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Characterization of thin SiO₂ and SiO_xN_y grown by thermal oxidation

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CHARACTERIZATION OF THIN SiO_2 AND SiO_xN_y GROWN BY THERMAL
OXIDATION

A Thesis

Presented to

The Faculty of the Department of

Chemical and Material Engineering

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Chemical Engineering

By

Jongchul Lim

December 2004

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**APPROVED FOR THE DEPARTMENT OF CHEMICAL AND
MATERIAL ENGINEERING**

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ABSTRACT

CHARACTERIZATION OF THIN SiO_2 AND SiO_xN_y GROWN BY THERMAL OXIDATION

By Jongchul Lim

Silicon dioxide (SiO_2) has been used as the gate dielectric insulator in Metal Oxide-Semiconductor (MOS) transistor for more than three decades. Silicon dioxide has excellent electrical and mechanical properties. As the feature size of MOS transistors gets smaller, thinner SiO_2 gates are required. However, as the gate oxide gets thinner, the reliability and quality of the oxide have become more difficult to control. Alternative gate materials have been required for the ultra-large-scale integration (ULSI) era. This report characterizes the quality and electrical properties of silicon oxynitride (SiO_xN_y) compared with SiO_2 . Four different thicknesses of SiO_2 films were prepared by a standard current thermal dry oxidation process, and three different thicknesses of SiO_xN_y films were prepared with N_2O gas. The thickness, capacitance, and leakage current of the films were measured. The SiO_2 films were grown for 5, 10, 20, 35 minutes at 1000°C , and the thicknesses of SiO_2 films were from 161 to $432\text{\AA}$. The SiO_xN_y films were grown for 45, 120, 300 minutes at 1000°C , and the thicknesses were from 96 to $210\text{\AA}$. For both films, the thickness variations increased as the thickness decreased. The capacitances of SiO_xN_y films were less than those of SiO_2 films. It contradicts the capacitance equation. The leakage current was reduced by using SiO_xN_y instead of SiO_2 .

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Table of Contents

List of Figures	ix
List of Tables	xi
1. Introduction	1
1.1 MOSFET (Metal-Oxide-Semiconductor Field Effect Transistor)	1
1.2 Ultra Thin Gate Oxide	2
1.3 Reliability of Ultra Thin Gate Oxide	3
2. Literature Review	4
2.1 Overview	4
2.2 Thermal Oxidation Kinetics and Mechanism of Silicon in Dry Oxygen	4
2.2.1 Deal-Grove Linear Parabolic Model	5
2.2.2 Oxidation Rate Enhancement Model	6
2.2.3 Parallel Oxidation Model	8
2.3 Effect of Nitrogen in Silicon Dioxide Films	9
2.3.1 Mechanism of Nitrogen in Silicon Dioxide	10
2.3.2 Dielectric Constant Enhancement	12
2.3.3 Boron Penetration Reduction	13
2.4 Methods for Growth of Silicon Oxynitride Film	15
2.4.1 Oxynitridation with N_2O Gas	16
2.4.2 Comparison of Nitrogen Concentration between N_2O and NO Gas Processes	19
2.5 Electrical analysis of SiO_xN_y film	20

2.6 Summary	23
3. RESEARCH OBJECTIVE AND JUSTIFICATION	24
3.1 Objective	24
3.2 Justifications	24
4. EXPERIMENTAL PRODECURE AND APPARATUS	26
4.1 Overview	26
4.2 Pre-oxidation wafer preparation	27
4.3 Thickness of SiO ₂ gate	27
4.4 Thickness measurement	28
4.5 Growth of silicon oxynitrde with N ₂ O gas	29
4.6 Electrical Characterization of SiO ₂ and SiO _x N _y	30
4.7 Fabrication of MOS capacitor	31
4.8 Capacitance measurement	32
4.9 Leakage current measurement	34
4.10 Materials and equipments	35
5. RESULTS AND DISCUSSIONS	37
5.1 Physical Characterization of SiO ₂	37
5.1.1 Overall uniformity of SiO ₂ filmas function of time	37
5.1.2 Uniformity of SiO ₂ film along the boat	38
5.1.3 Uniformity of SiO ₂ film across wafers	39
5.1.4 Growth rate of SiO ₂	40
5.2 Physical Characterization of SiO _x N _y with N ₂ O Gas	41

5.2.1 Overall uniformity of SiO_xN_y film	42
5.2.2 Uniformity of SiO_xN_y film along the boat	42
5.2.3 Uniformity of SiO_xN_y film across wafers	43
5.2.4 Growth rate of SiO_xN_y film	44
5.3 Capacitance Measurements	45
5.3.1 Maximum capacitance (C_{max}) comparison between SiO_2 and SiO_xN_y films	47
5.4 Leakage Current	48
6. CONCLUSIONS	51
7. FUTURE WORK	53
REFERENCES	54
APPENDIX: Raw thickness data of SiO_2 and SiO_xN_y films	56

List of Figures

Figure 1 Schematic of NMOS transistor	2
Figure 2 Oxide-thickness dependence of the growth rate for the oxidation	6
Figure 3 The parallel oxidation model to Si(100) oxidation kinetics	9
Figure 4 The dependence of interface-trap density on conditions of NO annealing	11
Figure 5 Model of the chemical structure of NO-annealed SiO ₂ /(100)Si	12
Figure 6 The ratio of the boron flux in the substrate for the oxynitride	14
Figure 7 Different nitridation methods	15
Figure 8 Nitrogen depth profile, measured using XPS, at two different flow velocities	17
Figure 9 Oxide thicknesses as a function of process temperature	18
Figure 10 Depth profile of the nitrogen concentration	19
Figure 11 Nitrogen depth profiles obtained by SIMS	20
Figure 12 CV characteristic for the 1000Å SiO _x N _y film on p-Si	22
Figure 13 CV characteristic for the 1500Å SiO _x N _y film on p-Si	22
Figure 14 Flow chart of experiments	26
Figure 15 Flow chart of silicon dioxide thickness control	28
Figure 16 The scheme of oxide thickness measurement on a wafer	29
Figure 17 Flow chart for oxinitridation of gate oxide	30
Figure 18 Flow chart of MOS capacitor fabrication	31
Figure 19 Capacitors made on a wafer	32
Figure 20 MOS capacitor CV plot	33
Figure 21 Flow chart of capacitance measurement	34

Figure 22 A wafer placed on the probe station	34
Figure 23 Schematic of the positions of wafers in a boat	38
Figure 24 The thickness profile of SiO_2 films along the boat	39
Figure 25 The thickness of SiO_2 films across wafers for various oxidation times	40
Figure 26 Oxidation rate vs. oxide thickness from experimental data, Deal-Grove linear parabolic model, and oxidation rate enhancement model	41
Figure 27 The thickness profile of SiO_xN_y films along the wafer carrier	43
Figure 28 The thickness of SiO_xN_y films across wafers for various oxidation time	44
Figure 29 Growth rate of SiO_xN_y film	45
Figure 30 Capacitances of SiO_2 with various thicknesses	46
Figure 31 Capacitances of SiO_xN_y for various thicknesses	46
Figure 32 Maximum capacitances (C_{max}) at various thicknesses of films	48
Figure 33 Leakage currents versus thickness of SiO_2 and SiO_xN_y	49
Figure 34 Leakage currents versus C_{max} for SiO_xN_y and SiO_2	50

List of Tables

Table 1 Roadmap for minimum feature size and equivalent dielectric thickness	3
Table 2 Pre-gate clean	27
Table 3 Materials used for the experiment	35
Table 4 Equipment	36
Table 5 Mean thickness, standard deviation, % of standard deviation from mean Thickness, and 95% confidence interval of SiO_2 for various oxidation times	37
Table 6 Mean thickness, standard deviation, % of standard deviation from mean thickness, and 95% confidence interval of SiO_xN_y for various oxidation times	42

1. INTRODUCTION

1.1 MOSFET (Metal-Oxide-Semiconductor Field Effect Transistor)

Since the first Integrated Circuit (IC) was invented 40 years ago, the device components in an integrated circuit chip have rapidly increased to tens of millions per square centimeter of silicon. This phenomenon has led to the shrinking of device geometries and to the increased complexity of the circuits. According to Moore's law, the numbers of transistors on a chip will double every two years [1].

A basic transistor is a four terminal switching device. The Metal Oxide Semiconductor (MOS) transistor was invented in the early 1960's [1]. Shown in Figure 1, a basic NMOS (N-type Metal-Oxide-Semiconductor) consists of four terminal regions: an input (source), an output (drain), a control terminal (gate) and a body. The region between the source and the drain is the active part of the device where the electrons flow under the gate. When a zero or negative voltage is applied on the gate, the circuit is in the open position and no current flows. Current flows when a positive voltage is applied on the gate. The positive voltage creates a vertical electric field across the gate oxide that will attract electrons to the surface of the silicon substrate. This changes the doping type from P to N, thus allowing current to flow from one n^+ region to another n^+ region.

Figure 1. Schematic of NMOS.

1.2 Ultra Thin Gate Oxide

Silicon dioxide (SiO_2) has been exclusively used as the gate dielectric insulator in the MOS transistor for more than three decades and exhibits unique electrical and mechanical properties. It adheres well on silicon, blocks the diffusion of dopants and many undesired impurities, is not reactive with most chemicals used in the silicon processing, and can be patterned and etched with specific chemicals or plasma. Additionally, SiO_2 provides good mobility of holes and electrons flowing in silicon at the silicon dioxide interface. As the geometry of the semiconductor devices has been shrinking through medium (MSI), large (LSI), very-large (VLSI), and now ultra-large-scale integration (ULSI), the thickness of SiO_2 films has decreased with each generation. The trend of reduction in lithography feature size and equivalent dielectric thickness is given in Table 1.

Table 1. Roadmap for minimum feature size and equivalent dielectric thickness.

Production Year	Minimum feature size (μm)	Equivalent dielectric thickness ($\text{\AA}$)
1997	0.25	40-50
1999	0.18	30-40
2001	0.15	20-30
2003	0.13	20-30
2006	0.10	15-20
2009	0.07	<15
2012	0.05	<10

For current high performance processors, the oxide thickness is less than $30\text{\AA}$. In ten years, the predicted oxide thickness should be less than $10\text{\AA}$ or about three atomic layers.

1.3 Reliability of Ultra Thin Gate Oxide

As the gate oxide gets thinner, the quality and reliability of the oxide have become more difficult to control. Aggressive scaling of the thickness of the gate insulator in MOS transistors has caused the quality and reliability of ultra thin dielectrics to assume greater importance [2][3][4]. High-performance CMOS products depend upon the reliability of ultra thin gate dielectrics. Silicon dioxide, and other potential gate dielectric materials, must withstand high electric fields, contain few electrical defects, and be robust with respect to damage during operation of the device. Gusev [6] have suggested that alternative gate dielectric materials will be required for sub- $0.25\mu\text{m}$ ULSI devices.

2. LITERATURE REVIEW

2.1 Overview

The 1997 National Technology Roadmap for Semiconductors identified several potential deficiencies for SiO₂ [8]. Increasing problems with dopant (boron) penetration through ultra-thin Silicon dioxide layers and direct tunneling for ultra-thin (<2nm) oxide films require materials for future gate dielectric applications with better diffusion barrier properties and higher dielectric constants [6][7][8]. Lightly nitrified silicon oxide, referred to as silicon oxynitride, is the most preferred alternative dielectric material. It has superior properties compared with those of SiO₂: better suppression of boron penetration and reduction of hot electron-induced degradation.

2.2 Thermal Oxidation Kinetics and Mechanism of Silicon in Dry Oxygen

The Deal-Grove linear parabolic model has been used to describe the kinetics of thick thermal oxidation for over two decades. However, it does not adequately describe the oxidation kinetics for oxides thinner than a few hundred angstroms [9]. Typically, the growth rate was higher than predicted by the linear parabolic model for layers thinner than 250Å [10]. Several mechanisms have been introduced to explain this rapid growth rate for a thin oxide. These new mechanisms include space-charge enhancement of the diffusing ionic species, rapid diffusion of oxidant through micro channels and micro pores in the oxide, varying diffusion coefficients, diffusion retardation by a blocking layers at the interface, parallel oxidation of two diffusing oxidants, oxidation rate

enhancement from an altered Si surface layer, and oxidation rate retardation from a buildup of fixed charge at the interface [11][12].

2.2.1 Deal-Grove Linear Parabolic Model

According to the linear parabolic model, oxide growth is the result of an oxidizing species diffusing through an existing layer of oxide and reacting with silicon atoms at the Si-SiO₂ interface to form SiO₂. The mechanism is based on three fluxes in series under steady-state conditions: flux from the gas to the oxide surface, flux through the oxide, and flux at the Si-SiO₂ interface. The growth rate (dx_{ox}/dt) is shown in Equation 1.

$$\frac{dX_{ox}}{dt} = \frac{B}{(2X_{ox} + A)} \quad \text{Equation 1}$$

$$\text{where } B = \frac{2DC^*}{N_1} \text{ and } A = 2D\left(\frac{1}{h} + \frac{1}{k_s}\right)$$

where D and C* are the diffusion coefficient and solubility of the oxidizing species in the oxide, respectively. N₁ is the number of oxidant molecules incorporated into a unit volume of the growing oxide, k_s is the surface reaction-rate constant, and h is the gas phase mass-transfer coefficient [9, 10]. This linear parabolic equation has been used to predict the growth for wet oxidation. However, the model does not accurately predict the growth rate of dry oxidation for thin oxide films. The actual growth rate is higher than that predicted for thin oxides less than 300Å thick. For thin oxides, the linear rate constant, B, shows a power-law dependence on oxygen partial pressure [9]. Due to these deficiencies, new oxide growth laws have been developed by some researchers.

2.2.2 Oxidation Rate Enhancement Model

Massoud [10] provided experimental data of oxidation rates in the thin oxide regime. The preoxidation cleaning was performed with an RCA clean. After cleaning, the wafers were then dried using nitrogen and immediately loaded in the oxidation furnace with argon flowing. The growth rate was measured *in situ* by a high temperature automated ellipsometer. The oxide thickness was measured from the onset of oxidation. In Figure 2, the oxidation rate vs. oxide thickness was plotted at several temperatures. As shown in Figure 2, the rate was higher than that predicted by the linear-parabolic model up to 250-350Å. Beyond this thickness, there was good agreement between the experimental data with the linear-parabolic model.

Figure 2. Oxide-thickness dependence of the growth rate for the oxidation.

Massoud [10] introduced an empirical rate law for dry oxidation based on their experimental data by adding two extra terms to the linear parabolic model. They assumed that the faster oxidation rate was the result of additional processes not accounting for the linear parabolic model. The additional processes were described as excess rates. Their expression of oxide growth rate is shown in Equation 2.

$$\frac{dX_{ox}}{dt} = \frac{B}{(2X_{ox} + A)} + C_1 e^{-(X_{ox}/L_1)} + C_2 e^{-(X_{ox}/L_2)} \quad \text{Equation 2}$$

The first term is the linear parabolic rate term, the second term is an initial phase term, and the third term is an intermediate phase term. C_1 and C_2 are pre-exponential constants of the initial and intermediate phases. L_1 and L_2 are characteristic lengths of the initial and intermediate phases. From their analysis, the initial phase term is only dependent on residual traces of impurities remaining on the surface after cleaning and the preoxidation procedure. That means that the initial phase term is closely related to wafer cleaning and surface preparation processes. Excluding the initial phase term results in errors of less than 5% in fitting the experimental data. It reduces the oxide growth rate to Equation 3.

$$\frac{dX_{ox}}{dt} = \frac{B}{(2X_{ox} + A)} + C_2 e^{-(X_{ox}/L_2)} \quad \text{Equation 3}$$

The characteristic length L_2 is independent of temperature, substrate orientation, substrate doping concentration, and the partial pressure of oxygen. The pre-exponential constant C_2 exhibits Arrhenius-type behavior with single activation energy, and is expressed in Equation 4.

$$C_2 = C_2^0 e^{-(\Delta E/kT)} \quad \text{Equation 4}$$

where C_2^0 is pre-exponential constant, ΔE is the activation energy, k is Boltzman constant, and T is the absolute temperature. The activation energy is a function of substrate doping concentration and of the partial pressure of oxygen in ambient pressure.

Hu [9] has defined that the linear rate constant of linear parabolic model, B/A , shows a power-law dependence on oxygen partial pressure. B/A is proportional to P^m , and the value of m is mostly between 0.6 and 0.8. The empirical rate law developed by Hu is shown in Equation 5.

$$\frac{dX}{dt} = \frac{B}{A} P^m + C_2 e^{-(X_{ox}/L_2)} \quad \text{Equation 5}$$

2.2.3 Parallel Oxidation Model

Han and Helms [12] introduced a parallel oxidation mechanism. The basic assumption is that if more than one diffusant is present, the oxidation rate should be a sum of the individual oxidation rates. The total oxidation rate can be expressed as

$$\frac{dX}{dt} = \frac{B_1}{2X_{ox} + A_1} + \frac{B_2}{2X_{ox} + A_2} \quad \text{Equation 6}$$

where the subscripts 1 and 2 refer to the two oxidizing species. The coefficients, B_i and the A_i , have corresponding definitions with the physical parameters in the linear parabolic model. The parameter B_1 , B_2 , and B_2/A_2 show Arrhenius-type behavior. The equation can be expressed as Equation 7.

$$B_i = B_i^0 e^{-\Delta E / kT} \quad \text{Equation 7}$$

where B_i refers to B_1 , B_2 , and B_2/A_2 . B_i^0 is pre-exponential constant, ΔE is activation energy, k is Boltzmann constant, and T is the absolute temperature, respectively.

Because A_1 is relatively small, $\sim 5 \text{ \AA}$, with $A_1=0$, Equation 6 can be reduced to Equation 8.

$$\frac{dX}{dt} = \frac{B_1}{2X_{ox}} + \frac{B_2}{2X_{ox} + A_2} \quad \text{Equation 8}$$

As shown in Figure 3, this equation fits to data of Massoud [10] with less than 4% standard deviation.

Figure 3. The parallel oxidation model to Si (100) oxidation kinetics.

2.3 Effect of Nitrogen in Silicon Dioxide Films

Nitrogen in a SiO_2 film provides some advantages and disadvantage over an SiO_2 film. Nitrogen could reduce the defect generation rate and boron penetration. However, incorporation of large amounts of nitrogen, more than one atomic percent, could cause

threshold voltage shift, and mobility and transconductance degradation [2]. In this chapter, the mechanism of nitrogen incorporation in a SiO₂ film, and the effect of nitrogen on dielectric constant and boron penetration are discussed.

2.3.1 Mechanism of Nitrogen in Silicon Dioxide

According to Gusev [6], an understanding of atomic-scale structure and electronic properties of dielectrics is required to find the optimal nitrogen profile in silicon oxynitride films. A recent publication from Kushida-Abdelghafar [13] studied atomic structure and electronic properties of nitrous-oxide-nitrided SiO₂/Si interface. SiO₂ films, 20 to 90 Å, on p-type Si (100) were grown by dry oxidation. The films were annealed in atmospheres from 1%-100% NO gas (with the remainder being N₂) at 900-950 °C. Electron spin resonance (ESR) analysis was used to find the nitrogen termination of dangling bonds at the Si/SiO₂ interface. In addition, the nitrogen bonds that are produced by nitridation were analyzed by x-ray photoelectron spectroscopy (XPS).

As seen in Figure 4, when NO annealing was performed in 10% NO atmosphere, about 90% of the traps were terminated by nitrogen. When the density of the traps are compared with that of pure SiO₂ film, about 15% of the Si atoms at SiO₂/Si interface were defective sites. So, a small atomic percentage of nitrogen at the interface is required to fill the interfacial traps.

Figure 4. The dependence of interface-trap density on conditions of NO annealing.

The physical form of an interfacial trap is a dangling bond at the interface. The characteristics of an interfacial dangling bond were measured with electron spin resonance (ESR). According to Kushida-Abdelghafar [13], the P_{b0} and P_{b1} centers were found at the Si/SiO₂ interface, and the interfacial dangling bonds were terminated by nitrogen. As seen in Figure 5(a), A P_{b0} center noted as (a) is a dangling bond in layer 0, and two P_{b1} centers noted as (b) and (c) respectively are dangling bonds in layer 1. In Figure 5(b), nitrogen directly bonds to P_{b0} or P_{b1} , and the O atom does not directly bond to the nitrogen.

Figure 5. Model of the chemical structure of NO-annealed SiO₂/(100)Si.

2.3.2 Dielectric Constant Enhancement

Recent publications suggest that the performance of CMOS-based devices depends on both concentration and distribution of the nitrogen atoms incorporated into the gate dielectric [6]. As the oxide thickness decreases, the leakage current increases, therefore it is desirable to reduce the leakage current for thin gate oxide and to maintain or increase the reliability of such films [7]. The dielectric constant of the oxynitride increases linearly with the percentage of nitrogen to oxygen from $\epsilon(\text{SiO}_2) = 3.8$ (0%) to $\epsilon(\text{Si}_3\text{N}_4) = 7.8$ (100%) [6]. With a higher dielectric constant, a thicker layer can be used. The effect of dielectric constant on dielectric thickness can be explained by the equivalent dielectric thickness. The equivalent dielectric thickness, t_{eq} , refers to the

thickness of any dielectric scaled by the ratio of its dielectric constant to that of silicon dioxide, Equation 9.

$$t_x = \frac{t_{eq} [\epsilon_x]}{\epsilon_{oxide}} \quad \text{Equation 9}$$

where t_{eq} and t_x are the equivalent oxide and physical thickness respectively, and ϵ_x and ϵ_{oxide} are the dielectric constant of dielectric material and silicon dioxide respectively.

2.3.3 Boron Penetration Reduction

According to Buchanan [2], the introduction of nitrogen can increase the thickness of the film which is desirable for increasing the reliability of the film, and reduce the “defect-generation rate” (P_{gen}). However, a nitrogen concentration of more than one percent close to the Si/SiO₂ interface leads to large flat-band or threshold-voltage shifts. A nitrogen concentration of less than one atomic percent close to the Si/SiO₂ interface is useful without degrading electrical properties and is desirable for controlling channel hot-electron degradation effects in MOSFET characteristics.

Nitrogen concentration smaller than one atomic percent is not sufficient to block the boron penetration from the p⁺ Si gate into the gate dielectric. Ellis and Buhrman [8] experimented and simulated boron diffusion into the SiO₂ with several concentrations of nitrogen. The thickness of the SiO₂ was 46Å for all four samples. Three different oxynitrides were grown on three inch prime-grade Si wafers in either a standard laminar flow furnace shown in sample # 2, or a rapid thermal processor shown in samples # 3 and # 4. Then 2000Å of in situ diborane-doped polycrystalline Si was deposited by low-

pressure chemical vapor deposition (LPCVD). The concentration of nitrogen in each sample was 0.4, 1.43, and 2.20 atomic percent, respectively. The highest concentration of nitrogen for all samples was at the SiO_2/Si interface. Sample #1 was pure silicon dioxide and was used to compare with the ratio of boron flux for three different oxynitrides. The ratio of boron flux for pure silicon dioxide was one. The boron profiles were measured with secondary ion mass spectroscopy. As shown in Figure 6, the vertical axis is the boron diffusion flux ratio compared with pure silicon dioxide, and the flux of boron was effectively reduced when the nitrogen concentration was more than one atomic percent. Also Buchanan [2] stated more than one atomic percent of nitrogen in SiO_2 is required to block the boron penetration at the $\text{SiO}_2/\text{poly Si}$ interface.

Figure 6. The ratio of the boron flux in the substrate for the oxynitride.

2.4 Methods for Growth of Silicon Oxynitride Film

Nitrogen may be incorporated into SiO_2 using either thermal oxidation/annealing or chemical and physical deposition methods as seen in Figure 7 [7]. Although NH_3 was the first of three gases used to produce thermal oxynitrides and had a superior barrier for boron penetration, it was largely supplanted by N_2O and NO for processing gate dielectrics [8]. Non-hydrogen nitrogen species (e.g., N_2O and NO) were even more efficient at increasing device reliability and reducing P_{gen} , since hydrogen was not introduced during the nitridation process. The introduction of N_2O and NO was found to reduce the defect-generation rate to a greater extent than NH_3 [2].

Figure 7. Different nitridation methods.

2.4.1 Oxynitridation with N₂O Gas

Oxynitridation in N₂O has two main advantages over oxynitridation in NO. One of the advantages is appropriate nitrogen concentration near the SiO_xNy/Si interface (typically 1% of atomic concentration). According to Ellis [8], the appropriate concentration of nitrogens are 1% of atomic concentration at the poly Si/SiO₂ interface and less than 1% of atomic concentration at the SiO₂/Si interface. The other advantage is that by simply replacing O₂ with N₂O in the furnace, the normal thermal oxidation process can be used [6]. However, the complexity of N₂O decomposition makes oxynitridation of N₂O difficult to control. The result of complete N₂O decomposition is a mixture of N₂, O₂, and NO. The decomposition is affected by gas flow rate, temperature, partial pressure of N₂O in the oxidizing ambient, reactor type and geometry, and impurity levels [8]. Ellis and Buhrman [8] studied the influence of flow rate on the concentration of nitrogen in the oxynitride film for furnace processing. For the furnace process, they measured the nitrogen depth profile by x-ray photoelectron spectroscopy (XPS), at two different flow velocities, 0.65 and 0.16 cm/s. Oxynitride films were prepared using a four step process: pure O₂ (5min), N₂O (30min), O₂ (30min), and N₂O (30 min), at 900°C. The reason for using two N₂O steps was to obtain bimodal nitrogen distribution in which the nitrogen incorporation or removal in either N₂O step could be monitored. As seen in Figure 8, they found the total nitrogen contents of the 0.65 cm/s oxynitride is approximately twice that of the 0.16 cm/s oxynitride and this phenomenon is attributed to the higher NO/O₂ ratio in the gas composition at the higher flow rate.

Figure 8. Nitrogen depth profile, measured using XPS, at two different flow velocities.

Lange [14] studied the growth rate and nitrogen concentration profile of SiO₂ film in N₂O atmosphere in a rapid thermal processor. It was assumed that the decomposition of N₂O gas consisted of two main decomposition reactions. Equation 10 shows the two main decomposition reactions associated with oxynitride growth.

In Figure 9, the oxide thickness, which is a function of process temperature, was displayed for oxidation times of 60, 300, and 480 seconds. For the short process time, a monotonic increase in thickness with increasing temperature was observed. For medium oxidation times, the thickness-temperature dependence ran through a transition region

with a plateau at approximately 1000°C. For the long process time, the oxide thickness drop occurred at about 1000°C, because at this temperature, N₂O decomposed with 91.1% N₂ and O₂ and a proportion of 8.9% of NO and N₂. At 900°C, the proportion of NO and N₂ decreases to 3.4%. It was assumed that the weakly reactive NO produced the interfacial nitrated layer. At about 1000°C, the formation of an interfacial nitrated layer occurred, and dropped the oxidation rate.

Figure 9. Oxide thicknesses as a function of process temperature.

In Figure 10, the depth profile of the nitrogen concentration for N₂O oxides, grown at a different temperature, was measured by SIMS. For comparison, a nitrogen depth profile of an RTP-O₂ oxide is shown. The thickness of all layers is 70Å. As seen in Figure 10, at 1150°C, the nitrogen concentration near the Si/SiO₂ interface was the

highest and closer to the interface. Also, the nitrogen concentrations at the surfaces were almost the same for all temperatures. From this result, at the higher temperature, the nitrogen concentration would be higher and closer at the interface.

Figure 10. Depth profile of the nitrogen concentration.

2.4.2 Comparison of Nitrogen Concentration between N₂O and NO Gas Processes

Lu [15] measured the nitrogen depth profiles for ~50Å silicon oxynitride films grown by different methods. The film (a) was grown by the thermal oxynitridation of Si in O₂ gas followed by NO annealing in a furnace, the film (b) was grown by the thermal oxynitridation in N₂O gas in a furnace, and the film (c) was grown by the thermal oxynitridation in N₂O gas in an RTP reactor, respectively. As seen in Figure 11, the

nitrogen concentration in the film (a) was the highest and closest to the SiO₂/Si substrate interface among the films. μm^{-3}

Figure 11. Nitrogen depth profiles obtained by SIMS.

2.5 Electrical analysis of SiO_xN_y film

One of the electrical analyses for the insulator-semiconductor interface and the bulk insulator material is the measurement of capacitance versus voltage (CV) characteristics. Flat-band shift and distortion of the measured CV characteristics from the ideal characteristic provide information about charge accumulation in the bulk insulator material and at various material interfaces [16].

O'Clock [16] measured CV characteristics of SiO_xN_y films on p-type Si. The SiO_xN_y samples were prepared using thermal nitridation of SiO₂ in pure ammonia at

atmospheric pressure. The oxide films were grown in pure oxide at 900°C and the thermal nitridation was accomplished at a temperature of 1100°C to 1200°C for approximately four hours. The CV characteristics were measured with an MSI-102 Mercury probe, HP 4280A C Meter/CV plotter, and a HP 9845A desktop computer. As seen in Figure 12 and 13, both films showed the negative flat-band voltage shifts associated with the CV characteristics. The shifts indicate the presence of positive charges at the insulator-semiconductor interface or the bulk insulator material. The type of hysteresis of measured CV curve indicates the presence of carrier trapping and detrapping mechanisms. The stretched-out CV curve shown in Figure 12 could be due to either the effects of surface states at the insulator-semiconductor interface or to effects associated with deep-level heavy metal impurities in the band gap. The pronounced C_{min} shown in Figure 13 could be associated with deep depletion in the semiconductor film or mobile ions in the insulating film.

Figure 12. CV characteristic for the 1000Å SiO_xN_y film on p-Si.

Figure 13. CV characteristic for the 1500Å SiO_xN_y film on p-Si.

2.6 Summary

As shown in the literature, the oxide growth rate for dry oxidation is higher than that predicted from the linear parabolic model in a particular thickness regime. If the gate oxide is less than 300 Å, the linear parabolic model is not valid. However, if the desired thickness is greater than 300 Å, the linear parabolic model is still applicable. The introduction of nitrogen in SiO₂ film can increase the film reliability and decrease the boron penetration into the film. The most important factors of silicon oxynitride are the appropriate concentrations of nitrogen at the Si/SiO₂ interface and the SiO₂/poly Si interface. For either the laminar flow furnace or rapid thermal processor (RTP), the flow rate and temperature are the most important process parameters. Among the three methods mentioned in this paper, NO annealing results in a superior gate oxide and is assumed to cause the interfacial nitrided layer. To find the nitrogen concentration profile, most researchers used x-ray photoelectron spectroscopy (XPS) or secondary ion mass spectroscopy (SIMS). To investigate the quality of a gate insulator, most researchers [2][14][15][16] used capacitance and voltage, CV measurement. CV measurement provides information about reliability of gate insulators and existence of impurities incorporated into the films.

3. RESEARCH OBJECTIVE AND JUSTIFICATION

3.1 Objective

The objective of this thesis is to develop a low leakage thin gate oxynitride used in MOS transistor processing. The performance of the thin gate oxynitride will be compared with a silicon dioxide gate of equivalent thickness. The comparison between the two gates will be based upon maximum capacitance and leakage current. Since the current silicon oxide gate utilized in the MOS transistors fabricated at SJSU is approximately 800Å thick, a silicon dioxide thin gate process needs to be defined. The growth of SiO₂ gate between 100-300Å was characterized in terms of growth rate and uniformity at fixed temperature, gas flow rate, and various oxidation times.

Thin silicon oxynitride gates, SiO_xN_y, between 100-300Å were grown at a fixed temperature, and a fixed N₂O gas flow rate. Time was varied to obtain oxynitrides of various thicknesses.

MOS capacitors were fabricated using the oxynitride and SiO₂ films. The leakage current and capacitance of the films were measured.

3.2 Justifications

For better performance of IC chips, a thinner oxide is desired. If the properties in a device are maintained as constants, a thinner gate oxide results in a higher source-drain current. The source-drain current is inversely proportional to the thickness of gate oxide, t_{ox} . Also, a higher current flow reduces the switching time, resulting in a faster device.

There are several problems that arise as the gate oxide gets smaller, such as boron penetration, high leakage current, and breakdown. It is well known that nitrogen in a silicon oxynitride can provide a barrier for boron penetration [8]. In addition, the high dielectric constant of oxynitride can reduce the leakage current. As transistor dimensions decrease, using a higher-k material can prevent the dielectric in the transistor from becoming so thin that leakage current reaches unacceptable levels because the physical thickness of dielectric insulator is proportional to dielectric constant.

4. EXPERIMENTAL PROCEDURE AND APPARATUS

4.1 Overview

The experiment consists of three phases: physical characterization of SiO_2 gate, physical characterization of nitrided gate, and electrical characterizations of SiO_2 and nitrided gates. The experiments for characterization of the gate oxide were based upon the current MATE 129 gate oxide process. The effect of oxidation time on silicon dioxide growth rate was investigated. The nitridation of gate oxide was performed under a set of conditions based upon reported values from literature. The oxynitride films were grown at three different oxidation times with a fixed N_2O gas flow rate. Finally, the electrical properties of silicon dioxide and silicon oxynitride were defined by measuring capacitances and leakage currents on MOS capacitors. The flow chart for these experiments is shown in Figure 14.

Figure 14. Flow chart of experiments.

4.2 Pre-oxidation wafer preparation

The gate oxides were grown on (100) p-type wafers using a Thermco Diffusion Furnace, Type B/A XL. Prior to oxidation, wafers were cleaned with a standard RCA process. The standard RCA clean is a four-step process: Standard Clean 1 (SC-1) followed by the Buffered Oxide Etch (BOE: $\text{H}_2\text{O}/\text{HF}$), Standard Clean 2 (SC-2), and spin dry. A detailed outline of the cleaning process is given in Table 2.

Table 2. Pre-gate clean. Source: Shop traveler, MATE 129, 2003.

Standard RCA	
Procedure	Parameters
<u>Clean step 1</u> Piranha dip + DI water rinse	-10min.Hot($T=110^\circ\text{C}$) H_2SO_4 (75%) + H_2O_2 (25%) -Dump rinser
<u>Clean step 2</u> BOE dip + DI water rinse	-Buffered Oxide Etch; 5 second max -Dump rinser
<u>Clean step 3</u> SC-2 step + DI water rinse	-10min.warm ($T=70^\circ\text{C}$) $\text{HCl}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ 1:1:6 -Dump rinser
<u>Clean step 4</u> Spin dry	Spin 2 minutes

4.3 Thickness of SiO_2 gate

The growth rate of silicon dioxide depends on oxidation time, gas composition, gas flow rate, and temperature. A growth rate relation was determined at a fixed temperature, fixed gas composition, and fixed gas flow rate. As a screen experiment, SiO_2 films were grown for 45 minutes. The thicknesses of films were thicker than a desired thickness, less than 300 Å. Thus, the thickness was determined at oxidation times

of 5, 10, 20, and 35 minutes. Four wafers were used at each oxidation time. The flow chart of the experiment is shown in Figure 15.

Figure 15. Flow chart of silicon dioxide thickness control.

4.4 Thickness measurement

The thickness was measured with a Nanometrics Nanospec 210 film thickness system. This system uses a scanned wavelength illumination source to determine the thickness and the refractive index of thin films. The spectrophotometer head scans a corrected spectrum by computing a ratio to a bare silicon reference previously stored. The resulting spectral data are used to determine the exact film thickness corresponding to the interference pattern. The wavelength range of this system is 370-800nm. The thickness was measured at nine points on the wafer. It is shown in Figure 16.

Figure 16. The scheme of oxide thickness measurement on a wafer.

The average thickness, the growth rate, and the uniformity were calculated for each oxidation run. The equation for growth rate is given in Equation 10.

$$Growthrate \left(\frac{\text{\AA}}{\text{min}} \right) = \frac{\text{Oxide thickness}}{\text{Oxidation time}} \quad \text{Equation 10}$$

For the uniformity of films, the mean thickness, standard deviation, and 95% confidence interval across the wafers were calculated.

4.5 Growth of silicon oxynitride with N₂O gas

The silicon oxynitride growth process was similar to the SiO₂ growth process. N₂O replaced O₂ as the oxidizing gas. Because the growth rate of silicon oxynitride under N₂O gas is much slower than the conventional oxidation process under O₂ gas, the oxidation time was much longer to get a compatible thickness with SiO₂. As a screen

experiment, silicon oxynitride films were grown for 20 minutes. There was no oxide detected after 20 minutes of growth. For that reason, longer oxidation times were required. Thus, silicon oxynitride films were grown under three different oxidation times: 45, 150, 300 minutes. The flow chart of the silicon oxynitride experiment is given in Figure 17.

Figure 17. Flow chart for oxynitridation of gate oxide.

4.6 Electrical characterization of SiO_2 and SiO_xN_y

The electrical characteristics were determined by measuring capacitances and leakage currents on MOS capacitors. Before measuring capacitances and leakage currents, MOS capacitors were fabricated on the wafers. Capacitances were measured from -5 volts to 2 volts and leakage currents were measured at 2 volts.

4.7 Fabrication of MOS capacitor

MOS capacitors of SiO_2 and SiO_xN_y were prepared by evaporating aluminum on top of the oxide films, through a copper template consisting of 36 holes. Each hole had an area of 0.079cm^2 . Aluminum was then evaporated on the back side of each wafer. The back side of each wafer was scratched with a diamond scribe before aluminum evaporation to ensure direct aluminum contact with the silicon substrate. After evaporation, the wafers were annealed in a furnace at 450°C for 30 minutes with mixed gas flow, consisting of 10% H_2 and 90% N_2 for better electrical contact between aluminum and Si. Figure 18 shows the flow chart of the MOS capacitance preparation, and Figure 19 shows the capacitors made on a wafer.

Figure 18. Flow chart of MOS capacitor fabrication.

Figure 19. Capacitors made on a wafer.

4.8 Capacitance measurement

Capacitance was measured with an HP 4140B PA meter/DC voltage source, an HP 4275A multi-frequency LCR meter, and a Signator probe station. A wafer was placed on the probe station with the front side of the wafer facing upward, and a probe was placed on a capacitor on the front side. The HP 4140 PA meter/DC voltage source swept from -5 volts to 2 volts at 10 kHz, with an increment of 0.1 volts for every 5 seconds. The HP 4275A multi-frequency LCR meter was connected with the back side of the wafer, and it displayed a capacitance at each voltage. Because the yield of the functional MOS capacitor was less than 100%, it was required to find working capacitors

for electrical testing. A working capacitor produces a capacitance versus voltage curve shown in Figure 20. The CV plot shown in Figure 20 is for a MOS capacitor made on an P type silicon substrate. A working capacitor has to show the pattern, corresponding to accumulation, to depletion, and to inversion, as shown in Figure 20.

Figure 20. MOS capacitor CV plot.

Once a working capacitor was found, an actual measurement took place on the capacitor. The capacitances at each voltage were read and plots of capacitances versus voltage curve were draw. Figure 21 shows the flow chart of capacitance measurement and Figure 22 shows a wafer placed on the probe station.

Figure 21. Flow chart of capacitance measurement.

Figure 22. A wafer placed on the probe station.

4.9 Leakage current measurement

Leakage current was measured with an HP 4145B semiconductor parameter analyzer. On the same probe station used for capacitance measurement, the probe was connected with the HP 4145. Leakage current was measured at 2 volts. To measure

leakage current, an IV curve was generated from -5V to 2V by using HP 4145. Then the current at 2V was read.

4.10 Materials and equipments

The following Tables 3 and 4 show the materials and equipment used for the experiment.

Table 3. Materials used for the experiment.

Description	Material used
Wafer	(100) P-type silicon wafer
RCA cleaning	H ₂ SO ₄ , H ₂ O ₂ , HF, and HCl
Oxidation	O ₂ and N ₂ gas
Oxynitridation	N ₂ O and N ₂ gas
Evaporation and annealing	Aluminum, 20%H ₂ and 80% N ₂ mixed gas

Table 4. Equipments.

1) Thermco B/AXL furnace
2) Nanometrics Nanospec 210 thin film thickness system
3) HP 4140 PA meter/DC voltage source
4) Aluminum evaporator
5) HP 4275A multi-frequency LCR meter
6) HP 4145B semiconductor parameter analyzer
7) HP 16058A test fixture
8) Signatone probe station

5. RESULTS AND DISCUSSIONS

5.1 Physical Characterization of SiO₂

From the thickness of SiO₂ experiment, the effect of oxidation time on silicon dioxide film growth was determined. SiO₂ films were grown for four different oxidation times; 5, 10, 20, and 35 minutes. After growing the SiO₂ film, thickness measurements were recorded on nine points per wafer.

5.1.1 Overall uniformity of SiO₂ film as function of time

Table 5 summarizes the results of the SiO₂ thickness characterization for each run of oxidation. All values were calculated for overall thicknesses for each oxidation time. Based upon calculated standard deviation and 95% confidence interval, the variations of film thickness is smaller for longer oxidation time. In the case of standard deviation, the variation was 15.5% for 5 minute oxidation and 2.8% for 35 minute oxidation from mean thicknesses.

Table 5. Mean thicknesses, standard deviations, and 95% confidence intervals of SiO₂ films for various oxidation times.

Oxidation Time (Min.)	Mean Thickness (Å)	Standard Deviation (Å)	% of Standard Deviation from mean thickness (%)	95% Confidence Interval (Å)
5	161.4	25.1	15.5	$154.8 \leq x \leq 168$
10	206.7	9.9	4.8	$203.5 \leq x \leq 209.9$
20	312.4	10.0	3.2	$309.1 \leq x \leq 315.7$
35	432.6	12	2.8	$428.7 \leq x \leq 436.5$

5.1.2 Uniformity of SiO₂ film along the boat

For thickness variations along the boat, the thicknesses of the center point of the wafers in a boat were plotted for each oxidation time. The center point is a representative sample of the wafer variation. The positions of wafers in a boat are described in Figure 23.

Figure 23. Schematic of the positions of wafers in a boat

As seen in Figure 24, the standard deviations of the thicknesses were smaller for longer oxidation time. There was no significant trend of thickness variation along the boat.

Figure 24. The thickness profile of SiO₂ films along the boat. The thickness of the center of each wafer is reported.

5.1.3 Uniformity of SiO₂ film across wafers

Examining the thickness variations across the wafers, it is important to compare wafers at the same position in the tube. Choosing a sample wafer to be representative to other wafers, a mean thickness of the wafer has to be similar to mean thicknesses of other wafers. By analyzing experimental data, the mean thickness of the first wafer for a 5minute oxidation time was too small compared to other wafers in the boat. The first wafer for a 5 minute oxidation time could not be used to compare the thickness variations across wafers. Other three wafers had similar thicknesses. For that reason, the thicknesses of the second wafers were plotted for each oxidation time. The second wafer

for each oxidation time is a representative sample of the wafer variation. As seen in Figure 25, the standard deviations of thickness were smaller at longer oxidation times.

Figure 25. The thicknesses of SiO_2 films across wafers for various oxidation times. The wafers chosen were the second wafers in the boat.

5.1.4 Growth rate of SiO_2

After measuring the thicknesses of films, growth rates were calculated based on Equation 10 and plotted. Figure 26 shows growth rates from experimental data, Deal-Grove linear parabolic model, and oxidation rate enhancement model. As shown in Figure 26, the oxidation rate from experimental data was higher than both models, while both the Deal Grove and enhanced model predict a similar growth rate over the range plotted in Figure 24. However, the pattern of growth rate from experimental data showed

a similar behavior to the Oxidation rate enhancement model. The pattern consisted of two growth rate regions which had a rapid growth rate in the thin oxide region, around 300Å, and a slow growth rate in the thick oxide region.

Figure 26. Oxidation rate vs. oxide thickness from experimental data, Deal-Grove linear parabolic model, and oxidation rate enhancement model.

5.2 Physical Characterization of SiO_xN_y with N_2O Gas

Silicon oxynitride (SiO_xN_y) films were grown at three different oxynitridation times by the dry thermal oxidation method with N_2O gas flow. For the physical characterization of the films, the thicknesses of the films were measured at nine points on each wafer according to Figure 16.

5.2.1 Overall uniformity of SiO_xN_y film

The mean thickness, standard deviation, and 95% confidence interval were calculated for each oxidation time. Similar to SiO_2 films, SiO_xN_y films showed more uniform film for longer oxidation time. As seen in Table 6, the standard deviation of SiO_xN_y films for 300 minute oxidation time was 5.3% compared to a 9.8% deviation for a 45 minute oxidation time.

Table 6. Mean thickness, standard deviation, and 95% confidence interval of SiO_xN_y for various oxidation times.

Oxidation Time (minutes)	Mean Thickness (Å)	Standard Deviation (Å)	% of Standard Deviation from mean thickness (%)	95% Confidence Interval (Å)
45	96	9.4	9.8	$92.9 \leq x \leq 99.1$
120	139.9	10.5	7.5	$136.5 \leq x \leq 143.3$
300	210.4	11.2	5.3	$206.7 \leq x \leq 214.1$

5.2.2 Uniformity of SiO_xN_y film along the boat

Examining variation along the boat, the center point of each wafer was chosen. As seen in Figure 27, a trend of thickness along the boat was observed that the first wafers, toward to the gas flow, showed the highest thicknesses compared to other wafers and the thicknesses of the films tended to decrease as the wafers were far from the flow. The variations of the wafers along the boat decreased with longer oxidation time.

Figure 27. The thickness profile of SiO_xN_y films along the boat. The thickness at the center of each wafer is reported.

5.2.3 Uniformity of SiO_xN_y film across wafers

Identical to the SiO_2 film, the second wafer in the boat for each oxidation time was chosen to plot thicknesses across the wafer. As seen in Figure 28, SiO_xN_y films also showed better uniformity across the wafer for longer oxidation times. The standard deviation of the thicknesses for 300 minute oxidation time was much smaller than that of 45 minute oxidation time.

Figure 28. The thicknesses of SiO_xN_y films across wafers for various oxidation times. The wafers chosen were the second wafers in the boat.

5.2.4 Growth rate of SiO_xN_y film

Growth rates of SiO_xN_y were calculated from thicknesses of SiO_xN_y corresponding to oxidation times. As seen on Figure 29, the growth rate of SiO_xN_y showed a similar pattern to SiO₂. The growth rate was high at the beginning and slowed down as the thickness increased. The growth rate at 100Å was almost three times faster than that at 200Å. However, the growth rate of SiO_xN_y film was much slower than that of SiO₂ film. One possible reason for the slow growth rate of SiO_xN_y film could be that if the concentrations of O₂ and NO gases decomposed from N₂O gas were low in the gas stream compared to the SiO₂ process and the main molecules associated in the oxidation

process were O_2 and NO gases, relatively low concentration of O_2 and NO gas in the stream could result in low growth rate compared to that of SiO_2 film. According to Gusev [6], the final concentrations of N_2 , O_2 , and NO gas in a furnace after decomposition of N_2O gas at 1223K were 61%, 27%, and 13%, respectively. The total concentration of NO and O_2 was 40% and was much smaller compared to 100% O_2 gas for the SiO_2 film.

Figure 29. Growth rate of SiO_xN_y film.

5.3 Capacitance Measurements

Capacitances were measured from -5V to 2V on 3-4 working capacitors. Figure 30 and 31 show the capacitances of SiO_2 and SiO_xN_y for various thicknesses, respectively.

Figure 30. Capacitances of SiO₂ with various thicknesses.

Figure 31. Capacitances of SiO_xN_y for various thicknesses.

For both films, the maximum capacitances were determined at -5V, and it was observed that the thinner the oxide, the higher the maximum capacitances. Also threshold voltage shifts were observed as the thickness changed for both films. However, no significant relationships were found between thicknesses and threshold voltage shifts. Along with threshold voltage shift, distortions of CV curves were also observed. The distortion of CV curve could be due to interface trapped charge, Q_{it} . Q_{it} is likely due to some type of incompletely oxidized silicon atom with unsatisfied or dangling bonds located in the oxide but very close to the interface. According to theory [1], the distortion of CV curve is mainly caused by Q_{it} .

5.3.1 Maximum capacitance (C_{max}) comparison between SiO_2 and SiO_xN_y films

One way to compare capacitance of two films is comparison of maximum capacitances.

$$C = \frac{keA}{d} \quad \text{Equation 11}$$

C is capacitance in Farads, k is dielectric constant of insulator, e is permeability constant, A is plate area in m^2 , and d is dielectric thickness (m), respectively. From equation 11, the capacitance is inversely proportional to the thickness of the insulator and proportional to the dielectric thickness. As seen on Figure 32, C_{max} decreased as the thickness increased for both SiO_2 and SiO_xN_y films. This is in agreement with Equation 11. However, the C_{max} of SiO_xN_y was less compared to that of SiO_2 at measured thicknesses even though the dielectric constant of SiO_xN_y film is greater than that of SiO_2 . This is in

contradiction to Equation 11. The gray box in Figure 32 indicates the data points where the comparison between SiO_2 and SiO_xN_y films took place.

Figure 32. Maximum capacitances ($C_{\max}$) at various thicknesses of films.

5.4 Leakage Current

Leakage currents were measured at 2V for both SiO_2 and SiO_xN_y films. 2V was used to protect the capacitor from failure. Each leakage current was the mean value of 3-4 capacitors for each thickness. According to theory, the leakage current increases as the thickness of an insulator decreases, and an insulator with high dielectric constant should have less leakage current compared to other insulators with lower dielectric constants [7]. As shown in Figure 33, the leakage current increased as the thickness decreased for both

films. It was also observed that the leakage currents of SiO_xN_y films were smaller than those of SiO_2 films at the measured thicknesses. The gray box in Figure 33 indicates the data points where the comparison between SiO_2 and SiO_xN_y films took place.

Figure 33. Leakage currents versus thicknesses of SiO_2 and SiO_xN_y films.

Examining the relationship between capacitance and leakage current, the plots of current C_{max} versus leakage were prepared. As shown in Figure 34, the data was analyzed in two regimes: thick and thin regimes. In the thick regime, thicker than $100\text{\AA}$, SiO_xN_y films showed lower capacitances than those of SiO_2 at given leakage currents. It was not expected. According to theory, a SiO_xN_y films should have higher capacitances than that of a SiO_2 film at a given leakage current [7]. However, in the thin regime, less than $100\text{\AA}$, the pattern of the relationship between capacitance and leakage current

showed that the capacitance of the SiO_xN_y film seemed to be greater than that of the SiO_2 film at the given leakage current. In the other word, a thin SiO_xN_y film, less than $100\text{\AA}$, would have a higher capacitance with a lower leakage current compared to a SiO_2 film at a given thickness.

Figure 34. $C_{\max}$ versus Leakage currents for SiO_2 and SiO_xN_y films.

6. CONCLUSIONS

Thin SiO_2 and SiO_xN_y films less than $250\text{\AA}$ can be grown in the SJSU IC Lab. The overall thickness uniformity was better for longer oxidation time for both SiO_2 and SiO_xN_y films. The uniformities of films across the wafers and along the boat were also better for longer oxidation time for both films. In Figure 27, it was observed that the first wafer of SiO_xN_y film which was near the front boundary had abnormally higher thicknesses than other wafers. The reason for thickness difference might be due to temperature difference throughout the axial direction of the tube. It is believed that the main factor causing temperature difference through the axial direction of the tube could be the decomposition of N_2O gas. The decomposition of N_2O gas is a highly exothermic reaction and more than 50% of N_2O gas was decomposed before it reached the first wafer in the boat. For that reason, the temperature near the front boundary between the front part of the tube and the flat zone might be higher than other parts of the flat zone. At the higher temperature, thicker films are expected.

The film growth rate decreased as thickness increased for both SiO_2 and SiO_xN_y films. The growth rate consisted of two regions for both films. Two regions were high growth rate in the thinner region and relatively slow growth rate in the thicker region. The film growth rate of SiO_2 was high compared to theory. However, the pattern of growth rate was similar to the oxidation rate enhancement model.

For thinner SiO_2 film, either less oxidation time or lower temperature can be used. However, using a short oxidation time of less than 5 minutes is not recommended because of difficulty in process control. A short oxidation time at a lower a temperature,

no lower than 800°C, would be the best choice for a thinner SiO₂ film. Growing SiO_xN_y with N₂O gas, using a high temperature is always preferred for complete decomposition of N₂O gas. In case of slow growth rate of SiO_xN_y film, either a higher gas flow rate or oxidation temperature can accelerate the growth rate.

The $C_{\max}$ of the films were increased as the thickness decreased for both SiO₂ and SiO_xN_y films, which was expected from theory. However, $C_{\max}$ values at different thicknesses were less for SiO_xN_y compared to those of SiO₂ films from the experiment data. This was not expected. According to the capacitance equation, the $C_{\max}$ of SiO_xN_y films should be higher than that of SiO₂ films, because the capacitance is proportional to dielectric constant and SiO_xN_y has greater dielectric constant than SiO₂. However, shown in Figure 34, the capacitance of the SiO_xN_y film, less than 100 Å would be greater than that of SiO₂.

By comparing leakage currents between equivalent thicknesses of SiO₂ and SiO_xN_y films, the leakage currents of SiO_xN_y films were less than those of SiO₂ films from the experiment data.

From the examination of relationship between capacitance and leakage current, the capacitances of SiO_xN_y films were lower than those of SiO₂ films at the given leakage currents in the thick regime, thicker than 100 Å. However, it was predicted that the capacitance of SiO_xN_y film would be higher than that of SiO₂ film, when the thickness of film was less than 100 Å.

7. FUTURE WORK

The future work related to this research should involve a more precise film thickness measurement and dielectric constant measurements. The thickness measurement instruments in the IC lab are not precise enough for either thin SiO_2 , less than $100\text{\AA}$, or thin SiO_xN_y films. In addition to film thickness measurement, a dielectric constant measurement for a thin film is required. After growing films, it is questionable whether the grown films are contamination-free SiO_2 or SiO_xN_y films. Because SiO_2 or SiO_xN_y film has its own dielectric constant, by measuring the dielectric constant of each film, it will assure the purity of the film.

With precise film thickness and dielectric constant, it will be helpful to build an actual device on a wafer with each film. The performance of devices made with each film will provide more detailed properties of the films.

Also, other types of gases, NH_3 or NO gas, can be used for growing SiO_xN_y film by thermal oxidation. Among the gases, NO gas will be the best choice because NH_3 gas has an issue associated with H_2O as a by-product. The oxidation process with NO gas consists of two step processes: oxidation with O_2 gas and re-oxidation with NO gas.

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APPENDIX: Raw thickness data of SiO₂ and SiO_xN_y films

A1. Thickness (Å) of SiO₂ films after 5minute oxidation.

	1	2	3	4	5	6	7	8	9
Wafer #1	104	104	110	122	134	132	132	135	132
Wafer #2	161	157	160	175	175	178	180	181	188
Wafer #3	160	159	161	169	171	171	174	179	188
Wafer #4	168	172	170	177	186	186	186	189	186

A2. Thickness (Å) of SiO₂ films after 10 minute oxidation.

	1	2	3	4	5	6	7	8	9
Wafer #5	239	225	204	203	215	204	193	203	199
Wafer #6	225	219	213	211	214	216	207	208	208
Wafer #7	213	201	192	202	204	202	198	200	202
Wafer #8	215	208	201	205	199	203	195	194	202

A3. Thickness (Å) of SiO₂ films after 20 minute oxidation.

	1	2	3	4	5	6	7	8	9
Wafer #9	306	311	309	318	321	318	333	337	331
Wafer #10	298	300	306	307	311	316	320	327	323
Wafer #11	296	300	306	301	304	313	315	317	319
Wafer #12	305	304	308	308	301	309	319	316	315

A4. Thickness (Å) of SiO₂ films after 35 minute oxidation.

	1	2	3	4	5	6	7	8	9
Wafer #13	431	436	436	431	438	434	436	441	446
Wafer #14	428	429	427	427	442	430	430	435	450
Wafer #15	440	440	442	436	443	443	440	444	461
Wafer #16	410	415	418	410	427	414	409	415	438

A5. Thicknesses ($\text{\AA}$) of SiO_xN_y films after 45 minute oxynitridation.

	1	2	3	4	5	6	7	8	9
#N1	104	105	112	103	101	128	95	94	105
#N2	97	91	96	93	82	108	85	84	91
#N3	92	92	94	95	86	107	87	83	92
#N4	96	96	99	94	88	108	90	89	94

A6. Thicknesses ($\text{\AA}$) of SiO_xN_y films after 120 minute oxynitridation.

	1	2	3	4	5	6	7	8	9
#N5	140	142	141	145	149	152	145	149	156
#N6	151	147	139	153	153	149	144	148	143
#N7	139	138	138	145	142	140	143	143	148
#N8	125	120	122	129	119	125	124	122	129

A7. Thicknesses ($\text{\AA}$) of SiO_xN_y films after 300 minute oxynitridation.

	1	2	3	4	5	6	7	8	9
#N9	222	219	217	223	224	228	222	225	231
#N10	217	212	216	216	213	219	208	213	228
#N11	203	195	200	203	200	213	197	203	213
#N12	195	193	199	198	194	200	200	203	213