellipsometry analyzes the changes in polarization state of monochromatic light that is reflected from the sample surface. A beam of linearly polarized light with the electric field E can be represented by two components. One is the s -direction taken to be normal to the direction of propagation and parallel to the sample surface. The other is p -direction is taken to be normal to the direction of propagation and contained in the plane of incidence. Normally, when polarized light is reflected from a sample surface, both the amplitude and the phase will be modified depending on the optical properties of the sample.

Fig. 4.2 shows the schematic geometry of the linearly polarized light with p and s polarizations encountering a system including medium 0, 1 and 2. The Fresnel coefficient for p and s components representing light from medium 0 to medium 1 are given as [107] (subscript 0, 1 and 2 are for corresponding mediums; subscript p and s are for corresponding polarizations)

$$r_{01p} = \frac{N_1 \cos \phi_0 - N_0 \cos \phi_1}{N_1 \cos \phi_0 + N_0 \cos \phi_1} \quad (4.10)$$

$$r_{01s} = \frac{N_0 \cos \phi_0 - N_1 \cos \phi_1}{N_0 \cos \phi_0 + N_1 \cos \phi_1} \quad (4.11)$$

where N is the complex refractive index corresponding to each medium with its subscript, and ϕ represents the incident angle. Similarly, coefficients representing light from medium 1 to 2 can be expressed as

$$r_{12p} = \frac{N_2 \cos \phi_1 - N_1 \cos \phi_2}{N_2 \cos \phi_1 + N_1 \cos \phi_2} \quad (4.12)$$

$$r_{12s} = \frac{N_1 \cos \phi_1 - N_2 \cos \phi_2}{N_1 \cos \phi_1 + N_2 \cos \phi_2} \quad (4.13)$$

where the each symbol has the meaning corresponding to its subscript. For the total system as illustrated in Fig.4.2, R_p and R_s are given as

$$R_p = \frac{r_{01p} + r_{12p} \exp(-j2\beta)}{1 + r_{01p} r_{12p} \exp(-j2\beta)} \quad (4.14)$$

$$R_s = \frac{r_{01s} + r_{12s} \exp(-j2\beta)}{1 + r_{01s} r_{12s} \exp(-j2\beta)} \quad (4.15)$$

The exponent β can be expressed with the thickness of medium 1, L_1 , the complex refractive index for medium 1, N_1 , and wavelength, λ , as

$$\beta = 2\pi \left(\frac{L_1}{\lambda} \right) N_1 \cos \phi_1 \quad (4.16)$$

Finally, for the optical system, the ratio ρ of the complex reflection coefficients is given by [107]

$$\rho = R_p / R_s = \tan(\psi) \exp(j\Delta), \quad (4.17)$$

where

$$\tan(\psi) = \frac{|R_p|}{|R_s|} \quad (4.18)$$

$$\text{and } \Delta = \Delta_{rp} - \Delta_{rs}$$

where Ψ and Δ are the ellipsometric angles.

Also Equ.4.17 can also be symbolized as

$$\rho = \tan(\psi) \exp(j\Delta) = \rho(N_0 N_1, N_2, L_1, \phi_0, \lambda) \quad (4.19)$$

Complex index for each medium is related to the ellipsometric angles. Thus, ellipsometry allows us to access the optical properties of the system. For a homogeneous medium, $N = n + jk$, where n is the real part of the refractive index, and k is the extinction coefficient. The absorption coefficient α is related to the k as

$$\alpha = \frac{4\pi k}{\lambda} \quad (4.20)$$

where λ is the wavelength in vacuum. The dielectric function ε of the medium is related to the refractive index in the following manner:

$$\varepsilon = \varepsilon_1 + j\varepsilon_2; \quad (4.21)$$

$$\varepsilon_1 = n^2 - k^2; \quad (4.22)$$

$$\varepsilon_2 = 2nk. \quad (4.23)$$

Therefore, from Ψ and Δ measured from ellipsometry, ρ , N , and L can be obtained as well as ε . The optical and dielectric properties of the material can be determined. To apply the above thin film analysis to our nc-Si embedded SiO₂ matrix, the Maxwell-Garnett effective medium approximation (EMA) [107, 108] is a good constraint with two constituents: nc-Si and SiO₂. In this approximation dielectric function of the film is expressed as a uniform mixture of the components, weighted by the relative fraction of each constituent according to

$$\frac{\epsilon_i - \epsilon_{\text{SiO}_2}}{\epsilon_i + 2\epsilon_{\text{SiO}_2}} = v_i \frac{\epsilon_{\text{nc-Si}} - \epsilon_{\text{SiO}_2}}{\epsilon_{\text{nc-Si}} + 2\epsilon_{\text{SiO}_2}} \quad (4.24)$$

where v_i is the volume fraction of the nanocrystals, ϵ_{SiO_2} is the dielectric function of host material SiO_2 , and $\epsilon_{\text{nc-Si}}$ is the dielectric function of Si nanocrystal. This approach is found to work very well for our nc-Si/ SiO_2 system. Depending on what is already known about the sample, the technique can probe a range of properties including the optical constants, dielectric functions and chemical composition. Based on the three-medium model analysis, the further application is the analysis of multi-layer thin films, which is more powerful to give information on depth profiles for our material system. Multi-layer modeling of our nc-Si/ SiO_2 system will be discussed in detail in **Section 4.3-4.5**.

4.2.3 Ellipsometric measurement

A spectroscopic ellipsometer (J. A. Woolam Co. VASE[®]) is used to determine the ellipsometric angles Ψ and Δ in the wavelength range of 400 to 1200 nm with the incident angle fixed at 75° . In Fig. 4.3 (a) and (b), the Ψ and Δ for different Si implantation doses are shown. With the injected Si ions increasing, the curves shift rightside. Both relative phase change and relative amplitude change are significant. It is clear that the substantial change in the structure of the SiO_2 film is brought on by the implanted Si atoms. As Si^+ ion implantation into SiO_2 produces shifts of $\Psi(\lambda)$ and $\Delta(\lambda)$ curves, these Si in the oxide can be detected based on a proper model. On the other hand, these shifts also reflect the modification of optical properties of the film. With a multi-layer model developed with EMA, both optical constants of nc-Si as a function of wavelength and the depth profiles of optical constants will be determined.

Fig. 4.3. Ellipsometric angle Ψ (a) and Δ (b) as a function of wavelength for various implantation doses. The curve without implantation is for the pure SiO_2 sample.

4.3 Dielectric Functions of Si Nanocrystals Embedded in SiO₂ Matrix

4.3.1 Background and Motivation

In the material system of SiO₂ matrix embedded with Si nanocrystals, the optical and dielectric properties for the nanocrystals should be different from those of bulk crystalline Si due to the size effect, and as the Si nanocrystals are isolated by the SiO₂ matrix the situation should be also different from that of a continued Si-nanocrystal film. Therefore, it would be interesting to examine the properties of the isolated nanocrystals embedded in SiO₂ matrix, and knowing the dielectric function of the nanocrystals isolated in SiO₂ matrix is definitely important to both solid-state physics and the applications. In this work, an approach to determine the dielectric function of Si nanocrystals embedded in SiO₂ matrix synthesized with Si ion beams has been developed. The approach is based on the effective medium approximation (EMA), and appropriate models are developed to simulate the secondary ion mass spectroscopy and spectroscopic ellipsometry measurements on the material system. The energy gap expansion of the Si nanocrystals due to the nanocrystal size effect has been obtained by modeling the real part of the dielectric function with the single-oscillator model. From the energy gap expansion, the nanocrystal size can be also obtained with two independent models known as the phenomenological model based on quantum confinement and the bond contraction model. The results from the two models are similar and are also consistent with transmission electron microscope and x-ray diffraction measurements.

4.3.2 Experimental

Sample preparation

550nm-thick SiO₂ films were grown on p-type Si (100) substrates by wet oxidation of Si at 1000 °C. The SiO₂ films were implanted with a dose of 1×10^{17} atoms/cm² of Si⁺ at 100 keV. The samples were annealed at 1000 °C in nitrogen gas for duration of 20 minutes. Upon such an annealing, one would expect the formation of Si nanocrystals in the SiO₂ film [17,30].

Characterization

TEM specimens were prepared as described in **Chapter 2** and were characterized with transmission electron microscope (Jeol JEM 2010). Fig.4.4 (a) shows the TEM image of nc-Si embedded in SiO₂ matrix. Lattice structures can be seen clearly for circled areas, which are considered as Si nanocrystals with the diameter of ~ 5 nm. In the most area of this image, there are no crystalline structures observed but all amorphous SiO₂. The mean size of the Si nanocrystals could be determined from full width of half maximum (FWHM) of the Bragg peak after correction for instrumental broadening in the XRD measurement [70] using Scherrer 's equation. Figure 4.4 (b) shows the XRD measurements for nc-Si embedded in SiO₂ matrix and the Pseudo-Voigt fit to the data, and nc-Si size obtained is ~ 4.6 nm. The depth distribution of Si nanocrystals in SiO₂ film was obtained from secondary ion mass spectroscopy (SIMS) measurement. Spectroscopic ellipsometry measurements were carried out to determine the ellipsometric angles Ψ and Δ in the wavelength range of 400 to 1200 nm.

(a)

(b)

Fig.4.4. (a) TEM image of nc-Si embedded in SiO₂ matrix; and (b) XRD measurement for nc-Si embedded in SiO₂ matrix and the Pseudo-Voigt fit to the data.

4.3.3 Result and Discussion

Our formalisms are based on the use of “ characteristic equations ” to describe the individual layers and the substrate. These equations relate the field components at the top of the film to those at the bottom. Results valid for a multi-layered structure are then obtained by multiplying the appropriate equations together in order through the stack as illustrated in Fig.4.5.

Fig.4.5. The model for the multi-layer SiO_x/Si reflective system.

Based on this multi-layer system, the approach proposed to divide our SiO₂ films containing Si nanocrystals is described as below. Fig.4.6 shows the volume fraction of Si nanocrystals in SiO₂ film as a function of depth is obtained from the SIMS measurement. As can be seen in Fig.4.6, nc-Si distributes from the surface to a depth of 250 nm, and there are few or no nanocrystals in the SiO₂ film beyond the depth of 250 nm. Therefore, the SiO₂ film can be approximately represented by the two layers, i.e., the first layer ($0 \leq \text{depth} \leq 250 \text{ nm}$), which contains Si nanocrystals, and the second layer ($\text{depth} > 250 \text{ nm}$), which is basically a pure SiO₂ layer. For the first layer, as the volume fraction of Si nanocrystals varies with the depth, the optical properties in this layer will also vary with the depth.

Fig.4.6. Volume fraction of Si nanocrystals embedded in SiO₂ film versus depth.

To model the optical properties of the first layer, it is divided into m sub-layers with equal thickness d_0 ($m = 25$, and $d_0 = 10 \text{ nm}$ in this study), namely sub-layer 1, sub-layer 2,..., sub-layer m in the sequence starting from the surface, and the volume

fraction of Si nanocrystals is considered constant within each sub-layer. Each sub-layer has its own complex refractive index, $N_i = n_i + jk_i$ ($i=1, 2, \dots, m$) where n_i and k_i are the refractive index and extinction coefficient for the i th sub-layer, respectively. Note that N_i is also a function of wavelength (λ). Therefore, in the ellipsometry analysis, the material system used in this study can be described with a $(m + 3)$ -phases model, *i.e.*, air/sub-layer 1/.../sub-layer m /pure SiO₂ layer (*i.e.* the second layer mentioned above)/Si substrate. Each phase is characterized by its complex refractive index, N_i ($i=0, 1, \dots, m, m+1, m+2$). Note that $N_0 = 1$ for air, $N_{m+1} = N_{\text{SiO}_2}$ (*i.e.* the SiO₂ complex refractive index) for the pure SiO₂ layer, and $N_{m+2} = N_{\text{Si}}$ (*i.e.* the Si complex refractive index) for the Si substrate. Therefore, for the total system, the ratio ρ of the complex reflection coefficients for the p and s polarizations is given by Eq.4.17, which is duplicated here for easy reference. [107]

$$\rho = R_p / R_s = \tan(\psi) \exp(j\Delta),$$

where Ψ and Δ are the ellipsometric angles. The complex reflection coefficient R_α ($\alpha = p, s$) for the p and s polarizations is given by

$$R_\alpha = (r_{0,1}^\alpha + R_{1,2}^\alpha X_1) / (1 + r_{0,1}^\alpha R_{1,2}^\alpha X_1), \quad (4.25)$$

where

$$X_1 = \exp(-j4\pi N_1 d_0 \cos \phi_1 / \lambda),$$

$$R_{1,2}^\alpha = (r_{1,2}^\alpha + R_{2,3}^\alpha X_2) / (1 + r_{1,2}^\alpha R_{2,3}^\alpha X_2),$$

$$X_2 = \exp(-j4\pi N_2 d_0 \cos \phi_2 / \lambda),$$

...

$$R_{(m-1),m}^\alpha = (r_{(m-1),m}^\alpha + r_{m,(m+1)}^\alpha X_m) / (1 + r_{(m-1),m}^\alpha r_{m,(m+1)}^\alpha X_m),$$

$$X_m = \exp(-j4\pi N_m d_0 \cos \phi_m / \lambda).$$

$$R_{m,(m+1)}^\alpha = (r_{m,(m+1)}^\alpha + r_{(m+1),(m+2)}^\alpha X_{m+1}) / (1 + r_{m,(m+1)}^\alpha r_{(m+1),(m+2)}^\alpha X_{m+1}),$$

$$X_{(m+1)} = \exp(-j4\pi N_{m+1} d_{\text{SiO}_2} \cos \phi_{m+1} / \lambda).$$

In the above equations, λ is the free-space wavelength of light, $r_{i,(i+1)}^\alpha$ ($i=0, 1, \dots, m, m+1, m+2$) is the Fresnel complex-amplitude reflection coefficient for α - ($\alpha=p, s$) polarized light at the interface between the i th phase and the $(i+1)$ th phase [106]; and the angles ϕ_i and the complex refractive index N_i ($i=0, 1, \dots, m, m+1, m+2$) are related by Snell's law.

$$N_0 \sin \phi_0 = N_1 \sin \phi_1 = \dots = N_{m+1} \sin \phi_{m+1}. \quad (4.26)$$

In the present study, ϕ_0 is fixed at 75° . Using these equations, finally the ellipsometric angles ψ and Δ can be expressed as functions of the parameters $N_1, N_2, \dots, N_m$, and λ [106,107], i.e.,

$$\psi = f_1(N_1, N_2, \dots, N_m, \lambda) \quad (4.27)$$

and

$$\Delta = f_2(N_1, N_2, \dots, N_m, \lambda). \quad (4.28)$$

Note that the functions f_1 and f_2 cannot be expressed as analytical formulas as they are very complicated for such a $(m+3)$ -phases system (here $m=25$). For the first layer mentioned above, it can be treated as a material system in which the SiO_2 is a host material while the Si nanocrystal is an inclusion embedded in the host material. Although the Si nanocrystal fraction varies with the depth and there may be a size distribution for the nanocrystals, for each sub-layer of the first layer, its effective complex dielectric function ε_i ($=N_i^2$, $i=1, 2, \dots, m$) can be calculated with Eq.4.24, which is duplicated here for easy reference.

$$\frac{\varepsilon_i - \varepsilon_{\text{SiO}_2}}{\varepsilon_i + 2\varepsilon_{\text{SiO}_2}} = v_i \frac{\varepsilon_{nc-Si} - \varepsilon_{\text{SiO}_2}}{\varepsilon_{nc-Si} + 2\varepsilon_{\text{SiO}_2}}$$

where v_i ($i=1, 2, \dots, m$) is the volume fraction of the nanocrystals in the i th sub-layer, $\varepsilon_{\text{SiO}_2}$ is the dielectric function of host material SiO_2 , and ε_{nc-Si} is the dielectric

function of Si nanocrystal. Here the nanocrystal size distribution is considered in terms of mean dielectric function. As the volume fraction (v_i) and ϵ_{SiO_2} are known, from Eq.(4.24) the effective complex dielectric function ϵ_i (and thus the complex refractive index N_i) for the i^{th} sub-layer ($i=1, 2, \dots, m$) can be expressed in terms of ϵ_{nc-Si} (or the complex refractive index of nc-Si, i.e. N_{nc-Si}). Therefore, Eqs. (4.27) and (4.28) can be rewritten in the form of

$$\psi = f_1'(N_{nc-Si}, \lambda) \quad (4.29)$$

and

$$\Delta = f_2'(N_{nc-Si}, \lambda). \quad (4.30)$$

Again the functions f_1' and f_2' cannot be expressed as analytical formulas as they are very complicated. For a given wavelength λ , an ellipsometric measurement yields a value of Ψ and Δ , and therefore N_{nc-Si} can be obtained by solving Eqs.(4.29) and (4.30). In this study, we use a spectral fitting in the wavelength range from 400 to 1200 nm to determine the N_{nc-Si} at each wavelength instead of solving the equations. The spectral fitting can avoid the problems of unstable or unreasonable values and difficulties associated with the peak structures of the measured $\Psi(\lambda)$ and $\Delta(\lambda)$ due to the measurement, model and calculation errors.

The above models and the fitting procedure are proven correct by applying them to a system of pure SiO_2 film on Si substrate (i.e., the volume fraction of nc-Si for each sub-layer equals to zero). As shown in Fig. 4.7, The fitting yields $v_i=0$ ($i=1, 2, \dots, m$) and the calculated (Ψ, Δ) fit the experimental (Ψ, Δ) perfectly over the whole spectral range (400 - 1200nm), demonstrating all the equations used and the computation program are correct and reliable.

Fig.4.7. Comparison of theoretical computation with experimental data for (a) Ψ and (b) Δ for a system of a pure SiO₂ film on Si substrate.

Fig.4.8. Comparison of ψ and Δ between calculation and measurement as functions of wavelength for the system of nc-Si embedded SiO_2 film on Si substrate.

After the verification of equations and the computation program, the spectral fitting was applied to the system of the nc-Si embedded SiO_2 film on Si substrate. Fig.4.8 shows the spectral fitting result, i.e., the comparison of the calculated Ψ and Δ based on Eqs.(4.29) and (4.30) with the measured Ψ and Δ in the wavelength range from 400 to 1200 nm. As can be seen in this figure, all the complicated spectral features of both Ψ and Δ can be fitted excellently. This indicates that the above approach is correct and the fitting is effective. The complex refractive index N_{nc-Si} (and thus the refractive index n and extinction coefficient k) of Si nanocrystals embedded in SiO_2 matrix obtained as a function of wavelength is shown in Fig.4.9. The real and imaginary parts of the complex dielectric function of nc-Si obtained are also shown in Fig.4.10 and Fig.4.11, respectively.

Fig.4.9. (a) for n and (b) for k of Si nanocrystals embedded in SiO₂ matrix as functions of wavelength. The dielectric suppression for both n and k due to the quantum size effect can be observed.

Fig.4.10. Real part of dielectric function of Si nanocrystals embedded in SiO₂ matrix as a function of wavelength. The modeling with Eq.4.31 yields an energy gap expansion of 5.1% and 6.3% for $E_{g0} = 4$ eV and 4.8 eV, respectively.

As can be seen in Figures (4.9) – (4.11), the optical constants and the dielectric function of the Si nanocrystals are reduced significantly compared to those of bulk crystalline Si. Here the reduction in the optical constants or the dielectric function is attributed to the energy gap expansion of the nanocrystals as a result of nanocrystal size effect. Based on the single-oscillator model, the change ($\Delta\epsilon_r$) of the real part of the dielectric function due to the energy gap change (ΔE_g) can be expressed below for a small energy gap change (i.e. $\Delta E_g/E_{g0} \ll 1$)

$$\frac{\Delta \varepsilon_r}{\varepsilon_{r0}} = -\frac{2(1 - \varepsilon_{r0}^{-1})}{1 - (E/E_{g0})^2} \left(\frac{\Delta E_g}{E_{g0}} \right), \quad (4.31)$$

where ε_{r0} and E_{g0} are the real part of dielectric function and energy gap of bulk crystalline Si, and E is photon energy. Note that the energy gap $E_g (= \hbar \omega_g$ where ω_g is the resonance frequency of the oscillator) in the single-oscillator model is not the same as the fundamental energy band gap of silicon. Tsu *et al* pointed out that the fundamental Γ - Δ gap at 1.1 eV plays almost no role in the dielectric function [113]. The energy gap E_{g0} for the dielectric function of bulk crystalline Si was set to be 4 eV in [113] while it was shown to be 4.8 eV in [114]. In this study, Eq.(4.31) is used to model the real part of the dielectric function of Si nanocrystals embedded in SiO_2 matrix, and the result is shown in Fig.4.10. The modeling yields an energy gap expansion of 5.1% and 6.3% for $E_{g0} = 4$ eV and 4.8 eV, respectively.

The nanocrystal size could be estimated from the energy gap change by using the bond contraction model [115] or the phenomenological model based on quantum confinement [116] on the size dependence of energy gap expansion. From the bond contraction model [115], if the surface bond contraction is significant for only the two outermost atomic layers of a spherical dot and the dot size (i.e. the diameter D) is much larger than the atomic diameter d , the energy gap expansion is given as

$$\frac{\Delta E_g}{E_{g0}} = \gamma_1' c_1 (c_1^{-m} - 1) + \gamma_2' c_2 (c_2^{-m} - 1) \quad (4.32)$$

where $\gamma_i' = \frac{3}{k} \left(1 - \frac{i-0.5}{k} \right)^2$ ($i = 1, 2$), $k = D/(2a)$, $m = 1$, $c_1 = 0.88$ and $c_2 = 0.96$ [115].

For $\Delta E_g/E_{g0} = 5.1\%$ which corresponds to $E_{g0} = 4$ eV, Eq.(4.32) yields the nanocrystal size $D = 4.1$ nm; and for $\Delta E_g/E_{g0} = 6.3\%$ which corresponds to $E_{g0} = 4.8$ eV, Eq.(4.32) yields the nanocrystal size $D = 3.1$ nm. On the other hand, from the phenomenological

model [116], which predicts the trend for quantum confinement, i.e. the inverse dependence of the expanded energy gap on the nanocrystal size, and in which a log-normal distribution of nanocrystal sizes is considered, ΔE_g is given by

$$\Delta E_g = \frac{C}{d_0^n} \left(\frac{d_m}{d_0} \right)^{n(2n+5)/3} \quad (4.33)$$

where d_0 (in nm) is the mean size of nanocrystals and d_m is the size for which the maximum occurs in the log-normal distribution, $n = 1.22$, $C = 3.9$ and $d_m/d_0 = 0.7$ [116]. For $\Delta E_g/E_{g0} = 5.1\%$ Eq.(4.33) yields the nanocrystal size $d_0 = 4.7$ nm; and for $\Delta E_g/E_{g0} = 6.3\%$ Eq.(4.33) yields $d_0 = 3.4$ nm. Obviously, the two models give similar results. These results are close to the value (~ 4.6 nm) obtained from XRD measurement shown in Fig1, and they also agree with the result reported in [17] for similar nc-Si formation conditions.

Fig. 4.11. Imaginary part of dielectric function of Si nanocrystals embedded in SiO₂ matrix as a function of wavelength.

Fig.4.12. Refractive index n and extinction coefficient k as a function of wavelength for nc-Si embedded in SiO₂ matrix (this work), bulk crystalline Si, amorphous Si [117], large aggrain polysilicon [118] and nc-Si layer (a hypothetical dense layer of *nc*-Si particles covered by their native oxide without voids) [117].

The optical constants $n_{nc-Si}(\lambda)$ and $k_{nc-Si}(\lambda)$ of the nc-Si embedded in SiO₂ matrix at various wavelengths are shown in Fig.4.12. In this figure, they are also compared with the optical constants of bulk crystalline Si, amorphous Si [117], large grain polysilicon [118] and nc-Si layer (a hypothetical dense layer of nc-Si particles covered by their native oxide without voids) [117]. As can be seen in this figure, the nc-Si optical constants obtained in this work are reduced compared to those of bulk crystalline Si, which is due to the energy gap expansion of the nanocrystals as a result of the quantum size effect [119]. The optical suppression due to the size effect can also be observed by comparison of refractive index from our result (~5 nm) and that from large grain polycrystalline Si (50-200nm in ref. [118]). It is also shown the difference between optical constants from isolated nc-Si in SiO₂ matrix and those from nc-Si film [117] as we expect at the beginning of the part. Hence, it can be concluded from Fig.4.12 that the nc-Si optical constants obtained in this work are reasonable.

In order to verify the optical modeling, the ellipsometric fitting is applied to the nc-Si embedded in a 50-nm SiO₂ film much thinner than the previous 550-nm SiO₂. But the nc-Si size is the same as that of the 550-nm SiO₂. The optical constants of the nc-Si yielded from the ellipsometric fitting are the same as those of nc-Si in 550-nm SiO₂, as shown in Figs.4.9-4.11. This means that optical constants of nc-Si are related to only the size of the nanocrystals but not the oxide thickness. Fig. 4.13 shows the ellipsometric angles (Ψ , Δ) from the experiment and calculation. The good fitting indicates optical properties obtained from this study are reliable.

Fig.4.13. Comparison of ψ and Δ between calculation and measurement as functions of wavelength for the system of nc-Si embedded in the 50-nm SiO_2 film grown on Si substrate.

4.3.4 Conclusion

In **Section 4.3**, we have developed an approach to determination of dielectric function of nc-Si embedded in SiO_2 matrix synthesized with Si ion implantation. The approach is based on the effective medium approximation, and appropriate models are developed to simulate the nc-Si depth profiles obtained from the SIMS measurement and the ellipsometric parameters measured in a wide range of wavelengths. The energy gap expansion of the nc-Si due to the size effect has been obtained by modeling the real part of the dielectric function with the single-oscillator model. From the energy gap expansion, the nanocrystal size can be also obtained with two independent models including the phenomenological model based on quantum confinement and the bond contraction model. The results from the two models are similar and are also consistent with the TEM and XRD measurements.

4.4 Determination of Depth Profile of Si Nanocrystals in SiO₂ Film with Ellipsometry

4.4.1 Background and Motivation

For applications such as light-emitting structures, single-electron memories, optical storage devices or waveguides [15, 25, 45, 46, 57, 60, 61, 96, 105, 122, 126, 123, 128], it is essential to have detailed information on the exact depth distribution of the Si nanocrystal concentration of the Si-doped SiO₂ films. In this part, we report an approach to determination of depth profiles of Si nanocrystal fraction of Si-implanted SiO₂ films based on spectroscopic ellipsometry (SE). In the SE analysis, a Si implanted SiO₂ film is divided into $m+1$ sub-layers (a better depth resolution for a larger m), and an effective medium approximation (EMA) is used to convert the depth profile of the complex refractive index to the depth profile of the nc-Si fraction. With this approach, the depth profiles of Si nanocrystal fraction have been determined quantitatively in an inexpensive and nondestructive way. The depth profiles of Si nanocrystal fraction obtained are in good agreement with secondary ion mass spectroscopy (SIMS) analysis, indicating that the approach is reliable.

4.4.2 Experimental

Sample preparation

550nm-thick SiO₂ films were grown on p-type Si (100) substrates by wet oxidation of Si at 1000 °C. The SiO₂ films were implanted with doses ranging from 2×10^{16} to 1×10^{17} atoms/cm² of Si⁺ at 50 keV. As revealed by the SE analysis and SIMS measurements discussed below, the Si nanocrystals distribute from the surface to a depth of about 250 nm.

Characterization

SE measurements before and after Si implantation were carried out in the wavelength range of 400 to 1200 nm. A continuous significant change in the ellipsometric angles ψ and Δ with the implant dose was observed. As discussed below, from these SE measurements, the depth profiles of nc-Si concentration in the SiO_x films was determined quantitatively. Fig. 4.14 shows the XRD pattern of the sample as well as the Pseudo-Voigt fitting. The mean size of nc-Si for this sample is ~ 4.3 nm determined with FWHM of the Bragg peak using Sherrer's equation [70]. It should be noted that the mean size of the 50keV Si-implanted sample is slightly smaller than that of 100keV Si-implanted sample used in previous part. And for the 1keV implanted samples the mean size ranges from 2.5 to 3 nm as determined by XRD measurements.

Fig. 4.14. XRD measurement for nc-Si embedded in SiO_2 (circles) and the Pseudo-Voigt fitting (solid line).

4.4.3 Result and Discussion

We start simulation from the use of the dielectric function of bulk crystalline Si for nc-Si. This is a test to study what level the size of nc-Si reduces to and to see whether the depth profile of nc-Si can be coarsely determined in a simpler way. Of course, as it is expected dielectric function will change according to the size reduction, dielectric function for nc-Si will be introduced into the simulation in the following part to obtain exact distribution of nc-Si in SiO_2 films.

As the concentration of nc-Si in the Si-implanted SiO_x films varies with the depth, namely, the x is a function of the depth, the optical properties of the films will also vary with the depth. To model the SiO_x films, the films are divided into $m+1$ sub-layers as **Section 4.3** mentioned. The x (≤ 2) is considered constant within each sub-

layer, and the corresponding x for the $m+1$ layers are $x_1, x_2, \dots, x_m, x_{m+1}$, respectively. Actually, the depth profile of x can be translated into the depth profile of nc-Si fraction in the films. Each sub-layer has its own complex refractive index. For example, for the i th sub-layer, its complex refractive index is $N_i = n_i + jk_i$ ($i=1, 2, \dots, m, m+1$) where n_i and k_i are the refractive index and extinction coefficient for the i th sub-layer, respectively. Note that the N_i is also a function of wavelength.

For SE analysis, an appropriate optical model is required. Based on the above discussions, we can use a $(m+3)$ -phase model the same with that in **Section 4.3**, i.e., air/sub-layer 1/.../sub-layer $m+1$ /Si substrate to describe the system of Si implanted SiO₂ film on Si substrate. Each phase is characterized by its complex refractive index, namely, N_i ($i=0, 1, \dots, m, m+1, m+2$). Note that $N_0 = 1$ for air, $N_{m+1} = N_{\text{SiO}_2}$ and $N_{m+2} = N_{\text{Si}}$ for the Si substrate. For the total system, the ratio ρ of the complex reflection coefficients for the p and s polarizations is given by Eq.4.17. The complex reflection coefficient R_α ($\alpha=p, s$) for the p and s polarizations is given by Eq.4.25. In this study, ϕ_0 is fixed at 75° . As $N_0 (=1)$, N_{m+1} ($=\text{SiO}_2$ complex refractive index) and N_{m+2} ($=\text{Si}$ complex refractive index) are known, for a given d , from the Eq.4.17 and Eq.4.25, Ψ and Δ can be symbolically written as $\Psi = f_3(N_0, N_1, N_2, \dots, N_m, N_{\text{SiO}_2}, N_{\text{Si}}, \lambda)$ and $\Delta = f_4(N_0, N_1, N_2, \dots, N_m, N_{\text{SiO}_2}, N_{\text{Si}}, \lambda)$. The functions f_3 and f_4 cannot be expressed as analytical formulae, but the Ψ and Δ can be calculated numerically. To determine the depth profile of the optical constants, one can search for one set of the parameters $(N_1, N_2, \dots, N_m)$, which are dependent of wavelength λ , by comparing the calculated (Ψ, Δ) with the experimental (Ψ, Δ) . To obtain the definite values of the complex refractive indices of the m sub-layers at various wavelengths, an appropriate constraint that is independent of wavelength, is required.

The constraint can be established by using an effective medium approximation (EMA) to relate the depth profile of the complex refractive index to the depth profile of the nc-Si fraction that is independent of wavelength. According to the EMA [107,112], the effective complex dielectric function of each sub-layer, $\epsilon_i (=N_i^2, i=1, 2, \dots, m)$, can be approximately calculated using Eq.4.24, which is duplicated here for easy reference.

$$\frac{\epsilon_i - \epsilon_{SiO_2}}{\epsilon_i + 2\epsilon_{SiO_2}} = v_i \frac{\epsilon_{nc-Si} - \epsilon_{SiO_2}}{\epsilon_{nc-Si} + 2\epsilon_{SiO_2}}$$

Each symbol in above equation has the same meaning as presented in **Section 4.3**. Then the depth profile of the complex refractive index is converted to the depth profile of the volume fraction (v_i). Note that the v_i is independent of the wavelength. Therefore, there are only m (the number of the sub-layers) unknown parameters, i.e., $v_1, v_2, \dots, v_m$ in the spectral fitting of experimental (Ψ, Δ) , which greatly reduces the complexity of the fitting. Obviously, a larger m means a better depth resolution but a longer computation time.

Finally, the depth distribution of the complex refractive index is converted to the depth distribution of the volume fraction (v_i). Thus (Ψ, Δ) can be symbolically written as

$$\Psi = f_3' (v_1, v_2, \dots, v_m, N_{nc-Si}, N_{Si}, \lambda) \quad (4.34)$$

and

$$\Delta = f_4' (v_1, v_2, \dots, v_m, N_{nc-Si}, N_{Si}, \lambda). \quad (4.35)$$

The functions f_3' and f_4' cannot be expressed as analytical formulae, but Ψ and Δ can be calculated numerically with the functions. As the complex refractive indexes of

SiO₂ and Si (i.e. N_{SiO_2} and N_{Si}) are well known, the complex refractive index of Si nanocrystal is obtained from dielectric function of bulk crystalline Si ($N = \sqrt{\epsilon}$). Then the depth profile of the nanocrystal concentration can be found by searching for one set of ($\nu_1, \nu_2, \dots, \nu_m$) such that the following error function

$$F = \sum [(\Psi_m^\lambda - \Psi_c^\lambda)^2 + (\Delta_m^\lambda - \Delta_c^\lambda)^2] \quad (4.36)$$

is a minimum for the whole measured spectral range, where Ψ_m^λ and Δ_m^λ are the measured Ψ and Δ values at λ , and Ψ_c^λ and Δ_c^λ are the calculated Ψ and Δ values with Eqs.(4.34) and (4.35), respectively, at the same wavelength.

One typical example using dielectric function of bulk Si for that of Si nanocrystal in the spectral fitting is shown in Fig.4.15 (a). As can be seen in this figure, all the complicated spectral features of both Ψ and Δ can be fitted basically. This indicates that the difference of dielectric functions between bulk crystalline Si and Si nanocrystal is not huge implying that the sizes of the nanocrystals are not too small (say, not less than 3 nm) in this study. Such a fitting can yield the depth profile of the volume fraction of nc-Si in the SiO₂ films. The volume fraction can be simply converted to the atom percentage that can be compared with the SIMS analysis. One example of the depth profile of the nc-Si concentration at percentage obtained is shown in Fig.4.15 (b). As shown in this figure, the depth profile obtained agrees well with the SIMS result.

Fig.4.15. (a) Typical example of spectral fitting of Ψ and Δ with the $(m+3)$ -phase model and the constraint that uses the EMA to convert the depth profile of the complex refractive index to the depth profile of the nc-Si fraction. (b) Comparison of the depth profiles of Si nanocrystal fraction obtained with the SE and SIMS analysis.

Further to the above study, to improve the above fitting procedure to SiO₂ films containing Si nanocrystals, we must know the dielectric function of Si nanocrystal. It is questionable to still use the dielectric function of bulk crystalline Si for the nanocrystal, as it is expected that with size reduction of a nanometric system its dielectric function will change. The dielectric function of Si nanocrystal can be calculated by using the simple formulas proposed in [115] which are duplicated in the following for easy reference. As a result of the band gap expansion (E_g) due to the reduction of nanocrystal size, the change ($\Delta \chi$) of the dielectric susceptibility is given by

$$\Delta \chi / \chi_0 = -2(\Delta E_g/E_{g0}), \quad (4.37)$$

and the change ($\Delta \epsilon_m$) of the imaginary part of the complex dielectric function is given as

$$\Delta \epsilon_m / \epsilon_{m0} = -2[E_{g0}/(E - E_{g0})](\Delta E_g/E_{g0}), \quad (4.38)$$

where χ_0 , ϵ_{m0} and E_{g0} are the corresponding physical parameters of bulk crystalline Si, and E is photon energy. It should be pointed out that the formulas are just a first order approximation valid for a small $\Delta E_g/E_{g0}$. To calculate the dielectric function of Si nanocrystal, the band gap change $\Delta E_g/E_{g0}$ should be known.

Bond contraction model [115,132] has been used to simulate the dielectric suppression due to the size reduction. From this model, if the surface bond contraction is significant for only the two outermost atomic layers of a spherical dot and the dot size (i.e. the diameter D) is much larger than the atomic diameter d , the band gap expansion is given as Eq.4.32. For a given nanocrystal size, E_g/E_{g0} can be calculated by using the model, and thus the dielectric function of the Si nanocrystal can be obtained with Eqs.(4.37) and (4.38). Therefore, the spectral fitting discussed above is

now carried out by searching for the nanocrystal size and one set of ($v_1, v_2, \dots, v_m$) such that the error function (F) is a minimum.

Fig.4.16. Fitting spectra for Ψ and Δ using the dielectric function of Si nanocrystal calculated with the bond contraction model.

Fig.4.16 shows the best fittings with the bond contraction model for ΔE_g . As can be seen clearly in Fig.4.16, these fittings, which have considered the nano-size effect on the band gap, are superior to the fitting with the dielectric function of bulk crystalline Si, indicating that the nano-size effect plays a role in the dielectric function. The depth profile of Si nanocrystal concentration obtained from the fittings based on the model is shown in Fig.4.17, and it is also compared in this figure with the depth profile obtained from the fitting using the dielectric function of bulk crystalline Si.

Fig.4.17. Depth profiles of Si nanocrystals obtained from the spectral fittings by using the dielectric function of bulk crystalline Si and the dielectric function of Si nanocrystal calculated with the bond contraction model.

As can be seen in Fig.4.17, the two depth profiles appear to be very similar (only some small difference exist in the peak regions of the profiles). The reason for this is that, as indicated by our calculations based on the bond contraction model, the difference of dielectric functions between the bulk crystalline Si and the Si nanocrystal is not large as the size of the Si nanocrystals is not very small. The fitting based on the bond contraction model yield a nanocrystal size of about 5 nm, which agrees with the result from XRD measurement. For such nanocrystal sizes, the bond contraction model gives a decrease of 9% in the real part and a decrease of 5% in the imaginary part of the dielectric function at the wavelength of 400 nm. Therefore, although the fittings can be improved by taking into account the small reductions in the dielectric function due to the size effect (as shown in Fig.4.15 (a) and Fig.4.16),

the reductions do not have a very significant impact on the depth profiles. The depth profiles agree with that from the secondary ion mass spectroscopy measurement as well. Fig.4.18 shows the comparison of the depth profile obtained from the spectral fitting based on the bond contraction model with that from the secondary ion mass spectroscopy measurement and that from TRIM code simulation. The good agreement indicates that the above approach for depth profiling is reliable.

Fig.4.18. Comparison of the results of SIMS and TRIM code with the depth profile obtained from the spectral fitting by using the dielectric function of Si nanocrystal calculated with bond contraction model.

4.4.4 Conclusion

In conclusion, we have developed an approach to determination of depth profiles of nc-Si fraction of Si-implanted SiO₂ films based on the SE. In the SE analysis, a Si implanted SiO₂ film is divided into $m+1$ sub-layers (a better depth profile resolution for a larger m), and an optical model of $(m+3)$ phases is used. In the spectral fitting of experimental Ψ and Δ , an effective medium approximation (EMA) is used to convert the depth profile of the complex refractive index to the depth profile of the nc-Si fraction, which greatly reduces the complexity of the fitting. With this approach, the depth profiles of nc-Si fraction in SiO₂ films are determined quantitatively in an inexpensive and nondestructive way. The depth profiles of Si nanocrystal obtained from the approach are in good agreement with the SIMS analysis and TRIM code simulation, indicating that the approach is reliable.

4.5 Depth Profiling of Optical Constants of SiO₂ Films Containing Si Nanocrystals

4.5.1 Background and Motivation

For optoelectronic and photonic applications of Si nanocrystals (nc-Si) embedded in SiO₂ matrix, the information of the depth profiles of the optical constants for the thin film system is necessary. In this work, one approach for depth profiling of optical constants for the thin film synthesized with ion implantation are developed. The nc-Si depth distribution obtained from secondary ion mass spectroscopy measurement is modeled with the approximation of many sub-layers, and for a given

wavelength the optical constants of each sub-layer are formulated with the nc-Si volume fraction in the sub-layer and the nc-Si optical constants as variables based on the effective medium approximation. After the above procedures the nc-Si optical constants are obtained from the spectral ellipsometric fittings. Finally the optical constants of each sub-layer are calculated, and thus the depth profiles of the optical constants for the SiO₂ thin film containing the nc-Si are obtained.

4.5.2 Experimental

Sample preparation

A 550nm-thick SiO₂ film, which was grown on p-type Si (100) substrates by wet oxidation of Si at 1000 °C, was implanted with the dose of 1×10^{17} atoms/cm² of Si⁺ at 100 keV. Following the ion implantation, a thermal annealing was carried out at 1000 °C in nitrogen gas. Here the annealing duration is 100 minutes in this study.

Characterization

X-ray diffraction (XRD) measurement indicates the formation of Si nanocrystals with a mean size of about 4.6 nm embedded in SiO₂ matrix as described in **Section 4.3**. The depth distribution of the nc-Si volume fraction in the SiO₂ film was obtained based on the depth profile of nc-Si secondary ion mass spectroscopy (SIMS) measurement. To obtain the profiles of optical constants of the material system, spectroscopic ellipsometry measurements were carried out in the wavelength range of 400 to 1200 nm.

4.5.3 Result and Discussion

Fig.4.19. (a) nc-Si depth distribution determined from SIMS measurement and the sub-layer approximation with $m = 25$; and (b) spectral ellipsometric fittings with $m = 25$.

To obtain exact depth profiles of optical constants for the SiO₂ films containing Si nanocrystals, dielectric functions of nc-Si should be used. And SIMS result gives detailed information about nc-Si distribution in SiO₂ films. Here we present a method to determination of profiles of optical constants based on SIMS result. As can be seen in Fig.4.19 (a), nc-Si distributes from the surface to a depth of 250 nm, and there are few or no nanocrystals in the SiO₂ film beyond the depth of 250 nm. Therefore, the SiO₂ film can be divided into two portions, i.e., the first portion ($0 \leq \text{depth} \leq 250 \text{ nm}$) that contains nc-Si, and the second portion ($\text{depth} > 250 \text{ nm}$) that is basically a pure SiO₂ layer. For the first portion, as the nc-Si volume fraction (ν) varies with the depth (x), the optical properties in this portion will also vary with x . To model the optical properties of the first portion ($0 \leq x \leq 250 \text{ nm}$), $\nu(x)$ is modeled with an m -sub-layers approximation, i.e., this portion is divided into m sub-layers with equal thickness d_0 , which are labeled as sub-layer 1, sub-layer 2,..., sub-layer m in the sequence starting from the surface. The average nc-Si volume fraction in each sub-layer is denoted with ν_i ($i = 1, 2, \dots, m$). Each sub-layer has its own complex refractive index, $N_i = n_i + jk_i$ ($i=1, 2, \dots, m$) where n_i and k_i are the refractive index and extinction coefficient for the i th sub-layer, respectively. Note that N_i is also a function of wavelength (λ).

Therefore, in the ellipsometry analysis, the material system used in this study can be described with a $(m + 3)$ -phases model, i.e., air/sub-layer 1/.../sub-layer m / pure SiO₂ layer (i.e. the second portion mentioned above)/Si substrate. Each phase is characterized by its complex refractive index, N_i ($i=0, 1, \dots, m, m+1, m+2$). Note that $N_0 = 1$ for air, $N_{m+1} = N_{\text{SiO}_2}$ (i.e., SiO₂ refractive index) for the second portion, and $N_{m+2} = N_{\text{Si}}$ (i.e., Si complex refractive index) for the Si substrate. As N_0 , N_{m+1} and N_{m+2} are known, for a fixed incident angle the ellipsometric angles Ψ and Δ can be

expressed as functions of the parameters $n_1, n_2, \dots, n_m, k_1, k_2, \dots, k_m$, and the wavelength λ [106,107], i.e.,

$$\Psi = f_5(n_1, n_2, \dots, n_m, k_1, k_2, \dots, k_m, \lambda) \quad (4.39)$$

and $\Delta = f_6(n_1, n_2, \dots, n_m, k_1, k_2, \dots, k_m, \lambda) \quad (4.40)$

where f_5 and f_6 are two complicated functions, which cannot be expressed as analytical formulas.

Each sub-layer can be treated as a material system in which the SiO_2 is a host material while the nc-Si is an inclusion embedded in the host material. From the effective medium approximation [107,119,133], the refractive index n_i and the extinction coefficient k_i for the i th sub-layer ($i = 1, 2, \dots, m$) can be obtained as follows

$$n_i = \left[\frac{\sqrt{(A^2 + B^2)(C^2 + D^2)} + (AC + BD)}{2(C^2 + D^2)} \right]^{1/2} n_{\text{SiO}_2} \quad (4.41)$$

$$k_i = \left[\frac{\sqrt{(A^2 + B^2)(C^2 + D^2)} - (AC + BD)}{2(C^2 + D^2)} \right]^{1/2} n_{\text{SiO}_2} \quad (4.42)$$

where $A = (1 + 2\nu_i)(n_{\text{nc-Si}}^2 - k_{\text{nc-Si}}^2) + 2(1 - \nu_i)n_{\text{SiO}_2}^2$

$$B = 2(1 + 2\nu_i)n_{\text{nc-Si}}k_{\text{nc-Si}}$$

$$C = (1 - \nu_i)(n_{\text{nc-Si}}^2 - k_{\text{nc-Si}}^2) + (2 + \nu_i)n_{\text{SiO}_2}^2$$

$$D = 2(1 - \nu_i)n_{\text{nc-Si}}k_{\text{nc-Si}}$$

In the above equations, $n_{\text{nc-Si}}$ and $k_{\text{nc-Si}}$ are the mean refractive index and extinction coefficient of the nc-Si (note that the influence of the nc-Si size distribution is considered in terms of the mean values), respectively, and n_{SiO_2} is the refractive index of SiO_2 . Note that all the parameters are dependent of wavelength. For a given wavelength λ , as the volume fraction (ν_i) and n_{SiO_2} are known, if the values of both $n_{\text{nc-Si}}$ and $k_{\text{nc-Si}}$ are given the calculation with equations (4.39)-(4.42) can yield the

values (Ψ_{cal} and Δ_{cal}) of the ellipsometric angles; and on the other hand, an ellipsometric measurement yields the experimental values (Ψ_{exp} and Δ_{exp}) of the ellipsometric angles. Therefore, the optical constants (n_{nc-Si} and k_{nc-Si}) of the Si nanocrystals at the wavelength can be found by comparing the calculated values (Ψ_{cal} and Δ_{cal}) with the experimental values (Ψ_{exp} and Δ_{exp}). In this study, we use a spectral fitting in the wavelength range from 400 to 1200 nm to determine the nc-Si optical constants at each wavelength. In the spectral fitting, the nc-Si optical constants at various wavelengths $\lambda_1, \lambda_2, \dots, \lambda_M$ (M is the number of wavelengths) can be found by searching for one set of $n_{nc-Si}(\lambda_1), n_{nc-Si}(\lambda_2), \dots, n_{nc-Si}(\lambda_M), k_{nc-Si}(\lambda_1), k_{nc-Si}(\lambda_2), \dots, k_{nc-Si}(\lambda_M)$ such that the error function below

$$F = \sum_{\lambda=\lambda_1}^{\lambda_M} [(\Psi_{exp}^{\lambda} - \Psi_{cal}^{\lambda})^2 + (\Delta_{exp}^{\lambda} - \Delta_{cal}^{\lambda})^2]$$

is a minimum for the whole measured spectral range, where Ψ_{exp}^{λ} and Δ_{exp}^{λ} are the measured values while Ψ_{cal}^{λ} and Δ_{cal}^{λ} are the calculated values at the wavelength λ .

Fig.4.20. Dependence of minimum value (F_{min}) of the error function on the number of sub-layers.

Obviously, for a given number of wavelengths, a smaller F means a better spectral fitting. The minimum value (F_{min}) of the error function corresponding to a best fitting depends on the number (m) of the sub-layers with a smaller F_{min} for a larger m , as shown in Fig.4.20. A larger m gives a better accuracy in the determination of the nc-Si optical constants and also a higher depth resolution in the depth profiling of the optical constants, but it leads to a longer computation time. Actually, we have found that $m = 20$ has already yielded a satisfactory fitting and there is no much improvement for a larger m (>20). Fig.4.19 (b) shows the spectral fitting with $m = 25$. As can be seen in this figure, all the complicated spectral features of both Ψ and Δ can be fitted excellently. This indicates that the above approach is correct and the fitting is effective.

Fig.4.21. Depth profiles of refractive index n and extinction coefficient k at the wavelength of 400 nm for the SiO_2 thin film containing nc-Si.

By using the nc-Si optical constants obtained from the spectral fitting with $m = 25$, the refractive index (n_i) and the extinction coefficient (k_i) of each sub-layer ($i=1, 2, \dots, m$) can be calculated with Eqs.(4.41) and (4.42), and thus the depth profiles of the optical constants (n and k) for the SiO_2 thin film containing the nc-Si are obtained. Fig.4.21 shows the depth profiles of the optical constants at the wavelength of 400 nm, and Fig.4.22 shows the 3D view of the refractive index and extinction coefficient as functions of both the depth and wavelength. As shown in Fig.4.22 for the wavelength of 400 nm, there are large changes in the optical constants in the depth range of $\sim 50\text{-}200$ nm with the maximum changes (the maximum change in the refractive index is about 0.32) occurring in the depth of about 130nm. In the region deeper than about 250nm, the optical constants are basically the same as those of pure SiO_2 . As shown in Fig.4.22, the changes of the optical constants due to the Si nanocrystals depend on the wavelength with larger changes at shorter wavelengths, and the wavelength dependence of the change of the extinction coefficient is much stronger than that of the refractive index. For long wavelengths (near-infrared to infrared), the extinction coefficient is very small (and thus there is no strong light absorption) in the depth range of $\sim 50\text{-}200$ nm although the refractive index in this region is significantly larger than that of pure SiO_2 .

The depth profiles can be roughly divided into three regions including the surface region (depth $< \sim 50\text{nm}$), the active region (depth of $\sim 50 - 200\text{nm}$) and the bulk region (depth $> \sim 200$ nm). As shown in the Fig. 4.21, the changes of the optical constants due to the nc-Si depend on the wavelength with larger changes at shorter wavelengths, and the wavelength dependence of the change of the extinction coefficient is much stronger than that of the refractive index. For all wavelengths, the

refractive index in the active region is significantly larger than that in the surface and bulk regions (the maximum difference could be as large as about 0.32). For short wave lengths, the extinction coefficient (and thus the absorption coefficient) in the active region is much higher than that in the surface and the bulk regions; however, for long wavelengths (near-infrared to infrared), the extinction coefficient is almost zero and thus there is almost no light absorption in all the three regions. This could provide a possibility of using the Si-implanted SiO_2 film as an optical waveguide for long-wavelength applications as the light could be confined and transmitted in the active region. And importantly, the refractive index and the extinction coefficient and their profiles can be accurately controlled through Si implantation. This provides the possibility of waveguiding and optical gain in the SiO_2 thin film structures with appropriate depth profiles of Si nanocrystals.

Fig.4.22. Refractive index n and extinction coefficient k as functions of both the depth and wavelength for the SiO_2 thin film containing nc-Si.

4.5.4 Conclusion

In **Section 4.5**, we have developed one quantitative approach of optical-constants profiling of SiO_2 film containing nc-Si synthesized with ion beam technique. This approach gives out the results analogous of the depth profile of nc-Si. The nc-Si depth distribution obtained from SIMS measurement is modeled with the approximation of many sub-layers, and for a given wavelength the optical constants of each sub-layer are formulated with the nc-Si volume fraction in the sub-layer and the nc-Si optical constants as variables based on the effective medium approximation. After the above procedures the nc-Si optical constants are obtained from the spectral ellipsometric fittings. Finally the optical constants of each sub-layer are calculated, and thus the depth profiles of the optical constants for the SiO_2 thin film containing nc-Si are obtained.

4.6 Summary for This Chapter

In this chapter, hardware and basic physics of spectroscopic ellipsometry have been introduced firstly. Based on SE analysis, we have developed an approach to determination of dielectric function of nc-Si embedded in SiO₂ matrix. This approach is based on effective medium approximation, and appropriate models are developed to simulate the nc-Si depth profiles obtained from the SIMS measurement and the ellipsometric angles. The energy gap expansion of the nc-Si due to the size effect has been obtained by modeling the real part of the dielectric function with the single-oscillator model. From the energy gap expansion, the nanocrystal size can be also obtained with two independent models including the phenomenological model and the bond contraction model. The results from the two models are similar and are also consistent with the TEM and XRD measurements.

In the ellipsometry analysis, the SiO₂ film with a depth distribution of Si nanocrystals is divided into $m+1$ sub-layers with a better depth resolution for a larger m , and each sub-layer is characterized by its nanocrystal concentration. As the dielectric function of SiO₂ is well known, the effective dielectric function of each sub-layer can be calculated with the effective medium approximation if the dielectric function of Si nanocrystal is also given. In the spectral fittings, the dielectric function of Si nanocrystal is calculated based on the bond contraction model for the band gap expansion due to the nanocrystal size reduction. The fittings yield the nanocrystal depth profile and the nanocrystal size as well. The depth profiles from the modeling are in good agreement with the SIMS measurement and TRIM simulation.

In **Section 4.5**, one quantitative approach of optical-constants profiling for SiO_2 film containing nc-Si have been developed. The nc-Si depth distribution obtained from SIMS measurement is modeled with the approximation of many sub-layers, and for a given wavelength the optical constants of each sub-layer are formulated with the nc-Si volume fraction in the sub-layer and the nc-Si optical constants as variables based on the effective medium approximation. The nc-Si optical constants are obtained from the spectral ellipsometric fittings. Finally the optical constants of each sub-layer are calculated, and thus the depth profiles of the optical constants for the SiO_2 thin film containing nc-Si are obtained. The results are analogous of depth profiles of nc-Si in SiO_2 films, demonstrating it is correct and reliable.

Chapter 5: XPS Characterization of nc-Si Embedded in SiO₂ Matrix

5.1 Introduction

X-ray photoelectron spectroscopy (XPS) can be used to probe the electronic and chemical structures of the nc-Si embedded in SiO₂ matrix, which play an important role in controlling the optical and electrical properties. In the beginning of this chapter, the instrumental basics of XPS will firstly be introduced as well as the photoemission mechanism and measurement capability.

In order to obtain the true chemical shift, electric charging should be corrected before anything can be said about chemical environment in the nc-Si/SiO₂ system. As large amount of nc-Si have been embedded into SiO₂, there should be a very large area of SiO₂/nc-Si interfaces. Therefore, in addition to the charging in the SiO₂ thin film, there is also very significant electric charging at the SiO₂/nc-Si interfaces during photoemission. The charging will cause a core-level shift to a higher binding energy. The true chemical shift can only be obtained by subtracting the charging energy from the measured value. A detailed study on charging in nc-Si/SiO₂ system is necessary both for the learning of charging ability of nc-Si/SiO₂ system and for the further exploration of true core level shift. In this study, it is found that the charging ability of the nc-Si embedded SiO₂ film is superior to that of pure SiO₂ film giving out the explanation of the use of nc-Si/SiO₂ as the charge storage layer for nano-memory devices. Annealing (both for various annealing durations and for different annealing

temperatures) leads to a decrease of electric charging, which is interpreted in terms of the decrease of amount of nc-Si and interface states in annealing processes.

For nanoscale particles such as nanocrystals and metal clusters, it has been frequently reported that the core levels measured with x-ray photoelectron spectroscopy shift with the reduction of particle sizes [134-141]. Various mechanisms have been proposed to explain the size-induced core-level shift [134, 137, 138]. However, Si 2p core-level shift of Si nanocrystals (nc-Si) embedded in SiO₂ matrix determined from x-ray photoelectron spectroscopy experiment is found to be due to the charging in the material system. After the correction for the charging effect, the core levels of the isolated nc-Si and the oxidation state Si⁴⁺ are the same as that of bulk silicon and pure SiO₂, respectively. The corrected nc-Si core level does not show a quantum size effect and a dependence on the nanocrystal formation.

It is generally believed that all the implanted Si ions will form into nanocrystals after high temperature annealing. However, the analysis of x-ray photoelectron spectroscopy shows that except the Si nanocrystals (the corresponding Si oxidation state is Si⁰) and the stoichiometric SiO₂ (the corresponding Si oxidation state is Si⁴⁺) there are still other Si suboxides corresponding to the three Si oxidation states Siⁿ⁺ (n = 1, 2 and 3) in the Si-implanted SiO₂ films after high temperature annealing, indicating that thermal annealing does not necessarily convert all the implanted Si ions into Si nanocrystals. Furthermore, by XPS analysis, we show a clear picture of the evolution of the oxidation states and the formation of Si nanocrystals with thermal annealing in the surface layer. The evolution of the concentrations of the five oxidation states with annealing is explained in terms of the thermal decompositions of

the suboxides corresponding to the three oxidation states Si^{n+} ($n = 1, 2$, and 3) and the thermal oxidation of the implanted Si. In addition, the relative concentration of each oxidation state at various depths is determined quantitatively from the XPS analysis. Annealing effects on depth distributions of the oxidation states are presented also.

5.2 XPS

X-ray photoelectron spectroscopy is a surface analysis technique, with which samples are irradiated by monochromatic soft x-rays and characteristic kinetic and binding energies of emitted core electrons are measured. In this part, the instrumentation of XPS will first be introduced giving out the general features of the spectrometer. Discussion on the photoelectron generation and detection will be carried out as well as how to analyze the XPS spectra. As nc-Si concentration varies with depth in the oxide, depth analysis by XPS is a useful technique to obtain the information on the core level changes as a function of the concentration of nc-Si and thus is stressed in this part.

5.2.1 Instrumentation of XPS

A Kratos AXIS spectrometer is employed in the whole study, which is equipped with monochromatic Al $K\alpha$ (1486.71 eV) for x-ray source. The XPS system used in this work in the School of Mechanical and Production Engineering, Nanyang Technological University is illustrated in Fig.5.0.

The XPS analysis is conducted with a UHV system with the pressure typically near 1×10^{-10} torr. Such a UHV environment is reached via a combination of pump systems. The use of a roughing pump and a turbomolecular pump can firstly attain the pressure near 10×10^{-7} torr. Subsequently, a pressure near 1×10^{-10} torr can be obtained by the main diffusion pumps with liquid nitrogen cooling system both for the chambers and the spectrometer. An ion pump is used for the x-ray anodes particularly. Further pumping for the system can be performed using two titanium sublimation pumps if necessary.

Fig. 5.0. The Kratos AXIS spectrometer for XPS measurement in School of Mechanical and Production Engineering, Nanyang Technological University.

The photoelectron selection is based on a hemispherical electron energy analyzer as shown in Fig. 5.1. The electrostatic potential between the two plates can be modulated, thus allowing electrons with a particular energy to pass through the plates to the detector. The higher resolution of the analyzer can be achieved by decreasing the

passing energy, but leading to the lower detection intensity. The detector which has a angle specific function that can map electrons with different distribution angles of $\pm 2^\circ$, $\pm 5^\circ$ or $\pm 7^\circ$.

Fig.5.1. Schematic illustration of measurement of photoelectrons. Only those photoelectrons having a particular kinetic energy equal to analyzer passing energy can be detected.

Sample translation and rotation are necessary in angle resolved XPS measurements, which can be performed by the manipulator. The sample introduction system is designed to allow rapid sample replacement without disturbing the vacuum in the main chamber, as the pump-down time is long. As characterization of nc-Si synthesized under different environments requires the measurement of many samples, sample changing must be facile and rapid as well as not disturb the vacuum in the main chamber. This sample introduction system consists of a load lock, which can be brought to the air to load samples and pumped down to $\sim 10^{-7}$ torr in a short time, and a swing arm, which is controlled magnetically to mount and shift the sample. Normally sample transfer can occur within 0.5 hour including the loading and vacuuming time.

XPS also allows measurements conducted at various temperatures. The sample can be cooled down to 180K as well as it can be heated to 500K. Cooling is realized with a liquid nitrogen dewar mounted on a copper block in the chamber. The sample heating is achieved by a filament mounted on the sample plate. A thermocouple is used to monitor the sample temperature contacting with a temperature controller embedded in the manipulator. The sample can also be biased or grounded to enable the shift of banding energy in a controllable manner.

Depth profile analysis with XPS can be performed by Ar ion sputtering. Elemental depth profiling of the surface layer and interfacial structure can be determined by sputtering off film surface layer by layer using an argon ion gun with 15 keV energy and a sputtering rate of 5 nm/min.

5.2.2 Fundamentals of XPS

Generation of photoelectron

Hertz first observed photoemission in 1887 and Einstein proposed the quantum mechanism for it in 1905. Photoelectron spectroscopy was first used for chemical footprint by Kai Siegbahn in 1967 with the application of high resolution electron energy detector and monochromatic x-ray sources. From then on, the investigation of the chemical environment of atoms was widely carried out by comparison of its binding energy with a reference compound using XPS.

The general process of generation of photoelectrons is shown in Fig.5.2. A standard Al anode is used to generate x-rays and the x-ray photon interacts with the core electron. The photoelectric effect leads to the escape of one photoelectron leaving a hole with positive charge in the core level. The kinetic energy of the resulting photoelectron is the difference between the energy of final excited charged state and the initial ground state energy of the particular electron in the core level interacting with the injecting photon. The XPS intensity is thus proportional to photoelectrons and the characteristic peak in the spectrum is corresponding to the atomic level at certain binding energy. This photoionization process can be expressed as

where A_0 is the isolated neutral atom, $h\nu$ is the photon, A^+ is the positive charged ion in the excited state and e^- is the photoelectron. From this reaction, it is important to note the final state of A^+ . With one photoelectron emission, the system is left a hole with unit positive charge. The proximity of a positive charge in deep core near the

nucleus is energetically unfavorable. A relaxation between nearby electrons and the hole may happen. The electronic relaxation occurs on the order of 10^{-16} s, and the nuclear geometric relaxation is approximately 10^{-13} s. As the photoelectron takes about 10^{-15} s to leave the system, the photoelectron is sensitive to the electronic relaxation. As a result, the XPS spectra are taken for the system with positive charges but not of the neutral state.

Fig.5.2. Illustration of the photoelectron generation process. (a) The ground state with the injecting x-ray photon; (b) photoelectric interaction between the photon and the electron in the specific core level; (c) The excited state with a photoelectron emission leaving a positive hole in the core level.

As illustrated in Fig. 5.3, with consideration of electronic charges, the binding energy (BE) of the photoelectron can be expressed as [142]

$$BE = h\nu - E_K - \phi_s - q\phi \quad (5.2)$$

where $h\nu$ is the x-ray photon, E_K is the kinetic energy of the photoelectron, Φ_s is the work function of the spectrometer, q is the electronic charge, and Φ is the surface potential. Figure 5.3 shows the energy diagram for a sample and the spectrometer under XPS measurement. The sample and the spectrometer are grounded together so that their respective Fermi levels are equal.

Fig.5.3. Energy diagrams of the sample and the spectrometer for XPS measurement.

Core level shift

As the photoelectrons originate from the deeply bound states at core levels, chemical bonding information about the atoms in the material system can be obtained. First, the core levels exhibit at characteristic binding energies, giving a footprint corresponding to the specific chemical structure, which make possible to identify the elements, compounds and characteristic bonding structures. Secondly, there are core

level shifts due to the chemical structure change, allowing researchers to examine the chemical environment of the atom. The shift of a core level can be attributed to electrostatics. The energy of a core electron is related to the attractive potential of the nucleus and the repulsive force from surrounding electrons in the material system. The electrons in the valence band will redistribute associated with the chemical environment. Consequently, the changes in density of electron states affect the binding energy of core electrons. For example, oxidation of Si involves removal of electrons and formation of stoichiometric SiO_2 , resulting in difficulties to remove another electron. As a result, the core level of SiO_2 is increased to a higher binding energy for ~ 4 eV relative to that of Si [143-146]. Fig. 5.4 shows the comparison of Si 2p spectra between bulk Si and SiO_2 film. A shift of ~ 4 eV can be clearly observed from the two spectra.

Fig. 5.4. XPS Si 2p spectra for bulk Si<100> and a SiO_2 film.

Surface sensitivity

Although x-ray photons can penetrate to several microns into the sample, the photoelectrons generated below a certain depth known as mean free path, undergo much inelastic energy loss collisions and thus only contribute to the background XPS spectrum. The photoelectrons generated near the surface escape without energy loss, contribute to the characteristic peaks of the core level of the element in the XPS spectrum. Each element or compound has its particular mean free path, λ , which is as a function of kinetic energy of the photoelectron. Fig. 5.5 shows the mean free path for elements as a function of the electron kinetic energy. Typically the photoelectron kinetic energies are ranging from 100 to 1000 eV, and thus λ values are within nanometers, making XPS a surface sensitive technique.

Fig. 5.5. Electron mean free path for numerous elements as a function of kinetic energy [147,148].

Method to analyze the XPS spectrum

XPS allows analysis of the very top surface, while it is difficult to analyze measured XPS spectrum because the energy of photoelectron electrons is greatly influenced by the chemical state of atoms. In the 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. By the deconvolution with the use of Gaussian function and the Lorentzian function, it is possible to isolate individual XPS peaks and perform the qualitative and quantitative analyses for every component accurately. As a fact, this method is dependent upon the initial guesswork, i.e., the number of peaks and their peak parameters [149]. Its scope and limitations have been pointed out in [150].

Fig.5.6 (a) and (b) show the XPS Si 2p core level peaks for the original spectrum and the spectrum after the peak deconvolution, respectively. As can be seen in the original spectrum, there appear only two peaks arising from SiO₂ structure and Si structure at ~105 eV and ~ 100.5 eV, respectively. However, there are obvious shoulders corresponding to specific structures in the raw spectrum, which cannot be reflected without peak-fitting analysis. To extract detailed chemical structure information from the XPS Si 2p peaks it is necessary to establish a suitable peak fitting procedure. As shown in Fig.5.6 (b), our procedure is based on the use of five Gaussian-shaped peaks of Siⁿ⁺ (n = 0, 1, 2, 3, and 4) to simulate the five silicon oxidation states corresponding to the five chemical structures of Si, Si₂O, SiO, Si₂O₃ and SiO₂, respectively. It has been reported that the five oxidation states exist in non-stoichiometric SiO_x (0 < x < 2) films [142 and 151], and they are also commonly

observed at SiO₂/Si interface [142, 153, 154, 237]. For the Si-rich SiO_x films formed by Si ion implantation into SiO₂ films in this study, it is also reasonable to assume the possible existence of the five silicon oxidation states. Fig. 5.7 shows the interface structure between nc-Si and SiO₂ as well as the five Si oxidation states. With the possible existence of the five oxidation states in mind, the peak of each oxidation state will be yielded from the fitting without any pre-adjudication, and such an approach has been proved to be able to provide us a reasonable picture of the changes of the chemical structures in the SiO_x film as a result of thermal annealing. The detailed discussion will be carried out in **Section 5.4 and 5.5**.

Fig. 5.6. Illustration of Si 2p peak deconvolution for (a) the original spectrum and (b) the deconvolution with five sub-peaks corresponding to Siⁿ⁺ (n=0, 1, 2, 3, and 4) .

Fig. 5.7. The interface structure and Si oxidation states between nc-Si and SiO₂.

Depth analysis

As discussed in **Chapter 4**, the concentration of nc-Si in the SiO₂ film varies with depth. Thus, it would be also useful to examine the chemical environment changes as a function of the concentration of nc-Si at various depths. The XPS spectra of the depth profile can be obtained by repeating the measurements after successive slight etching of nc-Si embedded SiO₂ films with argon sputtering.

Fig. 5.8. Si 2p spectra of four successive XPS measurements with Ar sputtering at the interface of SiO₂ film/Si substrate.

Fig. 5.8 shows the depth dependence of the XPS Si 2p spectrum for the interface of SiO₂/Si substrate. As illustrated, either the intensity of Si 2p (from substrate) or the Si 2p (from oxide) is observed to change as a function of depth. With sputtering on, the peak intensity of Si 2p (oxide) decreases as well as that of Si 2p (substrate) increases. The modification is due to the changes in the chemical state of the oxide film because concentration of Si⁴⁺ will be reduced as well as that of Si⁰ will be increased in the transition from SiO₂ film to the Si substrate. The analysis of nc-Si/ SiO₂ interface is similar to that of SiO₂ film/ Si substrate and will be studied detaily in **Section 5.4 and 5.5**.

5.3 Charging in the Material System

5.3.1 Background and Motivation

Many studies have been carried out on SiO₂/Si interface and nc-Si/SiO₂ systems with XPS [151, 153-163, 237]. However, some of researchers failed to point out whether they had considered charging effect [163], or some even said they found no charging or almost no effect of charging (<0.05 eV) in SiO₂ films [160-162]. Seiichi Iwata *et al* made the conclusion that charging occurs within SiO₂ film and at the interface of SiO₂/Si [142]. Before further investigation can be started, the true chemical shift must be determined by correction of charging effect. As large amount of nc-Si have been introduced into SiO₂, there should be a very large area of SiO₂/nc-Si interfaces. Therefore, in addition to the charging in the SiO₂ thin film, there is also very significant charging at the SiO₂/nc-Si interfaces in photoemission. The charging will cause a core-level shift to a higher binding energy. The true chemical shift can only be obtained by subtracting the charging energy from the measured core level. Hence a detailed study on the charging in our nc-Si/ SiO₂ material system is necessary. On the other hand, as nano-memory and single electron devices also work with charging/discharging in nc-Si/SiO₂ system, XPS result may be helpful to understand the operation mechanisms of these devices. In this section, Si 2p, O 1s and C 1s core levels are recorded to study the effects of annealing on surface charging in SiO₂ films containing Si nanocrystals. Due to the charging effect, Si 2p core level does not show any trend with annealing as well as O1s core level, indicating true core level shift can only be obtained after the correction of charging effects. It is also found the charging ability of the nc-Si embedded SiO₂ film is superior to that of pure SiO₂ film giving out

the explanation of the use of nc-Si/SiO₂ as the charge storage layer for nano-memory devices. Annealing (both for various annealing durations and for different annealing temperatures) leads to a decrease of charging, which is interpreted in terms of the decrease of amount of nc-Si and interface states in annealing processes.

5.3.2 Experimental

Sample preparation

30 nm SiO₂ thin films were grown on p-type Si wafers with (100) orientation by thermal oxidation in dry oxygen at 950 °C. Then Si ions were implanted into the SiO₂ films at the energy of 1keV with the dose of $8 \times 10^{16} \text{ cm}^{-2}$. The profile of excess Si in the SiO₂ thin film was measured with secondary ion mass spectroscopy (SIMS). The implanted Si distributes from the surface to the depth of ~ 15nm with the maximum concentration at the depth of ~ 5nm, as shown in Fig. 5.9. Thermal annealing was carried out in N₂ ambient at various annealing temperatures for different annealing time.

Characterization

The mean size of the nc-Si is determined from full width of half maximum (FWHM) of the Bragg peak after correction for instrumental broadening in the x-ray diffraction (XRD) measurement [70]. The nc-Si size obtained is from ~ 2.5 nm for the as-implanted sample to ~ 3 nm for the samples annealed at various temperatures for various durations. This result is similar to that from [73] in which it is reported that the nc-Si size slightly increases from 2.5 nm after 1 minute annealing to 3 nm after 16 hours annealing at the annealing temperature of 1100 °C. This very slow evolution is

due to the very low diffusion coefficient of Si in SiO₂. It should be noted that samples used in this study are different from those in **Chapter 4**. The 1keV Si-implanted samples here has a mean size of ~ 3 nm, while the 50 keV and 100 keV implanted samples used in **Chapter 4** have a mean size of 4-5 nm. XPS experiment was performed by using a Kratos AXIS spectrometer with monochromatic Al K α (1486.71 eV) X-ray radiation. For the study of the charging effect, Si 2*p* core-level spectra, C 1*s* spectra and O 1*s* spectra were recorded under the surface-scanning mode by XPS. An XPS survey spectrum from the nc-Si embedded SiO₂ film surface is shown in Fig.5.10. Si 2*p* and Si 2*s* peaks can be clearly observed, arising from the Siⁿ⁺ (n=0,1, 2, 3 and 4) states. The strongest O1*s* core level peak comes from the oxidation states. C1*s* core level is due to the carbon contamination, which exists at the oxide surface. Detailed discussions will be carried out below.

Fig.5.9. Si implantation profile determined from SIMS measurement.

Fig.5.10. A typical XPS survey spectra for the nc-Si embedded SiO₂ film.

5.3.3 Result and discussion

It has been proved for a long time that under x-ray excitation, charges can be generated in SiO₂ films or at the SiO₂/Si interface [142]. It is also reported in [164] that SiO₂ can withstand electric fields of 10^6 - 10^7 V/cm. That means there could be a voltage difference of 0.5-5V in a 5-nm thick SiO₂ film if sufficient charges were induced, demonstrating the existence of charging effect in SiO₂ or at SiO₂/ Si interface. The charging picture is shown in Fig. 5.11. During the XPS measurements, x-rays generate the photoelectrons leaving positive charges inside the sample, which makes it difficult to determine the true chemical shift by XPS. For the case of nc-Si/ SiO₂ system, a very large area of SiO₂/nc-Si interfaces is expected because of a large number of nc-Si embedded in SiO₂ matrix. Therefore, in addition to the charging in

the SiO_2 thin film, there should be very significant charging at the $\text{SiO}_2/\text{nc-Si}$ interfaces in photoemission. The charging will cause a core-level shift to a higher binding energy. At the same time, photoemission will also leave charges in the nanocrystals giving rise to a Coulomb charging energy that depends on the nanocrystal size, and the Coulomb charging energy will lead to a core-level shift to a higher binding energy.

Fig. 5.11. Illustration of charging inside the sample caused by x-rays during XPS measurements.

Fig. 5.12 shows the Si 2p spectra for the nc-Si/ SiO_2 system as a function of annealing time (a) and as a function of annealing temperature (b). As already introduced in **Section 5.2**, it is shown that the peak from Si^0 corresponding to nc-Si appears at ~ 100.5 eV, while that from Si^{4+} corresponding to SiO_2 structure locates at ~ 105 eV. There are no obvious trend of core levels both for annealing temperature and annealing time. But as compared to 103.8 eV for Si^{4+} of pure SiO_2 films, a shift to higher binding energy of ~ 1.2 eV is clearly observed. Such a shift is attributed to the more significant charging ability of the $\text{SiO}_2/\text{nc-Si}$ system, while in some literatures

[165,166], this phenomenon was explained in terms of permanent chemical state changes produced by x-ray irradiation. However, the O1s peaks, in Fig.5.13, are also observed to shift in the same direction corresponding to the Si 2p peaks, which indicates that there is electric charging but no chemical state change [142].

Fig. 5.12. Si 2p core level for (a) as a function of annealing time with the temperature fixed at 1000°C and for (b) as a function of annealing temperature with duration fixed for 20 min.

Fig. 5.13. O 1s core level for (a) as a function of annealing time with the temperature fixed at 1000°C and for (b) as a function of annealing temperature with duration fixed for 20 min.

If we conclude that the above results are due to electric charging, is it possible to correct for this effect and obtain the real chemical shift? One commonly used method by previous researchers is employment of adventitious carbon [167,168]. C 1s core

level peaks may be a choice to evaluate the charging effect, as adventitious carbon is usually detected on the sample surface and there are no carbon doped purposely in our nc-Si/SiO₂ samples. Fig. 5.14 shows C 1s core levels for different annealing temperatures and for various annealing durations. As can be seen, with doping of a large amount of nanocrystals the charging ability of the SiO₂ film is remarkably improved. A shift ranging from ~1.5 to ~2 eV to a higher binding energy from that of pure SiO₂ is always observed both in samples annealed for different durations and those annealed at different temperatures. Furthermore in figure 5.15, the charging is determined by subtracting the reference C 1s core level [169] from the measured C 1s core level.

$$\Delta E = BE_m - BE_{ref} \quad (5.3)$$

where ΔE is the charging energy; BE_m is the measured C 1s core level peak position; BE_{ref} is the reference C 1s core level equal to 284.6 eV [169]. For pure SiO₂ film, the surface charging is about 0.8 eV. The value is much less than ΔE for the nc-Si/SiO₂ system.

As XPS is a surface probing technique, the charging effect here is reflected from the surface layer of the nc-Si/SiO₂ films. The surface charging for the nc-Si embedded SiO₂ films shows a decrease both as a function of annealing temperature and as a function of annealing time, as illustrated in Fig. 5.15. For example in group one, after annealing at 1100 °C for 20 minutes, the C 1s core level shifts from 286.6 eV (the as-implanted sample) to a lower binding energy of ~ 286.2 eV, while the surface charging is changed from 2.0 eV to 1.6 eV. For the samples annealed for different durations, similar situation can be found. In Fig. 5.15 (a), surface charging for the sample in group two decreases from 2.1 eV to 1.9 eV after annealing at 1000 °C for

100minutes. This evolution of surface charging with annealing is explained in terms of the thermal oxidization of nc-Si due to the presence of residual oxygen and the decomposition of interface states. It may lead to growth of SiO₂ but reduction of the nc-Si and interface states, and thus the decrease of the charging ability for the surface layer of nc-Si/SiO₂ films. The annealing effect on the evolution of Si oxidation states will be discussed detaily in **Section 5.5**.

Fig. 5.14. C 1s core level for (a) as a function of annealing time with the temperature fixed at 1000 °C and for (b) as a function of annealing temperature with duration fixed for 20 min.

Fig.5.15. (a) Surface charging as a function of annealing time at 1000 °C and (b) as a function of annealing temperature. Surface charging for pure SiO₂ is 0.8 eV. Samples prepared with identical process are divided into two groups. Group one is characterized by XPS a few weeks earlier than group two.

It is also can be found in Fig. 5.15, even samples prepared with identical process show different charging effects. Differences of charging between identical samples are ranging from 0.1 to ~ 0.4 eV, which can be attributed to the amount of C present at sample surface and the measurement conditions as pointed out in [142].

5.3.4 Conclusion

In this section, XPS has been employed to study the charging effect in our nc-Si/SiO₂ system. The charging effect in the nc-Si/SiO₂ system due to photoemission is found to be much more significant than that in the pure SiO₂ system, indicating that the charging effect from the SiO₂ thin film is much less significant than that from the SiO₂ films containing nc-Si. Annealing reduces the charging ability of nc-Si embedded SiO₂ films, which is due to the thermal oxidation of nc-Si and the decomposition of interface states in annealing processes.

5.4 Core Level Shift

5.4.1 Background and Motivation

One of promising techniques for the incorporation of Si in SiO₂ films is Si ion implantation into SiO₂ films grown by thermal oxidation of Si substrate. With this technique, nc-Si is formed and isolated inside the robust SiO₂ matrix that provides good chemical and electrical passivation of the nanocrystals. Optical and electrical properties of the nc-Si embedded in SiO₂ matrix should be different from those of bulk crystalline Si as well as nc-Si thin films. Photoelectron spectroscopy can be used to probe the electronic and chemical structures of the nc-Si embedded in SiO₂ matrix,

which play an important role in controlling the optical and electrical properties. For nanoscale particles such as nanocrystals and metal clusters, it has been frequently reported that the core levels measured with x-ray photoelectron spectroscopy (XPS) shift with the reduction of particle sizes [134-141]. Various mechanisms have been proposed to explain the size-induced core-level shift. For example, the cluster size-dependence of Cu 2p core-level shift is explained in terms of the influence of initial- and final-state effects [137], Au 4f core-level shift of the supported gold clusters is experimentally found to be consistent with the size dependence of the charging energy of the clusters [138], and the size dependence of Si 2p core-level shift of porous silicon is explained by the bond contraction model [134]. In this study, Si 2p core-level shift of Si nanocrystals (nc-Si) embedded in SiO₂ matrix determined from x-ray photoelectron spectroscopy experiment is found to be due to the charging in the material system. After the correction for the charging effect, the core levels of the isolated nc-Si and the oxidation state Si⁴⁺ are the same as that of bulk silicon and pure SiO₂, respectively. The corrected nc-Si core level does not show a quantum size effect and a dependence on the nanocrystal formation.

5.4.2 Experimental

Sample preparation

30 nm SiO₂ thin films were grown on p-type Si wafers with (100) orientation by thermal oxidation in dry oxygen at 950 °C. Then Si ions were implanted into the SiO₂ films at the energy of 1keV with the dose of $8 \times 10^{16} \text{ cm}^{-2}$. The profile of excess Si in the SiO₂ thin film was measured with secondary ion mass spectroscopy (SIMS). The implanted Si distributes from the surface to the depth of ~ 15nm with the maximum

concentration at the depth of ~ 5 nm, and the subsequent annealing doesn't change the profile significantly. Thermal annealing was carried out in N_2 ambient at various annealing temperatures for different annealing time. For simplicity, here only the results of the annealing at 1000°C for various annealing durations ranging from 0 to 100 minutes are presented.

Characterization

The mean size of the nc-Si is determined from full width of half maximum (FWHM) of the Bragg peak in the XRD measurement. The nc-Si size obtained is from ~ 2.5 nm for the as-implanted sample to ~ 3 nm for the samples annealed at various temperatures for various durations. XPS experiment was performed by using a Kratos AXIS spectrometer with monochromatic Al $K\alpha$ (1486.71 eV) X-ray radiation. Si 2p core-level spectra were recorded. For the study of the charging effect, C 1s spectra from the sample surface and Au 4f spectra from the thick (~ 50 nm) or thin (~ 2 nm) gold films deposited on the samples were also recorded.

5.4.3 Result and Discussion

Fig. 5.16. Illustration of deconvolution of Si 2p spectrum for the as-implanted sample.

Figure 5.16 shows the XPS Si 2p core level peaks for the as-implanted sample. It has been reported that five oxidation states Si^{n+} ($n = 0, 1, 2, 3$, and 4) corresponding to the five chemical structures of Si, Si_2O , SiO, Si_2O_3 and SiO_2 , respectively, exist in non-stoichiometric SiO_x ($0 < x < 2$) films [151], and they are also commonly observed at SiO_2/Si interface [142,153,154,237]. For the Si-rich SiO_x films formed by Si ion implantation into SiO_2 films in this study, it is also reasonable to assume the possible existence of the five silicon oxidation states. With the possible existence of the five oxidation states in mind, the peak of each oxidation state will be yielded from the curve fitting based on the use of five Gaussian-shaped peaks of the five oxidation states without any pre-adjudication, and such an approach has been proved to be able to provide us a reasonable picture of the changes of the chemical structures in the SiO_x film as a result of thermal annealing. The Si 2p peak deconvolution of the above approach for the as-implanted is also shown in Fig.5.16.

Fig.5.17. Si^0 shifts relative to the Si 2p core level in bulk Si for the as-implanted sample (i.e. the annealing time is 0 minute) and the samples annealed at 1000 °C for various annealing time. The solid circles represent the uncorrected shifts and the open circles show the values after the correction for the charging effect.

The Si 2p binding energy of the nc-Si (or Si⁰) can be determined from the above peak deconvolution. The solid circles in Fig.5.17 represent the shifts of the Si⁰ 2p binding energy relative to the bulk Si 2p core level for the as-implanted sample (i.e. the annealing time is 0 minute) and the samples annealed at 1000 °C for durations ranging from 20 min to 100 min. A shift ranging from ~1.5 to ~2 eV to a higher binding energy is always observed. The shift doesn't have a trend of dependence on the nanocrystal size. For the as-implanted sample, the nanocrystal size is ~ 2.5 nm; for the samples annealed for durations of from 20 min to 100 min, the nanocrystal size is ~ 3 nm being almost the same for different annealing time. The shift for the as-implanted sample is ~ 2eV, it drops to ~1.5 eV for the annealing of 20 min, then it increases with the annealing time to get back to ~ 2 eV at the annealing of 60 min and it remains almost unchanged for further annealing. Therefore, it seems that the shift is not determined by the size effect that may originate from quantum confinement, initial- and final-state effects [137], Coulomb charging energy [138], or surface bond contraction [134]. The situation of other oxidation states Siⁿ⁺ (n = 1, 2, 3, and 4) is also similar to that of Si⁰ discussed here. The solid circles in Fig.5.18 show the Si⁴⁺ shift relative to the Si 2p core level in pure SiO₂. It can be concluded from the comparison of Fig.5.18 with Fig.5.17 that the Si⁴⁺ shift is actually the same as the Si⁰ shift. This suggests that the shifts are due to a change in the overall environment. As demonstrated below, the shifts originate from the charging in the material system.

It has been known for a long time that under x-ray irradiation, charges can accumulated at SiO₂/Si interface [142]. With a large number of nc-Si embedded in the SiO₂ matrix, there should be a very large area of SiO₂/nc-Si interfaces. Therefore, in addition to the charging in the SiO₂ thin film, there is also very significant charging

at the $\text{SiO}_2/\text{nc-Si}$ interfaces in photoemission. The charging will cause a core-level shift to a higher binding energy. At the same time, photoemission will also leave a charge in the nanocrystals giving rise to a Coulomb charging energy, and the Coulomb charging energy will lead to a core-level shift to a higher binding energy. The core-level shift in the pure SiO_2 thin film due to photoemission is found to be much smaller than that in the $\text{nc-Si}/\text{SiO}_2$ system, indicating that the charging effect from the SiO_2 thin film is much less significant than that from the combination of $\text{SiO}_2/\text{nc-Si}$ interfaces and the nanocrystals.

Fig. 5.18. Si^{4+} shifts relative to the Si 2p core level in pure SiO_2 thin film. The solid circles represent the uncorrected shifts and the open circles show the values after the correction for the charging effect. Note that the charging effect on the Si 2p core level in the pure SiO_2 thin film has been corrected.

To show the charging effect on the core-level shifts, C 1s spectra from the sample surface due to adventitious carbon and Au 4f spectra from the thick or thin gold films

deposited on the samples were also recorded. Fig.5.19 shows the shifts of the C 1s core level relative to C 1s reference for the sample without nc-Si (i.e. the pure SiO₂ thin film on Si substrate), the as-implanted sample and the sample annealed at 1000°C for 100 minutes after Si⁺ implantation. The shift in the sample without nc-Si is 0.8 eV, which is due to the charging in the 30 nm SiO₂ thin film on Si substrate [142], being much smaller than the shifts in the as-implanted and annealed samples. The shifts are 2 eV in both the as-implanted and annealed samples as illustrated in Fig.5.19, showing that the charging effect is greatly enhanced by the Si⁺ implantation.

Fig. 5.19. C 1s spectra recorded from the surfaces of the sample without nanocrystals (i.e. the pure SiO₂ thin film on Si substrate), the as-implanted sample and the sample annealed at 1000 °C for 100 minutes after the Si⁺ implantation.

The charging effect can be also revealed by monitoring the shifts of Au 4f core level in the thick and thin gold films. Fig.5.20 shows the Au 4f shifts (relative to the

gold reference) of the thick and thin gold films deposited on the samples identical to those for the C 1s measurement. As can be seen in Fig.5.20, for all the samples, the shifts of the thick gold films are either insignificant or very small indicating that the thick gold films can present the charging, but in contrast the shifts of the thin gold films are large. This again clearly shows that the XPS measurement itself can really cause a core-level shift as a result of the charging effect.

Fig.5.20. Au 4f spectra of the thick and thin gold films deposited on the samples identical to those for the C 1s measurements shown in Fig.5.19.

The charging effect has important consequence on the evaluation of the core-level shifts of nc-Si, and the correction for the charging effect must be made. As each Si 2p and C 1s spectra were recorded in the same XPS experiment on the same sample, the charging effect on the Si 2p core-level shift can be corrected by subtracting the C 1s

core-level shift from the raw data of the binding energy of Si^0 2p core level. Such corrections are shown in Fig.5.17 where the solid circles are for the raw data (i.e. before correction) while the open circles give the corrected values. A quite different picture is observed after the corrections. As shown in Fig.5.17, after the correction, the nc-Si core level shows no significant shift from that of bulk silicon within the measurement uncertainty, and it has no significant dependence on the nanocrystal formation and the nanocrystal size as well. Similar corrections have been made for Si^{4+} also, as shown in Fig.5.18. After the correction for the charging effect, the core level of Si^{4+} has also no significant shift from the Si 2p core level in pure SiO_2 thin film and no significant dependence on the annealing as well. These results suggest that the chemical statuses of Si^0 and Si^{4+} in the material system of nc-Si embedded in SiO_2 matrix are very similar or even identical to those of the corresponding oxidation states in bulk Si and pure SiO_2 thin film, respectively.

5.4.4 Conclusion

In conclusion, Si 2p core-level shift of nc-Si embedded in SiO_2 matrix is observed in XPS experiment. The shift of the nc-Si relative to the bulk Si 2p core level is found to be the same as the shift of the oxidation state Si^{4+} relative to the Si 2p core level in pure SiO_2 . It is demonstrated that the shifts are due to the charging in the material system. After the correction for the charging effect the core level of the isolated nc-Si is found to be the same as that of bulk silicon, and no quantum size effect and no dependence on the nanocrystal formation are observed. In addition, after the correction for the charging effect the core level of Si^{4+} has also no significant shift

from the Si 2p core level in pure SiO₂ thin film and shows no significant dependence on the thermal annealing as well.

5.5 Depth Profiling of Si Oxidation States

5.5.1 Background and Motivation

It is generally believed that all the implanted Si ions will form into nanocrystals after high temperature annealing. However, our analysis of x-ray photoelectron spectroscopy (XPS) shows that except the Si nanocrystals (the corresponding Si oxidation state is Si⁰) and the stoichiometric SiO₂ (the corresponding Si oxidation state is Si⁴⁺) there are still other Si suboxides corresponding to the three Si oxidation states Siⁿ⁺ (n = 1, 2 and 3) in the Si-implanted SiO₂ films after high temperature annealing, indicating that thermal annealing does not necessarily convert all the implanted Si ions into Si nanocrystals. The analysis of the XPS Si 2p peaks shows the existence of the five chemical structures corresponding to the Si oxidation states Siⁿ⁺ (n=0, 1, 2, 3, and 4) in the SiO₂ films, and the concentration of each oxidation state is determined quantitatively. The XPS results show a clear picture of the evolution of the Si oxidation states and the formation of Si nanocrystals as functions of annealing temperature and annealing time at surface layer. The evolution of the concentrations of the five oxidation states with annealing is explained in terms of the thermal decompositions of the suboxides and the thermal oxidation of the implanted Si. We also show that the depth distributions of the relative concentrations of all the five Si oxidation states can be quantitatively obtained from the XPS analysis, and an

investigation of annealing effects on both the oxidation states and their depth distributions is presented also.

5.5.2 Experimental

Sample preparation

30 nm SiO₂ thin films were grown on p-type Si wafers with (100) orientation by thermal oxidation in dry oxygen at 950 °C. Then Si ions were implanted into the SiO₂ films at the energy of 1keV with the dose of $8 \times 10^{16} \text{ cm}^{-2}$. Thermal annealing was carried out in N₂ ambient. For the experiment of annealing temperature, the temperature was varied from 500 to 1100°C but the annealing time was fixed at 20 minutes; for the experiment of annealing time, the time was varied from 0 to 100 minutes while the annealing temperature was kept at 1000 °C.

Characterization

The mean size of the nc-Si is determined from full width of half maximum (FWHM) of the Bragg peak in XRD measurement ranging from 2.5 to 3 nm. XPS analysis was performed by using a Kratos AXIS spectrometer with monochromatic Al K α (1486.71 eV) X-ray radiation. The depth profiling experiment was carried out with Ar ion sputtering. The Si 2*p* XPS peaks were analyzed by means of a computer program of gaussian peak fitting. From the decomposition of the Si 2*p* peaks, the relative concentrations of various components corresponding to different Si oxidation states Siⁿ⁺ (n = 0, 1, 2, 3, and 4) in the SiO₂ films were determined. Secondary ion mass spectroscopy (SIMS) has been used for elemental depth profiling of Si and O. Cs⁺ was used as the primary ion source in the SIMS measurement. As revealed by

SIMS and XPS characterization shown later, 1 keV Si^+ ion implantation led to the distribution of excess Si from the surface to a depth of about 15 nm.

5.5.3 Result and Discussion

Figure 5.23(a) and (b) show the XPS Si 2p core level peaks for the as-implanted sample and the sample that was annealed at 1000°C for 100 minutes, respectively. As the spectra were taken at sample surface, the Si substrate did not contribute to the spectra. To extract detailed chemical structure information from the XPS Si 2p peaks it is necessary to establish a suitable peak fitting procedure. As shown in Fig.5.23 and Fig.5.24, our procedure was based on the use of five Gaussian-shaped peaks of Si^{n+} ($n = 0, 1, 2, 3, \text{ and } 4$) to simulate the five silicon oxidation states corresponding to the five chemical structures of Si, Si_2O , SiO, Si_2O_3 and SiO_2 , respectively. It has been reported that the five oxidation states exist in non-stoichiometric SiO_x ($0 < x < 2$) films prepared by low pressure chemical vapor deposition (LPCVD) or by atmospheric pressure chemical vapor deposition (APCVD) [151], and they are also commonly observed at SiO_2/Si interface [142, 153, 154, 237]. For the Si-rich SiO_x films formed by Si ion implantation into SiO_2 films in this study, it is also reasonable to assume the possible existence of the five silicon oxidation states. With the possible existence of the five oxidation states in mind, the peak of each oxidation state will be yielded from the fitting without any pre-adjudication, and such an approach has been proved to be able to provide us a reasonable picture of the changes of the chemical structures.

Fig.5.21. Illustration of Si 2p peak deconvolution for (a) the as-implanted sample and (b) the sample annealed at 1000 °C for 100 minutes. Both of the samples were scanned for the surface layer.

As shown in Fig.5.21, the annealing effect on the chemical structures can be clearly demonstrated by the comparison of the Si 2p peak deconvolution between the as-implanted sample and the sample that was annealed at 1000°C for 100 minutes. As

shown in Fig.5.21 (a) for the as-implanted sample, the contributions of Si^0 , Si^{1+} , Si^{2+} and Si^{3+} are large, showing the coexistence of large amounts of Si nanoclusters/nanocrystals and the Si suboxides corresponding to the three oxidation states Si^{1+} , Si^{2+} and Si^{3+} in addition to the stoichiometric SiO_2 matrix in the SiOx films. However, after the annealing at 1000 °C for 100 minutes, as shown in Fig.5.21 (b), the contributions of the three oxidation states become small or even insignificant, and Si^{4+} and Si^0 are the dominant components after the annealing, suggesting the formation of Si nanocrystals embedded in the stoichiometric SiO_2 matrix. The result indicates that the annealing leads to the reductions of the three suboxides Si_2O , SiO and Si_2O_3 , being consistent with the picture of the thermal decompositions of the suboxides that is discussed below.

Fig.5.22. Changes of the concentrations of the five Si oxidation states Si^{n+} ($n = 0, 1, 2, 3$, and 4) in the surface layer with annealing temperature. The annealing time is fixed at 20 minutes.

It would be useful to examine quantitatively the changes of the concentrations of the five oxidation states with annealing. For this regard, as a first-order

approximation, the relative concentration (in percentage) of each oxidation state is obtained from the calculation of the ratio of $\frac{I_{Si^{n+}}}{I_{total}}$ ($n=0, 1, 2, 3$, and 4) where $I_{Si^{n+}}$ is the peak area of the oxidation state Si^{n+} and I_{total} is the total area ($= \sum_{i=0}^4 I_{Si^{i+}}$) of the Si 2p peaks. Fig.5.22 shows the changes of the concentrations of the five oxidation states with annealing temperature for a fixed annealing time of 20 minutes. For all annealing temperatures, with the increase of annealing temperature, the Si^{4+} concentration increases greatly, but the concentrations of all other oxidation states decrease. On the other hand, we have also measured the evolution of the concentrations of the five oxidation states with annealing time for the annealing temperature of $1000^{\circ}C$, and the result is shown in Fig.5.23. As can be seen in this figure, the Si^{4+} concentration has a very large increase after the first 20-minutes annealing but increases gently after longer annealing, while all other oxidation states Si^{n+} ($n = 0, 1, 2$ and 3) show a decrease in concentration with annealing time.

Fig.5.23. Evolution of the concentrations of the five Si oxidation states Si^{n+} ($n = 0, 1, 2, 3$, and 4) in the surface layer as a function of annealing time. The annealing temperature is fixed at $1000^{\circ}C$.

The above results are explained in the following. The thermal decomposition (or phase separation) of the Si suboxides Si_2O , SiO and Si_2O_3 corresponding to the oxidation states Si^{1+} , Si^{2+} and Si^{3+} , respectively, occurs during annealing to form more stable stoichiometric SiO_2 and Si nanocrystals, and the thermal decomposition can be described by [31,79]

where $x = 1/2, 1, 3/2$ for Si_2O , SiO and Si_2O_3 , respectively. Obviously, the thermal decomposition of the suboxides reduces the concentrations of the oxidization states Si^{1+} , Si^{2+} and Si^{3+} , and it also leads to the growth of SiO_2 and the formation of Si nanocrystals. On the other hand, thermal oxidation of the implanted Si during the annealing due to the presence of residual oxygen in the nitrogen atmosphere may also lead to the growth of SiO_2 but the reduction of the Si^0 concentration at the surface layer. The thermal decomposition and the oxidation explain the increase of the Si^{4+} concentration with annealing. However, although the thermal decomposition increases the Si^0 concentration, the thermal oxidation reduces the concentration.

Fig.5.24 shows the Si 2p peaks taken at the surface and at the depth of 5 nm of the Si-implanted SiO_2 film after the annealing. As can be seen in this figure, the shape of the peak for the surface is very different from that for the depth of 5 nm corresponding to the maximum concentration of implanted Si ions. The difference is due to both the depth distribution of the excess Si concentration and the depth variations of the relative concentrations of the five Si oxidation states Si^{n+} ($n=0, 1, 2, 3$, and 4), and the details will be discussed later. On the other hand, the Si depth distribution can be determined from the depth variation of the areas of the Si 2p and O 1s XPS peaks. After the correction with the appropriate atomic sensitivity factors,

the Si concentration is obtained from the calculation of the ratio of $\frac{I_{Si}}{I_{Si} + I_O}$ where

I_{Si} is the peak area of the Si 2p peak and I_O is the peak area of the O 1s peak. The sensitivity factor is checked by measuring the ratio of I_{Si}/I_O for pure SiO₂, which is 1:2.1 being close to 1:2 for the atomic ratio of silicon dioxide. The estimated accuracy of excess Si atomic percentage obtained from this approach is $\pm 5\%$. The depth distribution of Si concentration obtained from the above XPS calculation is shown in Fig.5.25. As can be seen in this figure, the depth distribution obtained from the XPS calculation is consistent with the SIMS result, indicating that the depth profiling with the XPS analysis is reliable. In addition, Fig.5.25 shows that the excess Si distributes from the surface to a depth of about 15 nm with a maximum Si concentration at a depth of about 5 nm.

As pointed out above, the depth variations of the relative concentrations of the five Si oxidation states Siⁿ⁺ (n=0, 1, 2, 3, and 4) contribute to the changes in the shape of the Si 2p peaks at different depths. In fact, the Si 2p peaks can be decomposed into five Gaussian-shaped peaks of the Si oxidation states Siⁿ⁺ (n =0, 1, 2, 3, and 4) corresponding to the five chemical structures of Si (Si nanocrystals or nanoclusters), Si₂O, SiO, Si₂O₃ and SiO₂, respectively. With the possible existence of the five oxidation states in mind, the peak of each oxidation state is yielded from the deconvolution of the Si 2p peaks by using a computer peak fitting program as described above, as shown in Fig.5.24. As can be seen in this figure, the relative peak areas of the all Si oxidation state at the surface are different from that at the depth of 5 nm. This indicates that the relative concentrations of the Si oxidation states vary with the depth.

Fig.5.24. Decomposition of the Si 2p peaks taken at the surface (a) and (b) at the depth of 5 nm of the Si-implanted SiO_2 film after the annealing.

Fig.5.25. Comparison of the Si depth distribution between the XPS analysis and the SIMS measurement.

The relative concentration of each oxidation state can be obtained from the calculation of the ratio of $\frac{I_{Si^{n+}}}{I_{total}}$ ($n=0,1,2,3$, and 4) where $I_{Si^{n+}}$ is the peak area of the oxidation state Si^{n+} and I_{total} is the total area ($= \sum_{i=0}^4 I_{Si^{n+}}$) of the Si 2p peaks.

Consequently, we obtain the depth profiles of the relative concentrations of all the five oxidation states for the annealed sample, as shown in Fig.5.26. It can be concluded from Fig.5.26 that the depth distributions of both Si^0 (which corresponds to Si nanocrystals as the x-ray diffraction measurement shows the formation of nanocrystals after the annealing) and the suboxides corresponding to Si^{n+} ($n=1, 2$, and 3) are basically the same as the distribution of the implanted Si^+ ions. Actually, Si^0

(corresponding to Si atoms or nanoclusters) and all the suboxides are also observed in the as-implanted sample. This indicates that both the Si^0 and the suboxides are formed during the ion implantation. Another important observation is that there is still the existence of the suboxides with significantly high concentrations. The suboxides may exist at the interfaces of SiO_2/Si nanocrystals, just like at the conventional SiO_2/Si interface [143,174].

Fig.5.26. Depth distributions of the relative concentrations of the five oxidation states Si^{n+} ($n = 0, 1, 2, 3$, and 4) for the annealed sample.

The annealing effect on the Si oxidation states and their depth distributions can be revealed through the comparison of the relative concentrations of the oxidation states between the as-implanted and annealed samples. Fig.5.27 shows the comparison at the surface, at the depth of ~ 5 nm corresponding to the peak implanted-Si

concentration and the depth of 15 nm where the implanted-Si concentration is very low. As shown in Fig.5.27 (a), the annealing has an obvious effect at the surface. The relative concentrations of the oxidation states including Si^0 , Si^{1+} , Si^{2+} and Si^{3+} are reduced significantly while the relative concentration of Si^{4+} increases dramatically. This situation could be attributed to the thermal reactions of oxygen with both silicon (Si^0) and the suboxides (Si^{1+} , Si^{2+} and Si^{3+}) or to the thermal decomposition of the suboxides during the annealing. Although the annealing was carried out in nitrogen gas (the purity of N_2 used in annealing is higher than 99.99%), it is still possible that some oxygen presented in the furnace during the annealing. Actually, the SIMS measurement shows the existence of some excess oxygen in the surface region of the annealed sample. The thermal reactions convert the silicon and the suboxides into the stoichiometric SiO_2 , and thus the relative concentrations of Si^0 , Si^{1+} , Si^{2+} and Si^{3+} decrease but the relative concentration of Si^{4+} increases. At a depth of ~ 5 nm illustrated in Fig. 5.27 (b), where there is no residual oxygen, the thermal decomposition (or phase separation) of the Si suboxides Si_2O , SiO and Si_2O_3 corresponding to the oxidation states Si^{1+} , Si^{2+} and Si^{3+} , respectively, occurs during annealing to form more stable stoichiometric SiO_2 and Si nanocrystals via Eq. (5.4), while the thermal oxidation does not happen. Hence, we can find the increase of concentrations of nc-Si and SiO_2 as well as the decrease of concentrations of the Si suboxides Si_2O , SiO and Si_2O_3 . However, as shown in Fig.5.27(c), the changes in the relative concentrations of the five oxidation states at the depths of 15 nm are not large (actually they are close to the measurement errors of the relative concentrations). This indicates that beyond the implantation region (i.e. the depth larger than ~ 15 nm) such thermal reactions are insignificant and the thermal annealing doesn't change the five oxidation states significantly.

Fig.5.27. Comparison of the relative concentrations of the five oxidation states between the as-implanted and annealed samples at the surface, at the depth of ~ 5 nm corresponding to the peak implanted-Si concentration and the depth of ~ 15 nm where the implanted-Si concentration is very low.

5.5.4 Conclusion

In this section, the XPS analysis shows that except the Si nanocrystals (the corresponding Si oxidation state is Si^0) and the stoichiometric SiO_2 (the corresponding Si oxidation state is Si^{4+}) there are still other suboxides corresponding to the three Si oxidation states Si^{n+} ($n = 1, 2$ and 3) in the Si-implanted SiO_2 films after high temperature annealing. This means that not all the implanted Si ions are converted to Si nanocrystals even after a thermal annealing at a high temperature. The analysis of the XPS Si 2p peaks is carried out to determine the concentrations of the five Si oxidation states Si^{n+} ($n = 0, 1, 2, 3$, and 4) in the SiO_x films. The XPS results clearly show the evolution of the chemical structures corresponding to the oxidation states as functions of annealing temperature and annealing time. The relative concentrations of the five oxidation states at various depths are also determined quantitatively from the XPS analysis. In addition, annealing effects on both the oxidation states and their depth distributions are also studied. It is shown that the thermal annealing can cause significant changes in the relative concentrations of the five oxidation states in the implantation region but such changes are insignificant beyond the implantation region. The annealing effect in the implantation region is explained in terms of the thermal reactions of the excess oxygen with both Si and the suboxides and the thermal decomposition of the suboxides.

5.6 Summary for This Chapter

In this chapter, the fundamentals and measurement capability of XPS have been firstly described as well as the method of spectrum analysis. Si 2p, O 1s and C 1s core levels have been recorded to study the charging effect in nc-Si/SiO₂ nanostructured films, showing that the charging effect in the nc-Si/SiO₂ nanostructured thin film due to photoemission is found to be much significant than that in the pure SiO₂ film, indicating that the charging effect from the SiO₂ thin film is much less significant than that from the SiO₂/nc-Si interfaces and nc-Si. The charging ability for the surface layer of the film is reduced by annealing, which is interpreted in terms of the thermal oxidation of nc-Si and the decomposition of interface states in annealing processes. The true core levels can only be obtained after the correction of charging effects.

Si 2p spectra are decomposed to study the core level shift. The core level shift of the nc-Si relative to the bulk Si 2p core level is found to be the same as the shift of the oxidation state Si⁴⁺ relative to the Si 2p core level in pure SiO₂. It is demonstrated that the shifts are due to the charging in the material system. After the correction for the charging effect the core level of the isolated nc-Si is found to be the same as that of bulk silicon, and no quantum size effect and no dependence on the nanocrystal formation are observed.

The analysis of the XPS Si 2p peaks shows the existence of the five chemical structures corresponding to the Si oxidation states Siⁿ⁺ (n = 0, 1, 2, 3, and 4) in the SiO₂ films, and the concentration of each oxidation states is determined quantitatively. The existence of suboxides indicates that not all the implanted Si ions are converted to

Si nanocrystals even after high temperature annealing. The XPS results show the evolution of the five Si oxidation states and the formation of Si nanocrystals as functions of annealing temperature and annealing time. The evolution of the concentrations of the five oxidation states at the surface layer with annealing is explained in terms of the thermal decompositions of the suboxides corresponding to the three oxidation states Si^{n+} ($n = 1, 2, \text{ and } 3$) and the thermal oxidation of the implanted Si. The relative concentrations of the five oxidation states at various depths are also determined quantitatively from the XPS analysis with sputtering. Annealing effects on the depth distributions of the oxidation states are also studied. It is shown that the thermal annealing can cause significant changes in the relative concentrations of the five oxidation states in the implantation region but such changes are insignificant beyond the implantation region. The annealing effect in the implantation region is explained in terms of the thermal reactions of the excess oxygen with both nc-Si and the suboxides and the thermal decomposition of the suboxides.

Chapter 6: Electrical Studies of Si Nanocrystal Embedded in SiO₂ Films

6.1 Introduction

While the investigation of optical and structural properties of SiO₂ films containing Si nanocrystals with various techniques, the electrical properties of such structures are of increasing interest with the application of nano-memory devices and single electron devices utilizing nanocrystals as charge storage elements [53, 61, 88, 94, 98, 175, 176, 181, 183, 236]. In such devices, a better understanding of charge trapping and carrier transport in SiO₂ matrix consisting of Si nanocrystals is thus very necessary.

In **Section 6.2**, C-V and I-V measurements are used to characterize the charge storage and charge transport properties in MOS structures with Si nanocrystals embedded in the gate oxide. Flat-band voltage shifts are found in MOS structures with nc-Si confined in a narrow region in the gate oxide due to the charge trapping in nanocrystals, allowing the application of nano-memory devices and single electron devices. Single electron tunneling is characterized by I-V measurements. The influence of nc-Si distribution on charge trapping and charge transport is also studied. For a MOS structure with nanocrystals embedded at oxide surface close to the metal gate, the influence of charge trapping in the nanocrystals on C-V characteristics for the nc-Si distribution of this study is very different from the situation for nanocrystals being confined in a narrow layer in the gate oxide. The charge trapping leads to a dramatic reduction in the capacitance magnitude, but no flat-band voltage shift can be

seen. Besides, very large tunneling current is observed in the MOS structures with nanocrystals distributing throughout the gate oxide, also showing different with I-V characteristics of capacitors with nanocrystals confined in the oxide. The differences in both charge storage and charge transport properties highlight the importance of the nc-Si distribution.

In **Section 6.3**, we report a study of the influence of charging and discharging in Si nanocrystals (nc-Si), which are embedded throughout the gate oxide in MOS structures, on the carrier transport of the MOS structures. Very large current are observed for the as-fabricated structures. However, charge trapping in the nanocrystals can reduce the tunneling current dramatically. The current reduction is attributed to the breaking of the nc-Si tunneling paths due to the charge trapping in the nc-Si. On the other hand, the trapped charges can also tunnel out from the nc-Si, leading to the recovery of the current.

In **Section 6.4**, we present that in contrast to the conventional situation in which charge trapping in silicon nanocrystals (nc-Si) confined in a narrow layer in the gate oxide of a metal-oxide-semiconductor (MOS) structure leads to a shift in capacitance-voltage (C-V) characteristic (i.e., a change in the flat-band voltage), charge trapping in nc-Si distributing throughout the gate oxide with its peak concentration located close to the gate leads to a dramatic reduction in the MOS capacitance. The reduced capacitance could be recovered after the release of the trapped charges by a small bias, ultra-violet light illumination or low temperature thermal annealing. The modulation of the capacitance magnitude by charging/discharging in the nc-Si

provides the possibility of a new type of memory devices application. Finally, a summary on the achievements in this chapter will be given out in **Section 6.5**.

6.2 C-V and I-V Characterization

6.2.1 Background and Motivation

Devices with nanocrystals confined in the gate oxide are possible candidates for nano-memory devices and single electron devices [44-48, 50, 66, 96]. In this work, we have characterized the electronic properties of MOS structures with nc-Si embedded in the SiO₂ films. C-V characteristics show that SiO₂ films with nc-Si confined in a narrow layer are able to store charges and thus are good candidates for non-volatile memory applications. Single electron tunneling can be observed by current-voltage (I-V) characteristics at room temperature.

On the other hand, we report a study of the influence of nc-Si distribution on the I-V and C-V characteristics of the MOS structures. It is found nc-Si distribution play a critical role in charge transport and charge storage properties by I-V and C-V characterization, respectively. Very large current and capacitance are observed for the MOS structures with nc-Si embedded throughout the gate oxide, showing substantial differences with the situation of devices with nc-Si confined in a narrow region in the gate oxide. The large tunneling current is attributed to tunneling path formed by nc-Si connecting metal gate to the substrate, while the change of MOS capacitance is explained in terms of the capacitance contribution from the nc-Si.

6.2.2 Experimental

Sample fabrication processes:

Process 1. Si ions were implanted at 1 keV with the dose of $8 \times 10^{16} \text{ cm}^{-2}$ into 30 nm SiO_2 films, which were grown on p-type substrate. Secondary Ion Mass Spectroscopy (SIMS) result shows Si ions distribute from the surface to the depth of 15 nm with the peak concentration at the depth of about 5 nm below the SiO_2 surface. Thermal annealing was carried out at 1000°C in N_2 ambient for 1 hour to induce the nc-Si formation. X-ray diffraction (XRD) measurement clearly shows the existence of nc-Si in the SiO_2 film. The broaden Bragg peaks clearly show nc-Si with a mean size of ~ 3 nm. Finally a 20 nm layer of aluminum was deposited on the oxide to form a gate electrode. Ohmic contact on the backside of the wafer was formed by a standard aluminum alloy process. The schematic illustration of the final structure is shown in Fig.6.1.

Fig.6.1. Schematic illustration of the MOS structure with nc-Si confined in a narrow layer in oxide synthesized with process 1.

Process 2. Si^+ ions were implanted at 10 keV with the dose of $8 \times 10^{16} \text{ cm}^{-2}$ into 30 nm SiO_2 films, which were grown on n-type substrate. Secondary Ion Mass

Spectroscopy (SIMS) result shows Si ions distribute from the surface to the depth of 25nm with the peak concentration at the depth of about 15 nm below the SiO₂ surface. Thermal annealing was carried out at 1000°C in N₂ ambient for 1 hour to induce the nc-Si formation. Finally a 20 nm layer of aluminum was deposited on the oxide to form a gate electrode. Ohmic contact on the backside of the wafer was formed by a standard aluminum alloy process. The schematic illustration of the final MOS structure is shown in Fig.6.2.

Fig.6.2. Schematic illustration of the MOS structure with nc-Si confined in a narrow layer in oxide synthesized with process 2.

Fig.6.3. Schematic illustration of the MOS structure with nc-Si distributing throughout the oxide synthesized with process 3.

Process 3. A 30 nm SiO₂ film was thermally grown on P-type (100) Si wafers in dry oxygen at 950 °C. Then Si⁺ ions with the dose of $3 \times 10^{16} \text{ cm}^{-2}$ were implanted into the SiO₂ at 14keV. From the transport and range of ions in matter (TRIM) simulations, the peak concentration was estimated to be at the depth of about 20 nm. Thermal annealing was carried out at 1000°C in N₂ ambient for 1 hour to induce nc-Si formation. The oxide layer was thinned in a HF solution of concentration of 50:1 with an etching rate of 10 nm/minute. 15 nm SiO₂ layer was removed such that the peak concentration of nc-Si is located close to the oxide surface. A 20 nm aluminum layer was then deposited to form the gate electrode. The wafer backside was coated with a layer of aluminum with the thickness of about 1 μm after removing the backside oxide. Finally, metal alloy process was conducted at 425 °C in N₂ ambient to form ohmic contacts. The nc-Si were found distributing throughout the gate oxide with peak concentration located near the gate. The schematic illustration of the MOS structure is shown in Fig.6.3.

All MOS structures synthesized by process 1, 2 and 3 were characterized by current-voltage (I-V) and capacitance-voltage (C-V) measurements using the Keithley 4200 semiconductor characterization system and the HP4284A LCR meter at the frequency of 1MHz, respectively.

6.2.3 Result and Discussion

Fig.6.4 and 6.5 show C-V curves of MOS structures synthesized with process1 and 2, respectively. Obvious flat-band voltage shifts can be observed after a negative voltage applied to the gate, while pure SiO₂ samples (i.e. without nanocrystals) show

no flat-band voltage shift (can be found in **Chapter 3**). These results demonstrate that charge trapping in the nanocrystals confined in a narrow layer in the gate oxide will lead to flat-band voltage shifts.

Fig. 6.4. C-V characteristics of the MOS structure containing nanocrystals confined a narrow region in the gate oxide synthesized with process 1.

Fig. 6.5. C-V characteristics of the MOS structure containing nanocrystals confined a narrow region in the gate oxide synthesized with process 2.

For a MOS capacitor with a gate oxide thickness of 15 nm and a gate area of $100 \times 100 \text{ } \mu\text{m}^2$, it has a capacitance of $\sim 23 \text{ pF}$ under strong accumulation if there is no nanocrystals embedded in the gate oxide. However, for the MOS capacitors synthesized with process 3, as can be seen in Fig.6.6, the capacitance is much larger than this value. Similar situation is observed under inversion. This indicates that the nanocrystals have a major contribution to the capacitance, if they are embedded at the oxide surface close to the metal gate. The situation is substantially different from the case that nc-Si are confined in a narrow layer in the oxide. The importance of nc-Si distribution should be noted.

Fig.6.6. C-V characteristics of the MOS structures before (i.e. the virgin case) and after applying +8V to the MOS structure for 10s.

The application of voltage can increase the capacitance of the MOS structure significantly, as shown in Fig. 6.6. The capacitance of the MOS structures was measured from depletion to inversion. The increases in the capacitance are due to the discharge of the previously trapped charges in the nc-Si, which were trapped during

the first C-V measurement, as a result of the application of the voltage. As shown in [193], the capacitance increases with the number of uncharged nanocrystals. Thus the discharge leads to a larger capacitance.

Fig.6.7. (a) Decrease and increase in the capacitance after two times of application of +8V for different durations; and (b) comparison of MOS capacitance between pure SiO₂ and SiO₂ containing nc-Si after the application of +8V for 120 s.

The charging and discharging in nc-Si, which are responsible for the scenario shown in Fig.6.7 (a), have serious impact on the C-V characteristics. In this figure, the application of +8V for 120s leads to the charge up of most of the nc-Si. As the number of uncharged nc-Si has decreased dramatically, the capacitance drops to a very low level ($\sim 600\text{fF}$), which is even smaller than the capacitance for pure SiO_2 MOS structure as shown in Fig. 6.7(b). After the second application of +8V for 40s, the current shows a recovery as shown in Fig. 6.7(a), indicating a large increase of the number of uncharged nc-Si. Due to the increase of the number of uncharged nc-Si, the capacitance increases accordingly, as shown in Fig.6.7 (a). It is clear from the above discussions that the changes in the capacitance are due to the discharging or charging of the nc-Si. More explanations are given below.

To explain the changes in the capacitance shown in Fig.6.6 and Fig.6.7, an equivalent capacitance model is proposed here. Charge could be stored in the three elements, i.e., the nanocrystals, the remaining gate oxide capacitor and the Si depletion layer as shown in Fig. 6. The corresponding capacitances of the elements are denoted by C_{nc} , C'_{ox} and C_D , respectively. The total capacitance C of the MOS structure is

$$C = \frac{(C_{nc} + C'_{ox})C_D}{(C_{nc} + C'_{ox}) + C_D} \quad (6.1)$$

As C_D is very large, the total capacitance is approximately equal to $(C_{nc} + C'_{ox})$. With charge trapping in the nanocrystals, the nanocrystal capacitance C_{nc} should decrease as the numbers of uncharged nanocrystals or available electronic states responding to the small AC signal in the C-V measurement are reduced. With a high concentration of Si nanocrystals in the gate oxide locating close to the gate, many SiO_2 structures close to the gate are replaced by the nc-Si, and the MOS capacitor

behavior is screened by the nc-Si. Thus, the remaining gate oxide capacitance C'_{ox} (i.e., the capacitance from SiO_2 excluding the capacitance from nc-Si) should be much smaller than the conventional gate oxide capacitance (C_{ox}) without nanocrystals. As C'_{ox} is very small but the virgin C under accumulation is much larger than the C_{ox} of a conventional MOS capacitor ($C_{ox} = \sim 23$ pF), the C_{nc} before charge trapping in the nanocrystals should be much larger than the C_{ox} . However, as the nanocrystals are charged up, the C_{nc} is reduced, and thus the total capacitance C is reduced. If almost all nanocrystals are charged up, then the C_{nc} will be very small, and thus the total capacitance C will be very small as the C'_{ox} is also very small. This explains the reduction of the capacitance to a very low level after the first application of +8V for 120s as shown in Fig.6.7 (a). On the other hand, the discharge of some charged nc-Si leads to the increase in the C_{nc} and thus gives rise to the total capacitance as shown in Fig.6.6. Further discussions on the charging/ discharging in nc-Si will be given out in **Section 6.4**.

Fig.6.8 shows I-V characteristics of the MOS structures with nanocrystals confined in a narrow layer in gate oxide. The devices are fabricated with process 1 and 2 corresponding to Fig.6.8 (a) and Fig.6.8 (b), respectively. Coulomb staircases of single electron tunneling are clearly seen in both figures. The electron transport is thus considered to occur via nanocrystals when gate voltage was swept from 0-4V. In Fig.6.8 (a), two steps in the I-V curves could be observed and each step corresponds to one electron charging state.

Fig.6.8. I-V characteristics of the MOS structures fabricated with process 1(a) and 2 (b). The nc-Si were confined in a narrow layer in the oxide.

Fig.6.9. I-V characteristics of the MOS structures fabricated with process 3 for (a) positive I-V scan and (b) negative I-V scan. The nc-Si were embedded throughout the gate oxide.

While for the capacitors with nanocrystals embedded throughout the gate oxide synthesized with process 3, the charge transport is substantially different with the situation of the capacitors synthesized with process 1 and 2. As can be seen in Fig.6.9 (a) and (b), very large current are observed in both positive and negative I-V characteristics for the as-fabricated structures. The current is over 7 orders higher than that for the pure SiO₂ film (i.e. without nc-Si) with identical oxide thickness, which has been shown in **Chapter 3**. This indicates that the nc-Si plays a key role in the current transport. Such high tunneling current can be attributed to the tunneling paths formed by the neutral (or uncharged) nc-Si connecting the Si substrate to the metal gate. The curves are found to follow a power law, which is similar to a typical post-breakdown I-V characteristic [99-103] of pure SiO₂ thin films. Detailed discussions on charge transport and modeling will be carried out in the **Section 6.3**.

6.2.4 Conclusion

MOS structures with nc-Si confined in a narrow layer in the oxide exhibit clear flat-band voltage shift due to charging trapping. Coulomb staircases due to single electron tunneling are obvious in I-V characteristics. These results demonstrate that non-volatile memory devices can be produced based on MOS structures with nc-Si confined in a narrow layer in the oxide. On the other hand, distribution of nc-Si plays a key role in both charge storage and charge transport properties. It is found that incorporation of Si nanocrystals at the gate oxide surface close to the metal gate increases the MOS capacitance greatly. However, the charge trapping in the nanocrystals reduces the capacitance dramatically, and after most of the nanocrystals are charged up the capacitance is even much smaller than that of a similar MOS

structure without nanocrystals. In I-V characteristics, the MOS structures with nc-Si embedded throughout the gate oxide show a very large tunneling current similar to a post-breakdown curve for pure SiO₂. Such a high current can be interpreted in terms of formation of tunneling paths by nc-Si connecting the metal gate to the substrate.

6.3 Carrier Transport via Nanocrystals

6.3.1 Background and Motivation

For the application of single electron devices, it is essential to have detailed information about the charge storage and carrier transport of the nc-Si in MOS structures. Some relevant research on this issue has been reported [89, 183, 200], but usually the studies were carried out with memory-cell structures with the nanocrystals confined in a narrow layer embedded in the gate dielectrics. However, it would be interesting to examine the effects of charge storage and charge transport when the nc-Si distributes throughout the whole gate dielectric. In this part, we report a study of the influence of charging and discharging in Si nanocrystals (nc-Si), which are embedded throughout the gate oxide in MOS structures, on the I-V characteristics of the MOS structures. Very large tunneling current has been observed for the as-fabricated structures, because carriers can transport via the tunneling path formed by nc-Si. However, 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 due to the charge trapping in the nc-Si. On the other hand, the trapped charges can also tunnel out from the nc-Si, leading to the recovery of the current.

6.3.2 Experimental

Sample preparation

Silicon wafers were (100) oriented, boron-doped with the concentration of $2 \times 10^{15} \text{cm}^{-3}$. Si^+ ions were implanted at 14keV with the dose of $3 \times 10^{16} \text{cm}^{-2}$ into 30 nm SiO_2 films, which were thermally grown on Si wafers in dry oxygen at 950 °C. The TRIM simulation shows that the Si ions distribute throughout the gate oxide with the peak concentration at the depth of about 20 nm below the SiO_2 surface, which is consistent with the Secondary Ion Mass Spectroscopy (SIMS) result (see Fig.6.10). Thermal annealing was carried out at 1000°C in N_2 ambient for 1 hour to induce the nc-Si formation. Then the oxide layer was thinned in a diluted HF solution, and a 15 nm oxide was etched off so that the nc-Si concentration peak is located close to the surface. Fig. 6.11 (a) and (b) show the Bragg peaks due to the nc-Si before and after the etching off 15nm oxide, respectively. For the both cases, the broaden Bragg peaks clearly show the existence of nc-Si (with a mean size of ~ 4 nm as determined from the Pseudo-Voigt fit). Finally a 20 nm layer of aluminum was deposited on the oxide to form a $100 \times 100 \mu\text{m}^2$ gate electrode. Ohmic contact on the backside of the wafer was formed by a standard aluminum alloy process.

Characterization

Current-voltage (I-V) and capacitance-voltage (C-V) measurements were performed with the Keithley 4200 semiconductor characterization system and the HP4284A LCR meter at the frequency of 1MHz, respectively. In discharging experiments, MOS structures were exposed to UV light at the wavelength of 365nm, or were annealed at a low temperature of 100 °C.

Fig.6.10. Depth profile for Si in the MOS structures in this work obtained by SIMS measurement.

Fig.6.11. XRD measurements for nc-Si embedded in SiO₂ thin films: (a) before etching off 15 nm oxide; and (b) after etching off 15 nm oxide (see the text).

6.3.3 Result and Discussion

The I-V characteristics shown in Fig. 6.12 were obtained by sweeping the voltage from 0 to +5V before and after applying +8V to the MOS structure for 10s. The curve for the virgin case (i.e., before the application of +8V) has been found to follow a power law, which is similar to a typical post-breakdown I-V characteristic of pure SiO₂ thin films. The current is over 7 orders higher than that for pure SiO₂ film with identical oxide thickness as shown in Fig. 6.13(b). This indicates that the nc-Si plays a key role in the current transport. As discussed below, the neutral (or uncharged) nc-Si can form tunneling paths connecting the Si substrate to the metal gate, and thus a large current can be expected. As shown in Fig. 6.12, the application of +8V for 10s leads to a significant increase in the current. The increases in the tunneling current are due to the discharge of the previously trapped charges in the nc-Si, which were trapped during the first I-V measurement, as a result of the application of the voltage. At the same time, as more uncharged nanocrystals are available due to the discharge, more tunneling paths are formed giving rise to an increase in the current.

Fig.6.12. I-V characteristics of the MOS structure before (i.e. the virgin case) and after applying +8V to the MOS structure for 10s.

On the other hand, the application of a voltage can also charge up the nc-Si, leading to a decrease in the current. It is shown in Fig. 6.13(a) the I-V characteristics for the following situations: 1) virgin; 2) after the first application of +8V for 120 s; and 3) the second application of +8V for 40 s. The application of +8V for 120 s leads to a dramatic current drop to a lower level (about 4 orders lower) in the voltage range of 0 to ~ 3 V in the I-V measurement. Such a current reduction can be explained in terms of the breaking of some tunneling paths due to the charge up in certain nanocrystals as a result of the application of the voltage. However, as can be seen in Fig.6.13 (a), the current jumps to a higher level when the measurement voltage is larger than ~ 3 V, indicating that the I-V measurement itself can also lead to the discharge of some charged nanocrystals modifying the current conduction. The second application of +8V for 40s leads to the recovery of the current almost to its value of the virgin situation in the measurement voltage range of 0 to ~ 1 V, but the current drops a little bit to the values of the first application of +8V for 120s in the measurement voltages larger than ~ 3 V. Similar situation can also be found in negative I-V characteristics shown in Fig. 6.14. It should be pointed out that the current unit in this graph is “-A”. Again these changes in the current are due to the changes in the tunneling paths as a result of charging and discharging in the nc-Si. The first application of +8V for 100s charges up of the nanocrystals, and thus the tunneling paths are blocked. The gate current is reduced to the level of -10^{-12} A. The second application of +8V discharges the nanocrystals. The tunneling paths were reformed. Thus a recovered current can be observed.

The effect of charging/discharging of nc-Si on the current conduction can be clearly illustrated with Fig.6.15. Electron tunneling can take place between adjacent

uncharged nanocrystals, and many such nanocrystals form tunneling paths connecting the Si substrate to the metal gate as shown in Fig. 6.15(a). The nc-Si can be charged or discharged under the influence of a voltage. If some of the nanocrystals in a tunneling path are charged up, then the tunneling path is blocked by the charged nanocrystals and thus the current path disappears, as shown in Fig. 6.15(b). Obviously, the current conduction of the MOS structure is determined by the tunneling paths, and thus the change of the current conduction is only the reflection of the disappearing/appearing of the tunneling paths due to the charging/discharging in the nc-Si.

Fig.6.13. (a) Demonstration of the decrease and increase in the tunneling current after two times of application of +8V for different durations; and (b) comparison of I-V characteristics between pure SiO₂ and SiO₂ containing nc-Si after the application of +8V for 120 s.

Fig.6.14. Negative I-V characteristics showing the decrease and increase in the tunneling current after two times of application of +8V for different durations.

The charges trapped in the nc-Si can be also released by UV illumination or low temperature annealing. As shown in Fig.6.16, the application of + 4V for 320s reduces the tunneling current to an extremely low value ($< 10^{-11}$ A); however, after 5 minutes of exposure to the UV light at the wavelength of 365 nm, the tunneling current increases remarkably to a high level even larger than the virgin case. This indicates that the UV illumination can release not only the charges that are trapped in the nc-Si during the application of the charging voltage but also the initial charges that are trapped in the nc-Si prior to the application of the voltage, thus forming more tunneling paths. Besides, similarly to the UV illumination, a low temperature annealing can also lead to the release of the trapped charges and thus a recovery of the tunneling current. Fig.6.17 shows the recovery of the tunneling current after the annealing at 100 °C for 10 minutes.

Fig.6.15.(a) Schematic illustration of the formation of tunneling paths between adjacent uncharged nanocrystals in the oxide; and (b) illustration of the blocked tunneling paths resulting from the charge trapping in some nanocrystals of the tunneling paths.

Fig.6.16. Changes in I-V characteristics due to the charging at +4V for 320s and the discharging under UV illumination for 5 minutes at the wavelength of 365nm.

Fig.6.17. Changes in tunneling current due to the charging at +4V for 320s and the discharging under low temperature annealing at 100°C for 10 minutes.

6.3.4 Conclusion

In this section, MOS structures containing nc-Si embedded throughout the gate oxide were fabricated by thinning the Si^+ implanted SiO_2 layer thermally grown on Si substrate. Very large current has been observed for the as-fabricated structures. It is observed that charge transport via the nc-Si can strongly modify the current conduction of the MOS structures. The charge trapping in the nanocrystals can reduce the current dramatically. The current reduction is attributed to the breaking of the nc-Si tunneling paths due to the charge trapping in the nc-Si. On the other hand, the trapped charges can also tunnel out from the nc-Si under a bias, UV illumination or low temperature annealing, leading to the recovery of the current.

6.4 Capacitance Modulation by Charging /Discharging in nc-Si

6.4.1 Background and Motivation

Nanocrystals (nc-Si) embedded in gate oxide of metal-oxide-semiconductor structures is expected to play an important role in memory devices due to the nanocrystals unique charging and discharging effect [59, 202-208]. Charging and discharging in nc-Si are indeed very important as they are directly related to data storage/retention in the memory cells. For memory applications, the nanocrystals are normally confined in a narrow layer embedded in the gate dielectrics near the Si substrate [46,207, 208]. However, it would be interesting to examine the charging and discharging in the nc-Si that distributes throughout the gate dielectric specially with the nc-Si peak concentration located near the gate. For the MOS structures with

such an nc-Si distribution, charging and discharging of the nc-Si are expected to be very easy to occur and thus they will have a significant impact on the electrical characteristics of the MOS structures. Indeed, for such MOS structures, an interesting phenomenon of capacitance modulation, namely, the dramatic reduction/recovery in the magnitude of the MOS capacitance by charging/discharging the nc-Si has been observed in this work. The charging can be performed by applying a voltage to the MOS structure, while the discharging can be done by applying a small bias with its polarity opposite to that of the charging voltage, ultra-violet (UV) light exposure or low temperature annealing. The modulation of the capacitance magnitude by charging/discharging in the nc-Si provides the possibility of a new type of memory device application.

6.4.2 Experimental

Sample preparation

To fabricate the MOS structures with nc-Si distributing throughout the gate oxide with its peak concentration located near the gate, a 30 nm SiO₂ film was thermally grown on P-type (100) Si wafers in dry oxygen at 950 °C. Then Si⁺ ions with the dose of $3 \times 10^{16} \text{ cm}^{-2}$ were implanted to the SiO₂ at 14keV. From the transport and range of ions in matter (TRIM) simulations, the peak concentration was estimated to be at the depth of about 20 nm. Thermal annealing was carried out at 1000 °C in N₂ ambient for 1 hour to induce nc-Si formation. The oxide layer was thinned in a HF solution of concentration of 50:1 with an etching rate of 10 nm/minute. 15 nm SiO₂ layer was removed such that the peak concentration of nc-Si is located close to the oxide surface. A 20 nm aluminum layer was then deposited to form the gate electrode. The

wafer backside was coated with a layer of aluminum with the thickness of about 1 μm after removing the backside oxide. Finally, metal alloy process was conducted at 425 $^{\circ}\text{C}$ in N_2 ambient to form ohmic contacts.

Characterization

The experiment of charging/discharging the nc-Si by applying a constant voltage to the MOS structures was performed with a Keithley 4200 semiconductor characterization system, and capacitance–voltage (C-V) measurement was carried out with a HP4284A LCR meter at the frequency of 1MHz. All the experiments were carried out at room temperature. In the discharging experiment, the MOS structures were biased at a low voltage with polarity opposite to that of the charging voltage, or were exposed to UV light at the wavelength of 365nm, or were annealed at a low temperature of 100 $^{\circ}\text{C}$.

6.4.3 Result and Discussion

For a MOS capacitor with a gate oxide thickness of 15 nm and a gate area of $100 \times 100 \mu\text{m}^2$, it has a capacitance of $\sim 23 \text{ pF}$ under strong accumulation at - 3V if there is no nanocrystals embedded in the gate oxide. However, as can be seen in Fig.6.19 (a) or Fig.6.19 (b), with the nc-Si distributing throughout the gate oxide the virgin capacitance (i.e., the capacitance before charge trapping in the nc-Si) is much larger than this value (~ 45 times larger). This can be explained with the equivalent capacitance circuit shown in Fig.6.18. Charge could be stored in the three elements of the MOS structures, i.e., the nanocrystals, the remaining gate oxide capacitor and the Si depletion layer. The corresponding capacitances of the elements are denoted by

C_{nc} , C'_{ox} and C_D , respectively. The total capacitance C of the MOS structure can be written as Eq.6.1.

$$C = \frac{(C_{nc} + C'_{ox})C_D}{(C_{nc} + C'_{ox}) + C_D}$$

As C_D is very large under accumulation at -3V, the total capacitance is approximately equal to $(C_{nc} + C'_{ox})$. Due to the existence of a high concentration of nc-Si in the gate oxide close to the gate, the remaining gate oxide capacitance C'_{ox} should be much smaller than the conventional gate oxide capacitance (C_{ox}) without the nc-Si (C'_{ox} is found to be less than ~ 700 fF). On the other hand, as the Si nanocrystals distribute throughout the gate oxide with their peak concentration located close to the gate, they easily respond to the small AC signal in the C-V measurement if they are uncharged or neutral (i.e., no charges trapped in them). The virgin C_{nc} (i.e., the nc-Si capacitance before charge trapping) should be very large due to the existence of a high concentration of nc-Si. Therefore, the MOS capacitance (C) is approximately equal to C_{nc} , and it will be very large when most of the nc-Si is uncharged.

Fig. 6.18. Equivalent capacitance circuit for the MOS structure with nc-Si embedded distributing in the gate oxide.

However, applying a constant voltage of + 4V or - 4V to the gate for 320 seconds reduces the MOS capacitance dramatically to a very low level (< 700 fF), as shown in Fig.6.19. The polarity of the gate voltage (either positive or negative) doesn't have a significant effect on the reduction of the capacitance. Obviously, the capacitance reduction can be explained in terms of the charge trapping in the nc-Si. With charge trapping in the nanocrystals, the nanocrystal capacitance C_{nc} should decrease as the numbers of uncharged nanocrystals or available electronic states responding to the small AC signal in the C-V measurement are reduced. If all the chargeable nanocrystals are charged up, then C_{nc} should approach zero. Thus the MOS capacitance is very small as it is now determined by the remaining gate oxide capacitance C'_{ox} (< 700 fF).

Note that the influence of charge trapping in the nanocrystals on C-V characteristics for the nc-Si distribution of this study is very different from the situation for nanocrystals being confined in a narrow layer in the gate oxide. In the latter case, the charge trapping in the nanocrystals leads to a shift of the C-V curve (i.e., a change in the flat-band voltage) [59, 207, 208] and as shown in Fig.6.4 and Fig. 6.5, but it doesn't change the capacitance magnitude under accumulation or inversion. In contrast, in the case of this study, the charge trapping leads to a dramatic reduction in the capacitance magnitude, but no flat-band voltage shift can be seen as the MOS capacitance is reduced to an extremely low level. Of course, as most of the nanocrystals are located near the gate, the charge trapping in the nanocrystals will not have a large contribution to the flat-band voltage. The difference between the two cases highlights the importance of the nc-Si distribution.

Fig.6.19. Changes in MOS capacitance due to charging/discharging in nc-Si. (a) charging at + 4V for 320s and discharging at - 2V for 160s; (b) charging at - 4V for 320s and discharging at + 2V for 160s.

On the other hand, if the charges trapped in the nc-Si are released, then C_{nc} should increase as the number of available electron states in the nc-Si that respond to the AC signal increases, and thus the MOS capacitance should increase. This has been confirmed in our experiment. As shown in Fig.6.19, applying a low voltage of 2V for 160s with the polarity (either positive or negative) opposite to that of the charging voltage leads to the recovery of the MOS capacitance, indicating that most of the charges trapped in the nc-Si have been released during the application of the voltage. If the discharging voltage is increased, the recovery time will be shorter. However, if the voltage is further increased to 4V or higher, the voltage may lead to discharging of nc-Si first but charging again later, corresponding to the first increase and then decrease in the MOS capacitance.

The charges trapped in the nc-Si can be also released by UV illumination or low temperature annealing. As shown in Fig.6.20, the application of + 4V for 320s reduces the MOS capacitance to an extremely low value (< 700 fF); however, after 5 minutes of exposure to the UV light at the wavelength of 365 nm, the capacitance increases dramatically to a high level even larger than the virgin capacitance. This indicates that the UV illumination can release not only the charges that are trapped in the nc-Si during the application of the charging voltage but also the initial charges that are trapped in the nc-Si prior to the application of the voltage (note that the C-V measurement at - 3V may have already caused some charge trapping in the nc-Si). On the other hand, similarly to the UV illumination, a low temperature annealing can also lead to the release of the trapped charges and thus a recovery of the MOS capacitance. Fig.6.21 shows the recovery of the MOS capacitance after the annealing at 100 °C for

10 minutes (a slight increase in the capacitance after the annealing indicates that some initial charges have been released also during the annealing).

Fig. 6.20. Changes in CV characteristics due to the charging at +4V for 320s and the discharging under UV illumination for 5 minutes at the wavelength of 365nm.

Fig.6.21. Changes in MOS capacitance due to the charging at +4V for 320s and the discharging under low temperature annealing at 100°C for 10 minutes.

It is found from the previous experiments that charging and discharging of the nc-Si could occur at the same voltage. This suggests that the capacitance modulation could be observed in time-domain capacitance measurement under a constant voltage. This is confirmed in our experiment. Fig. 6.22(a) shows the time-domain capacitance characteristic measured at -3 V. After about 250s, the MOS capacitance was reduced dramatically from the initial value of ~ 1.1 nF to a very low level (< 700 fF). In other words, the electrical state of the MOS device was switched from a high-capacitance state (State 1) to a low-capacitance state (State 2). As discussed early, the low capacitance corresponds to a charged state of the nc-Si, while the high capacitance corresponds to a discharged state of the nc-Si. Therefore, State 1 represents the discharged state and State 2 represents the charged state. State 2 can be maintained for ~ 120 s. Then the MOS device was switched to State 3 with a capacitance of ~ 0.4 nF, which is much larger than that of State 2 but lower than that of State 1. This indicates that not all the trapped charges associated with State 2 have been released and thus only a partial recovery of MOS capacitance can be achieved. If the time scale is extended, switching between different states, which is a random event, can be observed continuously. Similar capacitance modulation in the time-domain measurement can also be observed at positive gate voltage of +3V, as shown in Fig. 6.22 (b). In the case of Fig.6.22 (b), the capacitance of State 3 is ever larger than that of State 1. This indicates that not only the charges trapped in the nc-Si during the C-T measurement but also the initial charges trapped in the nc-Si prior to the C-T measurement are released.

Fig. 6.22. Capacitance modulations in C-T measurement at a constant voltage of -3 V (a) and +3 V (b).

As charging and discharging in the nc-Si depend on the applied voltage, the capacitance modulation should also depend on the voltage. This has been confirmed by our experiment, as shown in Fig. 6.23. The charging or discharging process is accelerated at a higher voltage, thus the capacitance modulation is easier to occur. This is evident from the comparison between the modulations at -3V (Fig. 6.22(a)) and at -6V (Fig. 6.22(a)). On the other hand, if the voltage is very low, the charging and discharging are not strong, and thus the modulation is not significant. Fig. 6.23 (b) shows such a case in which the capacitance modulation at -0.5V is insignificant.

The memory states can be changed by a charging or discharging operation at a relatively high voltage. The charging and discharging operation can be carried out with either positive or negative voltage. The charging or discharging time for a successful switching strongly depends on the magnitude of the voltage, and it is also affected by the memory structure. For the memory structure used in this study, the voltage should be larger than 2V; with the voltage of -6V, the charging time is ~40s, while the discharging time is ~30s, as shown in Fig.6.24. We believe the charging / discharging time can be dramatically reduced if the memory structure is optimized in terms of the device dimensions and the concentration and distribution of the nc-Si (note that the area of the current structure, which is $100 \times 100 \mu\text{m}^2$, is too large for a real memory device based on the effect reported here, but such a large area is necessary for our capacitance measurement).

Fig. 6.23. Capacitance modulations in C-T measurement at -6 V (a) and -0.5V (b).

6.4.4 Conclusion

In contrast to the conventional situation in which charge trapping in nc-Si confined in a narrow layer embedded in the gate oxide leads to a shift in C-V characteristic, charge trapping in nc-Si distributing throughout the gate oxide with its peak concentration located close to the gate leads to a dramatic reduction in the MOS capacitance. The reduced capacitance could be recovered after the release of the trapped charges by a small bias, UV light illumination or low temperature thermal annealing. The capacitance modulation by charging/discharging in the nc-Si provides the possibility of a new type of memory devices application.

6.5 Summary for This Chapter

In this chapter, we present a detailed study of the electronic properties of MOS structures with nc-Si embedded in the gate oxide using C-V and I-V measurements. For MOS capacitors with nc-Si confined in a narrow layer in the oxide, clear flat-band voltage shift due to charging trapping can be observed. Single electron tunneling in such a structure is characterized by I-V measurement. Results demonstrate that such structures are promising for memory device applications.

Carrier transport via nanocrystals is studied using MOS structures with nc-Si embedded throughout the gate oxide. Very large current has been observed for the as-fabricated structures, attributed to the tunneling paths formed by nanocrystals connecting gate to the substrate. The charge trapping in the nanocrystals can reduce the current dramatically. On the other hand, the trapped charges can also tunnel out from the nc-Si under a bias, UV illumination or low temperature annealing. Hence, the recovery of the current can be found. The current reduction is attributed to the breaking of the nc-Si tunneling paths due to the charge trapping in the nc-Si, while the recovery of the current can be interpreted in terms of the reformation of tunneling paths.

Incorporation of Si nanocrystals throughout the gate oxide with its peak concentration located close to the gate increases the MOS capacitance greatly. However, the charge trapping in the nanocrystals reduces the capacitance dramatically. The reduced capacitance could be recovered after the release of the trapped charges by a small bias, UV light illumination or low temperature thermal

annealing. An equivalent capacitance model is proposed to explain the phenomena observed. The capacitance modulation by charging/discharging in the nc-Si provides the possibility of a new type of memory device application.

Chapter 7: Conclusion and Recommendations

7.1 Conclusion

Aggressive down scaling of dimensions of the MOSFET perpetuated by the need for higher-integration and lower-power consumption ICs has compelled the realization of Si-based nano-memory devices and single electron devices. In addition, optical data transmission via Si-based optical ICs is the most promising way to overcome the bottleneck of interchip and intrachip communication. This study is concerned with the synthesis of thin SiO₂ films embedded with Si nanocrystals, which is fully compatible with modern CMOS technology. Such films are considered as candidates for Si-based light emitting devices and single electron devices. Further, we have explored the physical properties of these films, and the investigations enhance our understanding of the optical and structural properties of Si nanocrystals embedded in SiO₂ matrix as well as the relationship between the two properties. We have also conducted an electrical study, in which the influence of nc-Si distributions within the gate oxide on both charge storage and charge transport properties is investigated.

Si nanocrystals (nc-Si) embedded in SiO₂ films have been successfully synthesized by Si⁺ ion implantation into SiO₂ films that are thermally grown on Si substrates. Various techniques including ellipsometry, XPS, SIMS, XRD, TEM, PL, FTIR, and Raman scattering have been used to characterize these films. By ellipsometric analysis, we have developed a nondestructive and inexpensive approach to determination of the depth profile of nc-Si concentration, which is in good agreement with the results obtained by SIMS and TRIM simulation. TEM and XRD

measurements show a very slow evolution of nanocrystal size with annealing due to the low Si diffusion rate in SiO₂. By ellipsometry analysis and based on the effective medium approximation, one approach to determination of dielectric function and optical constants of Si nanocrystals embedded in SiO₂ matrix has been developed. Both the band gap expansion and dielectric suppression of the Si nanocrystals due to the quantum size effect have been obtained. The results are helpful to advance understanding of solid-state physics of nano-sphere and for Si nanocrystal applications. XPS core levels have been recorded to study the charging effect in nc-Si/SiO₂ films. It is found the charging ability of nc-Si/SiO₂ system is superior to that of pure SiO₂, showing that the charging effect is greatly enhanced by the introduction of Si into the SiO₂ matrix. Si 2p core-level shift of Si nanocrystals embedded in SiO₂ matrix determined from XPS experiment is found to be due to the charging in the material system. We have demonstrated that the true nc-Si core level can only be determined after the correction of charging effect. The analysis of the XPS Si 2p peaks shows the existence of the five chemical structures corresponding to the Si oxidation states Siⁿ⁺ (n = 0, 1, 2, 3, and 4) in the SiO₂ films. This means that not all the implanted Si ions are converted to Si nanocrystals even after a thermal annealing at a high temperature. Annealing effects on the oxidation states at various depths are also studied; the relative concentrations of the five oxidation states at various depths are determined quantitatively. It is demonstrated that nc-Si can be generated by the thermal decomposition of suboxides (Si¹⁺, Si²⁺, and Si³⁺) and the oxidation states Siⁿ⁺ (n=0, 1, 2, 3) can be oxidized by the excess oxygen present at oxide surface. These reactions leads to changes in the relative concentrations of the five oxidation states in the implantation region but such changes are insignificant beyond the implantation region.

For MOS capacitors with nc-Si confined in a narrow layer in the oxide, clear flat-band voltage shift due to charge trapping can be observed, demonstrating that such structures are promising for memory device applications. A new type of memory effect has been discovered by incorporation of Si nanocrystals throughout the gate oxide with its peak concentration located close to the gate: The charge trapping in nc-Si can modify the capacitance of such MOS structures, and detrapping of the charged nc-Si can lead to a recovery of the capacitance. This provides the possibility of a new type of memory device. The two types of memory effects are based on different nc-Si distributions within the oxide, and this thus highlights the importance of nc-Si distribution. Furthermore, charge transport via nanocrystals is also characterized by I-V measurements. It is observed that charge transport via the nc-Si can strongly modify the current conduction of the MOS structures. A carrier transport model has been proposed to explain the phenomena observed in current conduction characteristics.

7.2 Recommendations for Future Research

This work includes three major parts: synthesis of SiO₂ films containing Si nanocrystals, structural and optical characterization of SiO₂ films containing nc-Si and electrical characterization of SiO₂ films embedded with nc-Si with different distributions. To make the study more complete, the following research could be done:

- Other techniques such as sputtering, PECVD and laser ablation can be used to prepare nc-Si in SiO₂ films. Characterization of the films can be carried out with the techniques used in this work. Then the properties of the nc-Si thin

films prepared by these techniques are compared with those of the nc-Si embedded SiO₂ films prepared by Si⁺ implantation of this work, and relationship between the synthesis method and the nc-Si size, density and distribution should be studied. Proper methods should be developed to control the nanocrystal size, density and distribution.

- Electroluminescence (EL) devices such as light emission diodes (LEDs) are to be synthesized using nc-Si/SiO₂ as the active layer. The mechanism of EL should be studied: whether light emission is due to the electron-hole recombination within the nc-Si or via defects? Light emission efficiency of EL should be investigated: erbium (or some rare earth element) is to be doped into the nc-Si/SiO₂ layer to see if there is some improvement of the EL efficiency; LEDs with single active layer and multi active layers are to be fabricated to gain higher EL efficiency. Methods to improve the EL efficiency and to lower the onset voltage should finally be proposed.
- In order to finally realize single electron devices, a better understanding of single electron tunneling and Coulomb blockade effect is very important. As Coulomb blockade and single electron tunneling should be more significant at low temperatures, I-V and C-V measurements at low temperatures should be conducted on capacitors containing nc-Si to find more information about single electron tunneling, capacitance of nano-scale sphere and electrostatic energy of the nano-island. If possible, magnetic field will be applied when measuring I-V or C-V. The modulation of charging/discharging in quantum dot by magnetic force is also a very interesting topic.
- Future work also includes the fabrication and characterization of nc-Si nano-memory devices (i.e. MOSFETs with gate oxide containing nc-Si). The

influence of charge trapping in the nanocrystals on the device characteristics should be investigated. Studies on fabrication and characterization of nc-Si based single electron transistor (SET) should be carried out. In the fabrication processes for SETs, the removal of nearby nanocrystals is a more difficult task. One approach is to use photoresist lithography such as “nano-imprint” technology to allow only one or two nanocrystal embedded between the leads. The other is to *in-situ* control the nanocrystal deposition, i.e., the deposition should be terminated as soon as one nanocrystal bridges the leads. Characterizations should be focused on current transport behavior via nanocrystal in SETs. Information about energy needed to add or remove electrons to/from nanocrystal should be obtained also.

- First-principle calculation is a useful method to characterize electronic structures theoretically. Future work should include first-principle calculations to determine the band gap expansion, dielectric function suppression and XPS core level shifts due to the Si nanocrystal size reduction. Then the calculations should be compared with the experimental results obtained in this work.

Author's Publications

Journal Papers

1. Y. Liu, T. P. Chen, et al, "Influence of charge trapping in Si nanocrystals embedded throughout the gate oxide in MOS structures on I-V and C-V characteristics", *Electrochemical and Solid-State Letters (ECS)*, Vol.7, pp.G134-137, 2004.
2. Y. Liu, Y. Q. Fu, T. P. Chen, M. S. Tse, S. Fung, J. H. Hsieh, and X. H. Yang, "Depth profiling of Si oxidation states in Si-implanted SiO₂ films by x-ray photoelectron spectroscopy", *Japanese Journal of Applied Physics*, Vol. 42, Part 2, No. 11B, pp. L1394–L1396, 2003.
3. Y. Liu, T. P. Chen, Y.Q. Fu, M. S. Tse, J.H. Hsieh, P. F. Ho, and Y. C. Liu, "A Study on Si Nanocrystal Formation in Si-implanted SiO₂ films by X-Ray Photoelectron Spectroscopy", *Journal of Physics D: Applied Physics*, Vol.36, No.19, pp. L97-L100, 2003.
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9. T. P. Chen, Y. Liu, et al, "Optical-Constants Profiling of SiO₂ Thin Films Containing Si Nanocrystals ", *Journal of Applied Physics*, Vol.95, pp.8481-8483, 2004.
10. T. P. Chen, Y. Liu, et al, "Core-Level Shift of Si Nanocrystals in SiO₂ Matrix", *Journal of Physical Chemistry B*, Vol. 108, pp.16609-16612, 2004.
11. C. Y. Ng, T. P. Chen, Y. Liu, et al," Influence of Nitrogen on Tunneling Barrier Heights and Effective Masses of Electrons and Holes at Lightly-Nitrided SiO₂ /Si interface", *Journal of Applied Physics*, Vol.96 pp.5912-5914, 2004.
12. C. Y. Ng, V. S. W. Lim, T. P. Chen, H. W. Lau, Y. Liu, et al , " Visualizing Charge Transport in Silicon Nanocrystals Embedded In SiO₂ Films with Electrostatic Force Microscopy" , *Applied Physics Letters* , Vol.85, pp.2941-2943, 2004.
13. C. Y. Ng, T. P. Chen, Y. Liu, et al, "Modulation of Capacitance Magnitude by Charging/Discharging in Silicon Nanocrystals Distributed throughout the Gate Oxide in MOS Structures", *Electrochemical and Solid State Letters* ,accepted for publication.

14. Y. Liu, T. P. Chen et al, "Time-domain Capacitance Modulation due to Charging/Discharging in Si Nanocrystals Embedded in Gate Dielectric", *Applied Physics Letters* (submitted).

Conference Papers

1. Yang Liu, T. P. Chen, Man Siu Tse and Y. Q. Fu, "Evolutions and Distributions of Si Nanocrystals and Other Si Oxidation States in Si-implanted SiO₂ Films", SPIE's International Symposium on Microelectronics, MEMS, and Nanotechnology (BioMEMS and Nanotechnology), Dec. 10 - 12, 2003, Perth, Australia
2. T. P. Chen, Yang Liu and Man Siu Tse, "Optical Properties and Their Depth Profiling of Si Nanocrystals Embedded in SiO₂ Matrix", SPIE's International Symposium on Microelectronics, MEMS, and Nanotechnology (BioMEMS and Nanotechnology), Dec. 10 - 12, 2003, Perth, Australia
3. Chi Yung Ng, T. P. Chen Yang Liu, and Man Siu Tse, "Charging/discharging induced premature breakdown/recovery in Si Nanocrystals embedded in SiO₂ matrix", SPIE's International Symposium on Microelectronics, MEMS, and Nanotechnology (BioMEMS and Nanotechnology), Dec. 10 - 12, 2003, Perth, Australia
4. Y. Liu, T. P. Chen, Y.Q. Fu, and J.H. Hsieh, "Characterization of Si nanocrystals embedded in SiO₂ with x-ray photoelectron spectroscopy", The 2nd International Conference on Materials for Advanced Technologies (ICMAT) & IUMRS – International Conference in Asia 2003, 7-12 December, 2003, Singapore.
5. Y. Liu, T. P. Chen, M.S. Tse, P.F. Ho, A.L.K. Tan and Y.C. Liu, "Optical-Property Profiling of SiO₂ films Containing Si Nanocrystals Formed by Si⁺ Implantation", The

2nd International Conference on Materials for Advanced Technologies (ICMAT) & IUMRS – International Conference in Asia 2003, 7-12 December, 2003, Singapore.

6. Y. Liu, T. P. Chen, J.Y. Huang, A.L.K. Tan and Y.C.Liu, "Characterization of Si nanocrystal formation and optical constants", 2002 Conference on Optoelectronic and Microelectronic Materials and Devices (COMMAD2002), 11 - 13 December, Sydney, Australia.

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Appendix

In this part, some important technical details on the equipments used in this study are introduced. All processes are carried out in the cleanroom of the Microfabrication Laboratory of NTU.

(a) Cleaning process (Wet Bench)

The cleaning process was carried out at the wet benches in the Microfabrication Labor in NTU. Typical contaminants at silicon surfaces are molecular contaminants such as neutral and synthetic waxes, the resins and oils, ionic contaminants such as alkali ions, and atomic contaminants such as gold, silver and copper. In order to eliminate those contaminants and to grow oxides, Si wafers are normally cleaned with a standard chemical procedure:

1. Dipping in $\text{H}_2\text{SiO}_4:\text{H}_2\text{O}_2$ (1:1) solution at 100°C for 10 min to remove the contaminants listed above;
2. Washing in deionized water for 6 cycles;
3. Dipping in HF solution (1:10) for 10s to remove initial oxide;
4. Washing in deionized water for 6 cycles;
5. IPA drying to remove the moisture on the wafers.

(b) Oxide growth (MRL oxidation furnace)

Thermal oxidation of Si is one of the most important processes for the reliability and the performance of CMOS devices. In this study, oxides are thermally grown in a MRL oxidation furnace in a 150mm CMOS line in the Microfabrication Lab. Thermal oxide growth is illustrated in Fig. A1. The existing models for the thermal oxide

growth are based on the report in [238]. The basic idea is the assumption of steady state situation between two fluxes (i.e. $F_I = F_{II} = F$).

$$F_I = D \frac{dC}{dx} \approx \frac{D(C_0 - C_s)}{Tox} \quad (A1)$$

$$F_{II} = k_s C_s \quad (A2)$$

F_I represents the flux across the oxide, which is assumed to be purely diffusive; D is the diffusion coefficient of the oxidizing species; C_0 is the concentration of the oxidant at the oxide surface, C_s is the oxidant concentration in the oxide at the oxide/silicon interface; k_s is the chemical surface reaction rate. The flux of oxidant reaching the oxide/silicon interface is described by the differential equation from combining (A1) and (A2).

$$\frac{dTox}{dt} = \frac{F}{C_I} = \frac{DC_0 / C_I}{Tox + (D / k_s)} \quad (A3)$$

where C_I is the density of SiO_2 . The model for oxide growth is illustrated in Fig. A1.

Fig. A1. Illustration of thermal oxide growth and the model.

(c) Ion implantation (Varian EHP-220)

Ion implantation in this study is processed with an ion-implanter manufactured by Varian. Ion implantation is developed for use in semiconductor industries, which utilizes high energy ion beams to modify the electrical properties of materials. The ion implantation process is normally conducted in a vacuum chamber at very low pressure (10^{-4} - 10^{-5} Torr). Large numbers of ions (typically 10^{13} - 10^{17} ions/cm²) bombard and penetrate a surface, interacting with the substrate atoms immediately beneath the surface. Typical depth of ion penetration is a fraction of a micron. The interactions of the implanted ions with the material modify the surface, providing it with significantly different properties than the remainder of the material. Specific property changes depend on the selected ion beam treatment parameters including the particular ion species, energy, and total number of ions.

Ions are produced via a multi-step process in a system as shown schematically in figure A2. Ions are initially formed by stripping electrons from source atoms in plasma. Then ions are extracted and pass through a mass-analyzing magnet, which selects only those ions of desired specie, isotope, and charge state. The beam of ions is then accelerated using a potential gradient column. Typical ion energies range from a few keV to a few MeV. A series of electrostatic and magnetic lens elements make the final selection of the resulting ion beam and scans it over an area in the end station containing the wafer to be treated.

Main advantages are listed below:

1. Precise control of the introduced Si ions by adjusting the current.
2. Relatively low temperature processing.
3. The depth profile of Si nanocrystal can be controlled by the selection of implantation energy and dose.

4. The resulting nanostructured films are homogeneous and reproducible.

The disadvantages:

1. It is a relatively high-cost approach to synthesize nc-Si as compared to CVD and Co- sputtering.
2. For EL devices, a higher implantation dose leads to larger leakage currents and shorter EL time constants. [57]
3. Damages induced by ion implantation may affect the integrity of the oxide and thus the electrical characteristics of the devices. [97]

To improve EL efficiency and avoid device degradation, an optimal implantation dose should be determined experimentally, and a thermal annealing is necessary [57]. For memory devices, it is reported in [97] that annealing in diluted oxygen improves the charge storage ability and charge retention ability, because such a process improves the integrity of the oxide and narrows the size distribution of nanocrystals without affecting the mean size.

Fig.A2. Illustration of an ion implantation system.

(d) Metal deposition (BPS clusterline 200)

The metal films for electrodes were deposited with a BPS clusterline 200 sputtering system. A 3-inch aluminum target with the purity of 99.99% is used for deposition with a constant power of 200 W at 13.56 MHz. Before deposition, the deposition chamber should be vacuumed to a level of 10^{-6} mbar with a diffusion pump with a liquid nitrogen trap. Before depositing the electrodes, the target should be cleaned by pre-sputtering onto a shutter for 30 minutes. After the initial cleaning process, the real deposition starts by opening the shutter. The target-sample distance is fixed at 4cm. The process pressure is maintained at about 2 mbar. The substrate temperature is about 100 °C as a result of plasma heating. The film thickness is controlled by varying the deposition time. The parameters such as temperature, gas flow, gas pressure and reflected power are stable during the process. The final electrodes show a smooth and shining metallic surface under the microscope.