Growth and characterization of low-k dielectrics for multilevel interconnect applications

Wang, Minrui

2005

Wang, M. (2005). Growth and characterization of low-k dielectrics for multilevel interconnect applications. Master's thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/3674>

<https://doi.org/10.32657/10356/3674>

Nanyang Technological University

Downloaded on 26 Apr 2023 15:44:36 SGT

GROWTH AND CHARACTERIZATION OF LOW- k DIELECTRICS FOR MULTILEVEL INTERCONNECT APPLICATIONS

WANG MINRUI

SCHOOL OF ELECTRICAL & ELECTRONIC ENGINEERING
NANYANG TECHNOLOGICAL UNIVERSITY

2005

Growth and Characterization of Low- k Dielectrics for Multilevel Interconnect Applications

Wang Minrui

School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
Master of Engineering

2005

Acknowledgements

Acknowledgements

I would like to thank my supervisor, Associate Professor, Rusli, School of Electrical and Electronic Engineering, Nanyang Technological University, for the patient guidance and advice, personal inspiration and encouragement, and kind support in this period of my study. His erudition in plasma physics and carbon related materials gives me deep impression, which greatly enhances my knowledge in these fields.

I wish to express my heartfelt gratitude to Mr. Rakesh Kumar, Senior Technological Manager, Micro-Fabrication of Semiconductor Process Technologies, Institute of Microelectronics, for his strong and consistent support and encouragement.

I am very grateful to Dr. Li Chaoyong, Process Modules of Semiconductor Process Technologies, Institute of Microelectronics, for his valuable suggestion and tremendous support in the progress of the study. Thanks go to Ms. Wang Shurui for her assistance in AFM measurement, which is indispensable in my research work, Ms. Catherine Li Weihong for help in EDX measurements, and Ms. Stella Yuan Yijing for the annealing work. Very useful help to measure film thickness and refractive index comes from Dr. Yu Mingbin, Silicon Photonics & Devices of Semiconductor Process Technologies, Institute of Microelectronics, his strong background in material characterization and experimental skill impress me very much.

Acknowledgements

I also wish to express my appreciation to the colleagues from the PECVD group, for their help and precious friendship, their names will be remembered with gratitude: Mr. Narayanan Babu, Mr. Xie Jieli, and Dr. Wang Yihua. The co-operation from the Semiconductor Process Technologies lab, especially from Mrs. Lu Peiwei and others are also acknowledged.

I wish to thank my wife and my lovely daughter, to whom my love is beyond any words.

At last, I would like to acknowledge the support from Administration of Institute of Microelectronics for this study.

Table of Contents

Table of Contents

	Page
Acknowledgments	I
Table of contents	III
Summary	XII
Chapter 1: Introduction	1
1.1 Background	1
1.2 Motivation for the work	1
1.3 Objectives of the work	2
1.4 Organization of the report	3
1.5 References	4
Chapter 2: Literature review	5
2.1 Introduction	5
2.2 Interconnect delay	7
2.3 Definition of low k	8
2.4 Mechanism of dielectric constant reduction	9
2.5 Requirements of low k dielectric	10
2.6 Low dielectric technology approach	11
2.7 Fundamental of plasma enhanced chemical vapor deposition	13
2.8 Low constant dielectric application	14
2.9 References	17

Table of Contents

Chapter 3:	Experimental setup	19
3.1	Introduction	19
3.2	Plasma enhanced chemical vapor deposition (PECVD) system	20
3.3	Low k annealing system	23
3.4	Film inspection and characterization techniques	23
3.4.1	Unpatterned wafer inspection system	23
3.4.2	Spectrometric reflectance tool	24
3.4.3	Fourier transforms infrared absorption spectroscopy (FTIR)	24
3.4.4	Dielectric constant measurement - MIS structure	26
3.4.5	Atomic Force Microscopy (AFM)	26
3.4.6	Stress measurement	30
3.4.7	Energy Dispersive X-ray spectrometer (EDX)	32
3.5	Substrates	33
3.6	References	34
Chapter 4:	Optimization of process steps and the effects of oxygen in the growth process	35
4.1	Introduction	35
4.2.	Experimental details	37
4.3.	Results and discussion	37
4.3.1	Process reproducibility	37
4.3.2	Particle counts and element composition	38
4.3.3	Deposition rates	41

Table of Contents

4.3.4	Refractive index and dielectric constant	43
4.3.5	FTIR spectra	46
4.4	Conclusion	52
4.5	References	53
Chapter 5: Effects of annealing on low dielectric		
	constant carbon doped silicon oxide films	54
5.1	Introduction	54
5.2	Experimental details	54
5.3	Results and discussion	55
5.4	Conclusion	64
5.5	References	65
Chapter 6: Effects of changing process pressure		66
6.1	Introduction	66
6.2	Experimental details	66
6.3	Results and discussion	67
6.4	Conclusion	74
6.5	References	75
Chapter 7: Optical properties of the carbon doped oxide film		76
7.1	Introduction	76
7.2	Experimental details	77

Table of Contents

7.3	Results and discussion	78
7.3.1	FTIR spectra and dielectric constants of the SiO(C, H) film	78
7.3.2	Two-layer growth of the SiO(C, H) film	80
7.4	Conclusion	85
7.5	References	86
Chapter 8:	Conclusion and recommendations	87
8.1	Conclusion	87
8.2	Recommendations for further research	89
	Author's publications	90

Table of Contents

List of Figures

	Page
Figure 2.1: Technology evaluation and acceleration – Moore’s Law (1975)	5
Figure 2.2: Decrease in interconnect delay and improved performances are achieved using copper and low-k dielectrics	6
Figure 2.3: Capacitance occurs within and between metal layers	7
Figure 2.4: Cross-section of hierarchical scaling	16
Figure 3.1: Schematic diagram of inverse radial flow reactor with perforated electrode	21
Figure 3.2: Schematic diagram of PECVD configuration	21
Figure 3.3: Atomic Force Microscope system layout	27
Figure 3.4: Inter atomic force vs. distance curve	28
Figure 3.5: Diagram of stress measuring apparatus	32
Figure 4.1: The pre (a) and post-deposition (b) maps of wafer 3 in experiment 2 deposited using recipe CVD1 with a thickness of 3000 Å	39
Figure 4.2: (a) SEM image showing a particle embedded in the carbon doped silicon oxide films. (b) A typical EDX spectrum of the particles revealing the presence of Si, O and C	40
Figure 4.3: (a) Deposition rates of films with different thickness using recipe CVD1 and CVD2 in experiments 2 and 3 respectively,	

Table of Contents

and (b) deposition rates of films with different $O_2/3MS$	
flow ratios in experiment 4	42
Figure 4.4: (a) Refractive indices and (b) k values of the films deposited	
with different thickness using recipe CVD1 and CVD2	
in experiments 2 and 3 respectively	44
Figure 4.5: Refractive indices and k values of the films deposited	
with different $O_2/3MS$ flow ratios in experiment 4	45
Figure 4.6: FTIR spectra of the films deposited using recipe CVD1	
in experiment 2 with different film thickness	47
Figure 4.7: FTIR spectra of the films deposited using recipe CVD2	
in experiment 3 with different film thickness	47
Figure 4.8: (a) FTIR spectra of the films deposited with different	
$O_2/3MS$ flow ratios in experiment 4. (b) Enlarged FTIR	
spectra showing the main absorption bands	48
Figure 4.9: The integrated absorption area ratio of Si-CH ₃ and	
Si-O bonds plotted (a) as a function of thickness for films	
deposited in experiment 2 and 3, and (b) as a function of	
$O_2/3MS$ flow ratio for films deposited in experiment 4	50
Figure 4.10: The k values versus the Si-CH ₃ /Si-O integrated absorption	
area ratio for films deposited in experiments 2, 3 and 4	51
Figure 5.1: Thickness shrinkage after annealing treatment	
at different temperatures	56

Table of Contents

Figure 5.2: Refractive indices of the films as a function of the annealing temperature	56
Figure 5.3: Dielectric constant of the films as a function of the annealing temperature	58
Figure 5.4: Surface morphology of the films (a) as deposited, (b) annealing at 400°C, (c) annealing at 500°C, (d) annealing at 600°C, (e) annealing at 700°C	59
Figure 5.5: The change of root mean square roughness of the films as-deposited and annealed films	60
Figure 5.6: The FTIR spectra of as-deposited and annealed films	61
Figure 5.7: The integrated absorption area ratio of the Si-CH ₃ bonds to Si-O bonds for as-deposited and annealed films	62
Figure 5.8: The film stress for as-deposited and annealed films	63
Figure 6.1: Variation of deposition rate with changes of the deposition pressure	67
Figure 6.2: Refractive indices of the SiO(C, H) films on the deposition pressure	68
Figure 6.3: The dielectric constants of the SiO(C, H) films on the deposition pressure	69
Figure 6.4: The FTIR spectra of the SiO(C,H) films	70
Figure 6.5: The Si-CH ₃ /Si-O ratio of the SiO(C, H) films on the deposition pressure	71

Table of Contents

Figure 6.6: Surface morphology of the SiO(C, H) films prepared with varying deposition pressure of (a) 1.5Torr, (b) 2.0Torr, (c) 4.0Torr, (d) 6.0Torr and (e) 8.0Torr.	72
Figure 6.7: The root mean square (RMS) roughness of the SiO(C, H) films on the deposition pressure	73
Figure 7.1: FTIR spectra of the SiO(C,H) films deposited at different O ₂ /3MS flow ratios	79
Figure 7.2: Dielectric constants of the SiO(C,H) films as a function of the O ₂ /3MS flow ratio	79
Figure 7.3: The integrated FTIR absorption area ratio of the Si-CH ₃ bonds to Si-O bonds for SiO(C,H) films as a function of O ₂ /3MS flow ratio	80
Figure 7.4: The measured and simulated reflectance spectra of the SiO(C,H) film deposited with a O ₂ /3MS flow ratio of 100/600 using (a) one layer model and (b) two layer model	82
Figure 7.5: The refractive indices and extinction coefficients of the (a) lower layer and (b) upper layer of the SiO(C,H) film deposited with a O ₂ /3MS flow ratio of 100/600.	83
Figure 7.6: The thickness of the lower and upper layers of the SiO(C,H) films deposited at different O ₂ /3MS flow ratios	84

Table of Contents

List of tables

	Page
Table 2.1: Low k dielectric materials requirements	10
Table 2.2: Interconnect Technology Roadmap (ITRS' 2001)	14
Table 4.1: Summary of process steps of recipes CVD1 and CVD2	36
Table 4.2: The number of added-in particles on film surfaces. In experiments 2 and 3, wafers 1 to 5 correspond to films deposited with nominal thickness from 1000Å to 5000 Å. In experiment 4, wafers 1 to 7 correspond to films deposited with O ₂ /3MS flow ratios from 1/6 to 7/6	38
Table 7.1: SCI material model coefficients	81

Summary

Summary

This thesis focuses on the growth and characterization of carbon doped silicon oxide ($\text{SiO}(\text{C,H})$) low k dielectrics for multilevel interconnect applications.

$\text{SiO}(\text{C,H})$ films are formed by the plasma enhanced chemical vapor deposition (PECVD) technique using linear organosilicate trimethylsilane (3MS) as precursor and oxygen as oxidizer. The properties of this dielectric film have been investigated by energy dispersive x-ray (EDX) spectrometer, Fourier transform infrared (FTIR) absorption and atomic force microscopy (AFM). Other measurement tools applied include KLA-Tencor[®] SP1 for blanket wafer particle counts, Thermawave Opti-probe for thickness, uniformity and refractive index measurement, SSM[®] C-V system for k value measurement and FSM system for stress measurement.

The properties of the PECVD prepared $\text{SiO}(\text{C,H})$ films are dependent not only on the process parameters but also process sequences. The $\text{SiO}(\text{C,H})$ low k films deposited using an initial recipe labelled as CVD1 suffer from serious particle issue. To address the particle issue, we have optimized the oxygen and helium treatment process sequence, immediately before and after film deposition step. Using this new recipe CVD2, it has been found that the serious particle issue could be resolved. However this rearrangement compromises the other properties of the films in terms of a slight

Summary

increase in the dielectric constant and non-uniform deposition rate as a function of film thickness.

For films deposited with different O₂/3MS gas flow ratio, it is found that the deposition rate increases while the refractive index decreases with increasing oxygen concentration in the gas feed. Dielectric constant as low as 2.9 has been obtained for the as-deposited film with an optimized O₂/3MS flow ratio of 100/600. Thermal annealing has been found to reduce the dielectric constant of the films at 400 °C. The films are also found to be thermally stable up to as high as 500 °C in terms of their composition and chemical structure.

The effects of deposition pressure on the properties of SiO(C,H) films have also been investigated. An increase in the deposition pressure resulted in films with lower dielectric constants and refractive indices. A dielectric constant as low as 2.9 has been obtained for the film deposited at 8.0Torr and a high deposition rate of 5120 Å/min has been obtained for films deposited at 4.0Torr.

We have also studied the optical properties of the SiO(C,H) films. Their reflectivity were measured under normal incident and at 70° incident angle using polarized light, over a range of wavelengths from 200nm to 1700nm, to determine their optical constants (n and k) and thickness. It is found that the growth of SiO(C,H) films involves a two-layer process, in which a layer of thin SiC:H film is first formed, which

Summary

is then followed by the growth of SiO(C,H) film. We have proposed a growth mechanism to explain the two-layer growth process. Though the thin layer of SiC:H does not have much influence on the dielectric constants of the SiO(C,H) films, however, it may pose a potential challenge for these low k films in terms of advanced integration, such as acting as an unexpected etch stop layer.

Chapter 1: Introduction

1.1 Background

Continuous shrinking of interconnect pitch on integrated circuits increases wire resistance of smaller metal line and makes the crosstalk effects between closer metal space severer. Consequently these degrade interconnect RC delay and limit the high performance of integrated circuits (IC). In order to reduce the RC delay, it is necessary to decrease the capacitances among the metal lines by using low permittivity (low k) dielectrics as isolation material, besides using lower resistance metal interconnects. Hence, the International Technology Roadmap for Semiconductors (ITRS) calls for the implementation of low k materials. As a result, over the past few years, low dielectric materials have been under intensive research.

1.2 Motivation for the work

The implementation of low dielectric constant materials in ultra-large-scale integrated (ULSI) devices has been repeatedly delayed and the technology is taking much longer to move into production than originally planned [1,2]. Difficulties exist in retaining the low dielectric permittivity properties and compatibility during the integrated process. The challenges have proven to be substantial, requiring new

Chapter 1: Introduction

approaches for characterization and integration of low k materials with copper [3]. If the factors relating to the properties of low k materials have been fully understood right from the beginning, then the implementation of low dielectric constant materials may be as short as what it is expected to be.

1.3 Objectives of the work

This research topic will focus on the growth and characterization of low k dielectric thin films for multilevel interconnect applications, including the characterization of the material properties and the optimization of the process steps. Specifically, the dielectric that we will be investigating is carbon doped silicon oxide ($\text{SiO}(\text{C}, \text{H})$) thin films deposited using the plasma enhanced chemical vapor deposition (PECVD) process from organosilicon precursor trimethylsilane ($\text{C}_3\text{H}_9\text{Si}$, also referred to as 3MS) and oxygen. This dielectric is one of the most favorable low k materials due to their low k (<3) and their key electrical and integration characteristics being similar to those of SiO_2 [3]. The molecular structure of 3MS necessitates the use of an oxidant in the deposition process to provide a low k Si-O network [4]. The incorporation of carbon atoms serves to reduce the dielectric constant due to their reduced polarizability compared to silicon and oxygen [5].

The properties of the $\text{SiO}(\text{C}, \text{H})$ films depend on the process parameters such as the flow rate and process pressure. In this work, we will focus on:

Chapter 1: Introduction

- 1) optimizing the deposition process sequences,
- 2) evaluating the feed gas flow ratio impacts on the dielectric k value and other properties,
- 3) investigating the thermal stability of the low dielectric constant films by post annealing,
- 4) studying the process pressure effects on the dielectric k value and other properties and
- 5) studying their optical properties.

1.4 Organization of the report

In the physical order, the chapters of this thesis are arranged as follows:

Chapter one gives an introduction, detailing the background, motivation and objective of this study. Chapter two presents information about technology trend for low k/copper including the single and dual damascene schematics. Chapter three describes the experimental equipment and characterization tools used. Chapter four details the study of oxygen influences on SiO(C,H) films and considers the impact of process sequences on the properties of the films. Chapter five reports on the SiO(C,H) films prepared using different O₂/3MS flow ratios, and investigate their thermal stability through post-deposition annealing. Chapter six presents the study of the SiO(C,H) films under different process pressures. Chapter seven presents a study on the optical properties of the films. Chapter 8 presents the conclusion and future work of our study.

Chapter 1: Introduction

1.5 References

- 1 Katherine Derbyshire, Still waiting for low-k dielectrics, Semiconductor Manufacturing Magazine, January 2002 Vol. 3, No. 1.
- 2 Katherine Derbyshire, High frustration over low-k, Semiconductor Manufacturing Magazine, October 2003 Vol. 3, No. 10.
- 3 Laura Peters, Industry divides on low k dielectric choices, Semiconductor International, June 1998.
- 4 B. Narayanan, R. Kumar and P. D. Foo, "Properties of low-k SiCOH films prepared by plasma-enhanced chemical vapor deposition using trimethylsilane", Microelectronics Journal, Vol. 33, pp. 971 - 974, 2002.
- 5 Keith Buchanan, The evolution of interconnect technology for silicon integrated circuitry, 2002 GaAsMANTECH Conference.

Chapter 2: Literature review

Deleted: ¶

Chapter 2: Literature Review

Deleted: two¶

2.1 Introduction

Continuous improvement in integrated circuit feature size (miniaturization) and device performance (faster operating speed and higher packing density) have been achieved through multi-level metallization scheme. This trend in accordance with Moore's Law (the number of components per chip doubles every 18 months) [1] as shown in Fig. 2.1. Multi-level metallization allows increased functionality (transistor connectivity) whilst simultaneously decreases the average metal line length, the latter being having a large influence on the interconnect-related $R \times C$ (resistance $\times$ capacitance) signal propagation delay [2].

Figure 2.1: Technology evaluation and acceleration – Moore's Law (1975).

Deleted: 1

Chapter 2: Literature review

Deleted: ¶

The speed of IC devices is limited by the resistance of metal layers and the capacitance of dielectric insulating materials surrounding the metal lines. The speed of devices can also be limited by transistor dimensions, however, these are already very small in advanced processes, and are not longer the contributing factors to signal propagation delay. Figure 2.2 illustrates that the interconnect delay is beginning to dominate the overall device delay at 0.18 μm , therefore, it is important to switch to lower resistivity metals such as copper as well as low k dielectric materials [3].

Deleted: Literature survey¶

¶ What is low k?¶

¶

A low dielectric constant material can be defined as a dielectric material with dielectric constant close to or less than about 3.¶

¶

¶ Why low k?¶

Deleted: ¶

In modern integrated circuits the feature size is scaled down while the chip area is scaled up, hence delays due to resistance and capacitance of interconnecting lines become the predominant part of the total delay. This will increasingly limit the performance of high-speed logic chips.

Deleted: ig.

Deleted: dominance of interconnect RC delay over gate delay for as feature size beyond 180 nm.

Figure 2.2: Decrease in interconnect delay and improved performances are achieved using copper and low k dielectrics.

Deleted: 1

As device integration has been shown to be more difficult than predicted, the transition from SiO₂ (CVD $k = 4.1 - 4.2$) to new dielectric materials with $k < 3.0$ was delayed by about three years, compared to the initial semiconductor industry association Roadmap targets [4].

Chapter 2: Literature review

Deleted: ¶

2.2 Interconnect delay

Deleted: ¶

Interconnect delay is determined using the well-known formula:

$$T = RC \quad (2.1)$$

where R is the line resistance of the interconnect metal and C is the capacitance associated with the isolation dielectric. A schematic diagram of an interconnect is shown in Fig. 2.3.

Figure 11:

Deleted: RC delay Calculated gate and interconnect delay versus technology generation. [1y]¶

Deleted: RC

Deleted: related to the line resistance of the interconnect metal (R) and capacitance associated with the isolation dielectric (C).

Deleted: as

Deleted: . [000]

Figure 2.3: Capacitance occurs within and between metal layers [5].

The total resistance R of the metal line can be expressed as

$$R = 2\rho L / (PT) \quad (2.2)$$

where ρ is the resistivity of the metal line, L is length of the interconnect line,

P is the pitch or line spacing, and T is the thickness of the line.

There are two types of capacitance: the vertical layer-to-layer capacitance C_v and the lateral line-to-line capacitance C_{LL} . The total capacitance C can be expressed as

Deleted: ¶

Deleted: .

Deleted: /(

Deleted:

Deleted: 1

Deleted: .

Deleted: .

Deleted: .

Deleted: spacing ,

Deleted: .

Deleted: ¶

Deleted: .

Deleted: types of capacitance

Deleted: s

Deleted: ,

Deleted: namely

Deleted: .

Deleted: L

Chapter 2: Literature review

Deleted: ¶

$$C=2(C_k+C_{LL})=2k\epsilon_o(2LT/P+LP/2T) \quad (2.3)$$

Deleted: .

Deleted: L

Deleted:)=

Deleted: (

Deleted:)

Deleted: (

Deleted:)

Deleted: .

Deleted: 2

Deleted: . where

Deleted: .

Deleted: .

Deleted: E

where k is the dielectric constant or relative permittivity and $\epsilon_o = 8.85 \times 10^{-12}$ F/m is the permittivity of vacuum.

Combining equations (2.1), (2.2) and (2.3), yields the equation for interconnect delay

$$T=RC=2\rho k\epsilon_o L^2(4/P^2+1/T^2) \quad (2.4)$$

Deleted: .

Deleted: (

Deleted:)

Deleted: (

Deleted:

Deleted: 3

Deleted: ¶

Deleted: 3

Deleted: increasing

Deleted: hus

Deleted:)

Deleted: .

Equation (2.4) shows that the common chip geometry drivers, that is, decreasing P and T , will result in larger RC delay. Furthermore, increasing system complexity and size of die are causing L to increase [5]. Therefore, the RC delay can only be reduced by decreasing ρ and k . Hence, besides using copper metallization, there is a need for low dielectric constant (low k) materials to replace conventional SiO_2 .

2.3 Definition of low k

The dielectric constant of a dielectric is defined as the ratio of its permittivity to the permittivity of vacuum. A dielectric material having relatively greater insulating property than silicon dioxide (SiO_2), usually with a $k < 3.9$ is termed as a low dielectric constant material [6]. In practice, low k materials are mostly defined as dielectrics with a bulk dielectric constant below 3.0 [7].

Chapter 2: Literature review

Deleted: ¶

2.4 Mechanism of dielectric constant reduction

There are two primary approaches towards achieving low dielectric constant materials. The first approach is to reduce polarizability by lowering the electronic, ionic, and/or the orientation contribution [8]. The electronic component refers to the oscillation of electrons in chemical bonds and/or in the extended super molecular structure. The latter two components constitute the nuclear response and are important at lower frequencies ($<10^{13}$ Hz), while the electronic response dominates at higher frequencies (4.74×10^{14} Hz). At typical device operating frequencies, currently $<10^9$ Hz, all three components contribute to the dielectric constant and must be minimized for optimum performance [4]. The second approach is to increase the porosity and reduce the mass density [8], as this will lower the dielectric constant. The lower dielectric constant of non-polar organic polymers (~ 2.0 - 2.8) relative to SiO_2 (3.9 - 4.2) is partly due to the presence of lighter C and H atoms versus Si and O atoms, as well as the low packing density (~ 1.0 g/cm³) relative to the denser tetrahedral silica network (~ 2.4 g/cm³). The incorporation of non-polar and space-occupying groups such as methyl will also increase free volume in a silica network [4].

The $\text{SiO}(\text{C,H})$ films investigated in this work utilize a combination of both approaches. However, the reduction in dielectric constant is usually achieved at the expense of other desirable material properties and this can make integration more difficult. In both cases the reduced network bonding and reduced density contribute negatively to the film's mechanical properties [9]. Two unavoidable consequences will be resulted from the reduction in k value. Firstly, the films are not as hard, with

Chapter 2: Literature review

Deleted: ¶

negative implication for chemical and mechanical polishing process and wire bonding, and secondly their thermal conductivity is significantly lower than that of SiO₂ [10].

Potential low k materials can be categorised into different groups such as fluorosilicates, organo-silicates and organic polymers. They are also distinguished by the deposition technique used for the growth, such as CVD low k and spin-on low k [6]. Among the CVD low k dielectrics with values of $k < 3.0$, the main contenders are amorphous materials that comprise Si, C, O and H atoms, which are deposited in conventional PECVD tools. They are known by different names which include SiCOH, SiO(C,H), carbon doped oxides (CDO), organosilicate glasses (OSG), silicon – oxycarbide [11]. Throughout this thesis we will use the generic term carbon doped silicon oxide (SiO(C,H)) to refer to the investigated films.

2.5 Requirements of low k dielectric

Deleted: ¶

Deleted:
Figure [000]:Total capacitance
of metal lines [2w],¶

¶
Other advantages of low k
materials¶

¶
Mechanism of dielectric constant
reduction¶

¶
Low dielectric technology
approach¶

¶
Low k dielectrics have been
proposed having varying
compositions, some carbon based
and other silicon based. A
carbon based material is meant a
material containing more carbon
than either or both of silicon or
oxygen. Most carbon based low k
materials are fundamentally
organic polymers. In contrast, a
silicon based material contains
more silicon than carbon and is
typically based on SiO₂ or Si₃N₄
[3, 4y]. ¶

Chapter 2: Literature review

Deleted: ¶

Cu/low k interconnect has been under extensive investigation for a number of years [12]. Table 2.1 shows the requirements for low k materials [13]. Many materials offer lower dielectric constants, but few of these candidates can compete with SiO_2 in terms of the other properties relevant to process integration listed in Table 2.1 [7]. It is found that not many silicon-based materials have low permittivity, and very few carbon-based materials show good thermal stability, good adhesion to metal, resistance to plasma processing and no out-gassing or moisture adsorption. Therefore, it is a challenge to develop a suitable low k material that can meet all these

Deleted: . ¶
Actually

Deleted: -

Deleted: -

Deleted:

Deleted: ¶

requirements.

Thermal	Mechanical	Chemical	Electrical
High thermal Stability	Film thickness uniformity	High chemical resistance	Low dissipation
Low thermal expansion	Adhesion	High etch selectivity	Low leakage
High thermal conductivity	Low stress	Low solubility of H_2O	Low charge trapping
Low thermal shrinkage	High tensile modulus	Low gas permeability	High reliability
	High hardness	High purity	
	Low shrinkage	No metal corrosion	
	High crack resistance		

Table 2.1: Low k dielectric materials requirements.

Deleted: Table 11 Low- k dielectric materials requirements. [7y]¶

2.6 Low dielectric technology approach

Chapter 2: Literature review

Deleted: ¶

As the industry moves toward the 0.13 μm generation and beyond, first generation low k materials such as fluorine-doped silicate glass (FSG, $k=3.5 \sim 3.7$) will be replaced by the second generation low k films, with dielectric constant below 3.0, to allow the continued miniaturization of integrated circuits and to provide higher speed and performance [8,14].

Recently, many researchers have proposed various organic and inorganic materials as alternatives to SiO_2 . Organic materials have more significant integration problems than inorganic materials, such as poor adhesion, thermal instability and low resistance to O_2 plasma. Films made from inorganic materials have better thermal and mechanical stability, as well as better film adhesion during integration processing. However, they generally have higher dielectric constants and more serious moisture absorption than organic materials, and as a result they require additional liner and capping layer. Therefore, $\text{SiO}(\text{C,H})$, a hybrid type film between organic and inorganic materials has become a favorable low dielectric constant material suitable for ULSI process integration [15].

In $\text{SiO}(\text{C,H})$, carbon is introduced, typically in the form of methyl ($-\text{CH}_3$) groups, bonded to Si atoms, and effectively terminate a proportion of the Si-O bonds. This results in a reduction in the polarizability of the bonds, and a corresponding decrease in the k value. This material, formed from plasma enhanced chemical vapor deposition (PECVD) process by oxidizing methylsilane, is physically porous. The porous structure contributes to a decrease in the material mass density, and further lowers the k value. However, the porosity also induces some undesirable integration

Deleted: esees

Deleted: un

Deleted: an overall "loosing" of the lattice,

Deleted: a

Deleted: in

Deleted:

Deleted: the film density

Deleted: [7, 8y]

Deleted: ese

Deleted: s

Deleted: are

Deleted: grown

Deleted:

Deleted:

Deleted: k value

Chapter 2: Literature review

Deleted: ¶

problems.

SiO(C,H) materials have attracted considerable attention in the replacement of SiO₂ as the interlayer dielectric (ILD) and are expected to be a more cost-effective solution for the immediate low-k needs primarily due to:

- Shorter lead-time for process development.
- Re-use of existing tool-set.
- Process extendibility to Cu-Damascene using conventional CVD

Formatted: Bullets and Numbering

equipment and silicon-based materials.

- Superior thermal and mechanical stability over the organic materials,
making process integration relatively straightforward [16].

Deleted: ¶
¶

In this study, we will focus on the growth and characterization of SiO(C,H) low k dielectrics for multilevel applications, deposited by the plasma enhanced chemical vapor deposition (PECVD) process using organosilane trimethylsilane (3MS) as the precursors and oxygen (O₂) as the oxidizer.

Deleted: ¶

2.7 Fundamental of plasma enhanced chemical vapor deposition

The plasma enhanced chemical vapor deposition (PECVD) of thin films is widely used in microelectronics manufacturing. The PECVD process are generally carried out at pressures of 1mTorr to 20Torr, substrate temperatures in the range of 100 to 500°C, rf power densities < 0.5W-cm⁻², electron mean free paths of <0.1cm, and average electron energies of 1 to 6 eV [17].

When a plasma is initiated by the applied rf power, energy from the rf electric field is coupled into the reactant gases via the kinetic energy of a few free electrons. These electrons will gain energy rapidly through the electric field and lose energy slowly through elastic collisions. The high-energy electrons are capable of inelastic collisions that cause the reactant gas molecules to dissociate and ionize, producing secondary electrons by various electron-impact reactions. Next, these reactive species are transported from the plasma to the substrate surface concurrently with the

occurrence of many elastic and inelastic collision in both the plasma and sheath regions. Following that is the absorption and /or reaction of reactive species at the substrate surface. Finally, the reactive species and / or reaction products are incorporated into the deposited films or re-emitted from surface back to the gas phase.

In general, the PECVD process can be qualitatively summarized below [18]:

- Transport of reactants to the growth region.
- Mass transport of reactants to the wafer surface.
- Adsorption of reactants.
- Physical-chemical reactions yielding the solid film and reaction byproducts.
- Desorption of byproducts.
- Mass transport of byproducts to the main gas stream.
- Transport of byproducts away from the growth region.

Chapter 2: Literature review

Deleted: ¶

In plasma enhanced CVD processing, physical and chemical properties of the deposited film can be controlled by not only changing the type of reactive species, but also varying deposition parameters such as temperature, rf power, pressure, reactant gas mixture ratio, and type of reactant.

2.8 Low constant dielectric application

The International Technology Roadmap for Semiconductors (ITRS) calls for the implementation of low k materials. Table 2.2 shows the interconnect technology

requirements (ITRS 2001 Edition, Interconnect) [19].

YEAR OF PRODUCTION	2001	2002	2003	2004	2005	2006	2007
MPU/ASIC 1/2 PITCH (nm)	150	130	107	90	80	70	65
Number of metal levels	8	8	8	9	10	10	10
Number of optional levels - ground planes/capacitors	2	2	4	4	4	4	4
Local wiring pitch (nm)	350	295	245	210	185	170	150
Local wiring A/R (for Cu)	1.6	1.6	1.6	1.7	1.7	1.7	1.7
Intermediate wiring pitch (nm)	450	380	320	265	240	215	195
Intermediate wiring dual Damascene A/R (Cu wire/via)	1.6/1.4	1.6/1.4	1.7/1.5	1.7/1.5	1.7/1.5	1.7/1.6	1.8/1.6
Global wiring dual Damascene A/R (Cu wire/via)	2.0/1.8	2.0/1.8	2.1/1.9	2.1/1.9	2.2/2.0	2.2/2.0	2.2/2.0
Interlevel metal insulator - effective dielectric constant (k)	3.0-3.6	3.0-3.6	3.0-3.6	2.6-3.1	2.6-3.1	2.6-3.1	2.3-2.7
Interlevel metal insulator (minimum expected) - bulk dielectric constant (k)	<2.7	<2.7	<2.7	<2.4	<2.4	<2.4	<2.1

	Solutions exist & are being optimised
	Solutions are known
	Solutions are NOT known

Table 2.2: Interconnect Technology Requirements (ITRS' 2001)

Deleted: 1

Figure 2.4 highlights a hierarchical scaling methodology that has been broadly

Chapter 2: Literature review

Deleted: ¶

adopted. Local wiring levels are relatively unaffected by the traditional scaling. Implementation of copper and low k materials allows scaling of intermediate wiring levels and minimizes impact on wiring delay.

Low k materials are expected to be used between metal layers insulation as interlayer dielectric (ILD) and between adjacent metal lines as inter-metal dielectric (IMD), especially for interline isolation between the metal lines on the same level. They have an added advantage of facilitating manufacture of higher performance integrated circuit devices with minimal increase in chip size. The reduced capacitance

of these materials permits the shrinkage of spacing between metal lines to between 0.18 μ m. In addition, the use of copper / low k structure makes it possible to reduce

the number of interconnect levels. According to Jon Dahm, SEMATECH's (Austin, Texas), modeling has shown that by switching from Al/SiO₂ to copper / low k interconnect technology, the number of metal levels can be reduced from 14 to 9 [20].

Chapter 2: Literature review

Deleted: ¶

Deleted: AAA

Figure 2.4: Cross-section of hierarchical scaling

2.9 References

1. B. Narayanan, R. Kumar and P. D. Foo, "Properties of low-k SiCOH films prepared by plasma-enhanced chemical vapor deposition using trimethylsilane", *Microelectronics Journal*, Vol. 33, pp. 971 - 974, 2002.
2. Keith Buchanan, The evolution of interconnect technology for silicon integrated circuitry, 2002 GaAsMANTECH Conference.
3. Laura Peters, Pursuing the perfect low k dielectric, *Semiconductor International*, September 1998.
4. Josh H. Golden, Microbar Inc., Sunnyvale, Calif. Craig J. Hawker, Designing porous low-k dielectrics, *Semiconductor International*, 5/1/2001.

5. Michael E. Clarke, "Introducing low-k dielectrics into semiconductor processing", Mykrolis Corporation, Billerica, Massachusetts, <<http://www.mykrolis.com>>.
6. R. Singh and R.K. Ulrich, High and low dielectric constant materials, The Electrochemical Society Interface, summer 1999, Pages 26-30.
7. Katherine Derbyshire, Still waiting for low-k dielectrics, Semiconductor Manufacturing Magazine, January 2002 Vol. 3, No. 1.
8. David Cheung, Black Diamond CVD low k films for copper damascene, Low k dielectric materials technology, SEMICON West 1999, Pages F1-F10.
9. Mark ONeill, Aaron Lukas, Raymond Vrtis, Jean Vincent, Brian Peterson, Mark Bitner and Eugene Karwacki, Low-k Materials by Design, Semiconductor International, 6/1/2002.
10. Laura Peters, Industry divides on low k dielectric choices, Semiconductor International, June 1998.
11. Alfred Grill and Deborah A. Neumayer, Structure of low dielectric constant to extreme low dielectric constant SiCOH films: Fourier transform infrared spectroscopy characterization, Journal of Applied Physics, Volume 94, Issue 10, pp. 6697-6707
12. Copper/Low-k Interconnect in Integrated Circuits, Motivations, Trends and Difficulties, Reza Navid, Department of Electrical Engineering and Computer Science University of Michigan; Term Paper for EECS 598, Nanotechnology.
13. Development of Black Diamond™ Plasma Etching for Dual-Damascene

Metallization of VLSI, Ng Beng Teck, Industry Attachment Report at Institute of Microelectronics, Singapore.
14. Ben Pang, Wai-fan Yau, Peter Lee and Mehul Naik, A new CVD process for damascene low k applications, Semiconductor Fabtech – 10th Edition, Pages 285-289.
15. Chang Shil Yang, Kyoung Suk Oh, Jai Yon Ryu, Doo Chul Kim, Jing Shou-Yong, Chi Kyu Choi, Heon-Ju Lee, Se Hun Um and Hong Young Chang, A study on the formation and characteristics of the Si---O---C---H composite thin films with low dielectric constant for advanced semiconductor devices, [Thin Solid Films](#) , [Volume 390](#), [Issues 1-2](#) , Pages 113-118.
16. Lee, P.W.; Chi-I Lang; Sugiarto, D.; Li-Qun Xia; Gotuaco, M.; Yieh, E.; Multi-generation CVD low κ films for 0.13 μm and beyond, Solid-State and Integrated-Circuit Technology, 2001. Proceedings. 6th International

Chapter 2: Literature review

Deleted: ¶

Conference on, Volume:1, 22-25Oct. 2001 , Page(s): 358 -363 vol.1.

17. D.R. Cote etc al., Plasma-assisted chemical vapor deposition of dielectric thin film for ULSI semiconductor circuits, IBM J. RES. DEVELOP. VOL. 43 NO. ½ January/March 1999, Pages 5-39.
18. Stephen M. Rossmagel, Jerome J. Cuomo and William D. Westwood, Handbook of Plasma Processing Technology, Noyes Publications, 1990, page 266.
19. The International Technology Roadmap Semiconductors: 2001, Semiconductor Industry Association, San Jose, CA.
20. Peter Singer, Copper goes mainstream, low k to follow, Semiconductor International, Vol. 20, Issue 13, (1997), p67

Chapter 3: Experimental Setup

3.1 Introduction

In this work, a commercial plasma enhanced chemical vapor deposition (PECVD) system — Applied Materials CENTURA 5200 system has been used for deposition of carbon doped silicon oxide (SiO(C,H)) low dielectric thin films. Dow Corning's Semiconductor Grade linear silicon-source gas Trimethylsilane (3MS) has been used as the precursor and oxygen gas as the oxidizer. The post-annealing of the films were carried out using the TEL α SERIES LP – CVD from Tokyo Electron Limited.

Many different characterization tools were used to investigate the properties of the films. The defects on film surface were measured using scattered-light and defect compositions were analysed using energy dispersive x-ray spectrometer (EDX). The film thickness and refractive index were measured using spectrometric reflectance spectrophotometry. Dielectric constant measurements were carried out using a Si/insulator/mercury probe structure. The atomic bonding and their relative concentrations in the films were characterized by the Fourier Transform Infrared (FTIR) spectroscopy. The film surface morphology was investigated using Atomic force microscopy (AFM). The stresses of as-deposited and annealed films were determined using FSM 7800iTC.

This chapter will present a description of the deposition system used, and a general overview of the above characterization tools and their working principles.

3.2 Plasma enhanced chemical vapor deposition (PECVD) system

PECVD is a process where plasma is used to lower the temperature required to deposit films onto wafers. During the deposition process, gases containing the insulator chemistry are decomposed and ionized by the plasma, and react on the heated wafer surface, forming a thin film of solid material. Energy sources such as heat and radio frequency (rf) power are used alone or in combination to achieve this reaction. The advantage of the PECVD process is that it allows the use of low deposition temperature, avoiding defect formation in the underlying silicon substrate, dopant diffusion and degradation of the metal layers [1].

The Applied Materials CENTURA 5200 system 200mm deposition chamber is a radial flow reactor. The chamber basic type is CVD, chamber variant is D × Z and chamber effective volume is 5450cc.

A schematic diagram of the inverse radial flow reactor with perforated electrode used in this experiment is described in Fig. 3.1[2]. The Centura system uses a 13.56MHz compact rf delivery system consisting of a RF/DC generator and multi-function adaptor. The generator rf output impedance range is 50 – 400 Ω and over 1000W output power at nominal line. A dry pump Edwards IQDP 80 is used to achieve a base pressure of 24mTorr. The schematic diagram of the PECVD configuration shown in Fig. 3.2.

Chapter 3: Experimental setup

Figure 3.1: Schematic diagram of the inverse radial flow reactor with perforated electrode.

Figure 3.2: Schematic diagram of the PECVD system.

Chapter 3: Experimental setup

In the experiment, the substrate temperature was maintained at 350°C, rf power at 600W, and the discharge was struck between two 26.3 cm diameter electrodes spaced 300mil apart. Unless otherwise specified, the process pressure was fixed at 4.0Torr, O₂ flow at 100sccm and 3MS flow at 600sccm. The precursors used were linear organosilicate trimethylsilane (3MS) and oxygen (O₂). Upon deposition, the wafers were exposed to a continuous N₂ flow of 350sccm for 120 seconds to cool them down to room temperature.

During the deposition process, the wafers were loaded onto the lower electrically grounded electrode. The perforated upper electrode is connected to the rf generator through an impedance matching network. The plasma is generated between two parallel circular electrodes. The reactants are fed in from the upper electrode, with the gas flow directed radially outward. Working gases trimethylsilane (3MS) and Oxygen (O₂) are fed into the chamber via mass flow controllers (MFCs).

As film deposition occurs on the chamber wall as well as on the substrate during the growth process [3], the process chamber has to be cleaned after each growth. A plasma formed from source gases of C₂F₆, NF₃ and O₂ was used to clean the chamber and the completion of this process is monitored by an *in-situ* optical emission spectroscopy (OES) end point detector.

Chapter 3: Experimental setup

3.3 Low k annealing system

The low k furnace used for the annealing of samples is a vertical LPCVD system ALPHA – 8S – ZVFNS from Tokyo Electron Limited, Japan. The temperature ramping up rate is 50°C/min and ramping down rate is 9°C/min. The over-shoot is less than 5°C and stability is within 1°C. The process gas used during the annealing is nitrogen (N₂) with a gas flow rate of 1000sccm. The annealing pressure is 7.0Torr.

3.4 Film inspection and characterization techniques

3.4.1 Unpatterned wafer inspection system

The unpatterned wafer inspection system used in this study is Surfscan[®] SP1 from KLA Tencor. It is designed to perform highly sensitive inspection of unpatterned silicon wafer surfaces. It uses a system of fixed illumination and collection optics to illuminate the wafer surface, collect and analyze the scattered light. The illumination is derived from an argon ion laser that operates at 30 mW power with a wavelength of 488nm. Since defects and irregularities on and in the wafer surface affect the scattering power of the surface, therefore variations in the intensity of the scattered light can be correlated with surface features. The system processes the scattered-light signal to produce data that identifies the size and location of surface features [4].

The Surfscan SP1 has five scan data collection channels: Dark field wide normal, dark field narrow normal, dark field narrow oblique, dark field wide oblique

Chapter 3: Experimental setup

and bright field channel. Point defects detected in both the dark field wide channel and the dark field narrow channel can be displayed as composite data.

3.4.2 Spectrometric reflectance tool

The spectrometric reflectance tool used in this study is the Opti-Probe 5240i system from Thermo-wave. It is a non-destructive dielectric film thickness measurement tool used for the measurement of thin film thickness (d) and refractive index (optical constants, n) by measuring the reflected light and modelling the film parameters. It performs this function by integrating three film measurement techniques: reflectivity as a function of incident angle (beam profile reflectometry), reflectivity as a function of wavelength (spectrometry), and changes in polarization state (ellipsometry). The refractive indices presented in this work are taken at a specific wavelength of $6730\text{\AA}$ for comparison purpose across different films. The system allow a simultaneous measurement of thickness and refractive index, and hence eliminates errors involved in other techniques that measure thickness across the wafer while assuming a constant refractive index [5].

3.4.3 Fourier transform infrared absorption spectroscopy (FTIR)

Infrared absorption spectroscopy is a common and useful tool in material characterization. For solid material or gas molecule, the interaction between atoms causes vibrations or rotations. From quantum mechanical consideration, it is known that the rotational and vibrational energy levels are not continuous and that only those

Chapter 3: Experimental setup

transition, which obey the selection rule, are allowed. Therefore, a specific bond (or molecule) has its characteristic rotational and vibrational energy levels and transitional energy, which can be used for identification of the bonding structure (or molecule) by its absorption spectrum.

When radiation passes through a sample, the light can be absorbed only if the energy and hence the frequency corresponds to the energy difference between two quantum levels in the sample. This is described by the Bohr frequency condition:

$$\Delta E = E_2 - E_1 = h\nu \quad (3.1)$$

where h is Plank's constant and ν is the frequency of the light in Hz.

In classical electromagnetic theory, the periodic variation of the dipole moment of a vibrating molecule results in absorption of radiation of the same frequency as that of the oscillation of the dipole moment. Normally, the energy difference between two quantum levels is so small that the corresponding frequency is in the infrared range [6].

In order to obtain the absorption of the thin film alone, the absorption by substrate should be subtracted. Therefore, a bare substrate is needed as a reference in every measurement. In this work, the infrared spectra were measured using a Bio-Rad's QS2200 FTIR spectrometer in the mid-infrared region from 400 to 4000 cm^{-1} , with a resolution of 4 cm^{-1} . Since absorbance is also proportional to sample thickness, the integrated area ratio of the Si-CH₃ to Si-O-Si peak absorbance will be used as a measure of the carbon content in the films for samples with different thickness.

Chapter 3: Experimental setup

3.4.4 Dielectric constant measurement - MIS structure

Metal oxide semiconductor (MOS) C-V measurements traditionally have been used to measure the characteristics of an oxide with a known dielectric constant. Conversely, the value for k can be determined using the Si/insulator/mercury (MIS) probe structure, provided the thickness of the dielectric film and the contact area are known, according to a parallel plate capacitor model :

$$k = \frac{C_{ox} W_{ox}}{\epsilon_o A_G} \quad (3.2)$$

where C_{ox} is the accumulation region of capacitance, W_{ox} is the thickness of dielectric film, ϵ_o is the permittivity of free space and A_G is the electrical contact area [7].

The mercury probe SSM 495 CV system (Solid State Measurements, Inc.) used for k value measurements is an automatic mercury probe capacitance-voltage (CV) measurement system. C_{ox} were measured using the SSM's standard forward/reverse bias C-V measurement module at 0.926MHz in this study. Dielectric constants were automatically calculated based on the accumulation region of the capacitance-voltage curve obtained.

3.4.5 Atomic Force Microscopy (AFM)

Atomic force microscope (AFM) probes the surface of a sample, with a sharp tip, a couple of microns long and often less than 100Å in diameter. The tip is located at the free end of a cantilever that is 100 to 200µm long. Forces between the tip and

Chapter 3: Experimental setup

the sample surface cause the cantilever to bend or deflect. A detector measures the cantilever deflection as the tip is scanned over the sample. The magnitude of deflection is captured by a laser that reflects at an oblique angle from the very end of the cantilever. The measured cantilever deflections allow a computer to generate a map of the surface topography. This topographic image of the surface is produced by the variations in tip height recorded by scanning repeatedly across the sample. Figure 3.3 gives a briefly description how AFM works.

Figure 3.3: Atomic Force Microscope system layout.

There are three primary modes of AFM [8]: contact mode, non-contact mode and tapping mode, as can be seen from Fig. 3.4.

Chapter 3: Experimental setup

Figure 3.4: Inter atomic force vs. distance curve.

Contact mode is the most common method of operation of the AFM. As the name suggests, the tip and sample remain in the close contact as the scanning proceeds. The term “contact” refers to the repulsive regime of the inter-atomic force curve (see Fig. 3.4), which lies above the x-axis. One of the drawbacks of remaining in contact with the sample is that there exist large lateral forces on the sample as the tip is dragged over the specimen.

Tapping mode (or intermittent-contact) is the next common mode used in AFM. It is similar to contact mode, except that the cantilever is oscillated at its resonant frequency (often hundreds of kilohertz) and positioned above the surface so that it only taps the surface for a very small fraction of its oscillation period. This

Chapter 3: Experimental setup

mode is still contact with the sample in the sense defined earlier, but the very short time over which this contact occurs means that the lateral forces (friction or drag) are dramatically reduced as the tip scans over the surface. When imaging poorly immobilized or soft samples, tapping mode may be a far better choice than the contact mode for imaging. In general, it has been found that tapping mode is more effective than non-contact (which will be elucidated later) for imaging larger scan sizes that may include greater variation in sample topography. Tapping mode AFM has become an important AFM technique since it overcomes some of the limitations of both contact and non-contact AFM.

Non-contact operation is another method that may be employed in AFM application. The cantilever must be oscillated above the surface of the sample at such a distance that we are no longer in the repulsive regime of the inter-atomic force curve but in the attractive regime. In this mode, the system vibrates a stiff cantilever near its resonant frequency with an amplitude of a few tens of angstroms. Then it detects changes in the resonant frequency or vibration amplitude as the tip comes near the sample surface. The sensitivity of this detection scheme provides sub-angstroms vertical resolution in the image, as with contact mode. The resonant frequency of a cantilever varies as the square root of its spring constant while its spring constant varies with the force gradient experienced by the cantilever. Finally the force gradient, which is the slope of the force versus distance curve shown in Fig. 3.4, changes with the tip-to-sample separation. Thus, changes in the resonant frequency of a cantilever can be used as measure of changes in the force gradient, which reflects changes in the tip-to-sample spacing or sample topography. One of the advantages of this mode of

Chapter 3: Experimental setup

AFM is does not suffer the tip or sample degradation effects. It is preferable to use non-contact mode AFM for measuring soft samples.

During all AFM measurements, roughness is one of the most important parameters to be determined. Roughness measurements can be performed over an entire image or a selected portion. The root mean square (RMS) roughness is the standard deviation of the Z value within a given area,

$$\text{RMS} = \sqrt{\frac{\sum_{i=1}^N (Z_i - Z_{ave})^2}{N}} \quad (3.3)$$

where Z_{ave} is the average Z value within the given area, Z_i is the current Z value, and N is the number of points within a given area.

The AFM system used in this study is Dimension 3000 series from Digital Instruments. Tapping mode AFM technique has been used to scan $0.5\mu\text{m} \times 0.5\mu\text{m}$ area of the samples to investigate the roughness of as-deposited and annealed films.

3.4.6 Stress measurement

Stresses in as-deposited and annealed films were determined using the FSM 7800iTC from Frontier Semiconductor Measurements. The basic principle of stress measurement is that a laser beam is reflected from the surface of the wafer and the displacement of the reflected beam is measured as the wafer is scanned [9].

Chapter 3: Experimental setup

The FSM 7800iTC uses a laser optical lever to measure the change in curvature induced in a wafer due to the deposited film. A schematic of the configuration is illustrated in Fig. 3.5. The laser scans the surface of the wafer and the beam is deflected by the wafer surface, reflected off a mirror, and detected by a precision position detector. A clean, blank wafer is measured prior to film deposition, the results are then compared to those taken on the same sample after film deposition.

The radius of curvature of the sample is determined from the slope of a straight line fitted to the scan data calculated from the before and after deposition scan data.

$$R = 2L \delta x / \delta z \quad (3.4)$$

The film stress, S is then calculated using the following equation:

$$S = ED^2 / 6(1-\nu)RT \quad (3.5)$$

where E is Young's modulus of the substrate, ν is Poisson's ratio of the substrate, D is thickness of the substrate, R is net radius of curvature, and T is thickness of the film ($T \ll D$).

Chapter 3: Experimental setup

Figure 3.5: Diagram of measuring apparatus.

3.4.7 Energy Dispersive X-ray Spectrometer (EDX)

EDX is used in electron microscopy to provide information about the element composition of irradiate material. An electron beam from the SEM irradiates the defect during the time that the system performs the EDX measurement. This enables defect material analysis with high spatial resolution. EDX is normally performed at 45° tilt and an accelerating voltage of 5 keV or above to optimize EDX acquisition time (approximately 10 seconds). During the EDX scan, a real time spectrum is monitored in the materials analysis window, and the spectral peak energies are used for material identification, which is performed following the acquisition of data according to the analysis procedure.

The energy dispersive X-ray spectrometer (EDX) used in this study is the SEMVision system from Applied Materials [10]. It supports automatic review, classification and material analysis performed on unpatterned wafers. The instrument

Chapter 3: Experimental setup

aligns the wafer, uses an optical microscope to find the defects, redetects the defects using the scanning electron microscope (SEM), classifies the defect and automatically performs energy dispersive X-ray spectrometer (EDX) on the defect so as to analyze the results and identify the defect.

3.5 Substrates

In this study, bare Si wafers were used for film deposition and characterization. The properties of the wafers used are as follows:

Wafer category: Test wafer

Substrate: Si

Wafer size/Diameter: 200mm

Type/orientation: P/<100>

Dopant: Boron

Resistivity: 1-50 Ohm-cm

Thickness: 700-750 μ m

The substrates used are commercial production grade wafers and require no cleaning before deposition.

Chapter 3: Experimental setup

3.6 References

1. Fabio Iacona, Giulio Ceriola and Francesco La Via, Structural properties of SiO₂ films prepared by plasma-enhanced chemical vapor deposition, Materials Science in Semiconductor Processing , Volume 4, Issues 1-3, Pages 43-46.
2. Stephen M. Rossnagel, Jerome J. Cuomo and William D. Westwood, Handbook of Plasma Processing Technology, Noyes Publications, 1990, page 266.
3. Josh H. Golden, Microbar Inc., Sunnyvale, Calif. Craig J. Hawker, Designing porous low-k dielectrics, Semiconductor International, 5/1/2001.
4. “Surfscan® SP1 unpatterned wafer inspection system user manual” of KL Tencor Corporation, #512516-27, Rev. A 6/98, , 1998.
5. “Opti-Probe 5240i system user manual” by Therma-wave.
6. Shen Xuechu, Optical Properties of Semiconductor Materials (in Chinese), p21. Scientific Press (P.R.China) (1992).
7. Dimension™ of Low-k Dielectrics, Solid State Measurements, Inc., 2001.
8. “Dimension™ 5000 Scanning Probe Microscope Instruction Manual” of Digital Instruments, Version 4.22ce – 01MAR97.
9. “FSM 7800TC operation manual” of Frontier Semiconductor Measurement Inc., Rev.1,1999.
10. “SEMVision user’s manual”, by Applied Materials PDC (process diagnostics and control), version 1 – Rev. A, March 2001.

Chapter 4: Optimization of Process Steps and the Effects of Oxygen in the Growth Process

4.1 Introduction

In this chapter, we present results on the deposition of carbon doped silicon oxide ($\text{SiO}(\text{C,H})$) thin films using the plasma enhanced chemical vapour deposition (PECVD) process with source gases trimethylsilane ($\text{C}_3\text{H}_8\text{Si}$, also referred to as 3MS) and oxygen (O_2). Using a process recipe, known as CVD1, $\text{SiO}(\text{C,H})$ films with dielectric constant as low as 3.0 have been obtained. The key process steps involved in this recipe are shown in Table 4.1. However, these films suffer from high post particle counts, which can reach up to 70000 on 8-inch wafers. A new recipe CVD2, which is a modified version of recipe CVD1, has been applied successfully to reduce the particle counts to about 50 or much less, within the specification required of such films. The key steps of recipe CVD2 are also shown in Table 4.1 for comparison.

The main differences between the two recipes are as follows: 1) different oxygen (O_2) flow rates are used in the stabilization step (step A) and oxygen treatment step (step B), which are 200sccm in recipe CVD1 and 700sccm in recipe CVD2; 2) the pump down step (step C) that is part of recipe CVD1 is omitted in recipe CVD2. Since there is no pump down step in recipe CVD2, the O_2 flow rate was set at 700sccm in steps A and B, so as to maintain a constant total flow rate from step B to step D, where the total flow rate of O_2 and 3MS is also 700sccm. This will help ensure minimum disruption to the plasma during the transition between the process steps.

Chapter 4: Optimization of process steps and the effects of oxygen in the growth process

Except for the above differences, the other process steps and parameters used in the two recipes are identical. Indeed, the omission of step C in recipe CVD2 is responsible for the reduction in the post particle counts, as shall be seen.

		Recipe CVD1		Recipe CVD2	
Process step	Step description	Precursor (sccm)	Process pressure (Torr)	Precursor (sccm)	Process pressure (Torr)
A	Stabilisation	O ₂ =200	4.0	O ₂ =700	4.0
B	Oxygen (O ₂) treatment	O ₂ =200	4.0	O ₂ =700	4.0
C	Pump down	YES		NO	
D	Film deposition	O ₂ =100 3MS=600	4.0	O ₂ =100 3MS=600	4.0
E	Pump down	YES		YES	
F	Helium treatment	He=1300	8.7	He=1300	8.7
G	Pump down	YES		YES	

Table 4.1: Summary of process steps of recipes CVD1 and CVD2

It was also found that films deposited using recipe CVD2 have slightly different properties compared to those deposited using recipe CVD1, despite that all the parameters for the actual deposition process (step D) in the two recipes are identical. Investigations have shown that the residual oxygen derived from the process steps prior to the actual film deposition in recipe CVD2 is responsible for the differences observed. This suggests that oxygen has substantial influences on the properties of carbon doped silicon oxide films. In this work, we compare the two recipes, in terms of the critical process steps and their effects on the properties of the films. We have also investigated in detail the influences of oxygen (O₂) on SiO(C,H) films. This work provides us with a better understanding of the dielectric properties of

Chapter 4: Optimization of process steps and the effects of oxygen in the growth process

SiO(C,H) films in relation to the deposition process, and how they can be optimized for use in deep submicron integrated circuit technology.

4.2. Experimental details

Four groups of experiments have been carried out: 1) 5 samples deposited by both recipes CVD1 and CVD2 with film thickness of 5000 Å to ascertain reproducibility and also for statistical analysis; 2) 5 samples deposited by recipe CVD1 with nominal thickness ranging from 1000 Å to 5000 Å, in step of 1000 Å; 3) 5 samples deposited by recipe CVD2 with nominal thickness ranging from 1000 Å to 5000 Å, in step of 1000 Å; 4) 7 samples deposited by recipe CVD2 with different O₂/3MS flow ratios from 1/6 to 7/6 over a period of 44 seconds. In this experiment, the flow rate of O₂ was varied while that of 3MS was kept constant at 600sccm. All the films were deposited on p-type <100> orientation bare silicon 8-inch wafers, with a deposition temperature of 350°C, process pressure of 4.0 Torr and RF power of 600W.

4.3. Results and discussion

4.3.1 Process reproducibility

The average dielectric constant k and refractive index n of the films deposited using recipe CVD1 in experiment 1 are 2.98 and 1.41 respectively. The corresponding standard deviations of these parameters are 1.83×10^{-3} and 4.48×10^{-3} . For the films

Chapter 4: Optimization of process steps and the effects of oxygen in the growth process

deposited using recipe CVD2 in the same experiment, the average k and n values are 3.05 and 1.41 respectively, and the corresponding standard deviations are 4.47×10^{-3} and 5.36×10^{-4} . These results confirmed that this carbon doped silicon oxide low dielectric films deposited using the PECVD process in this work are highly reproducible.

4.3.2 Particle counts and element composition

Particle contamination or random defects are the primary concern for low k material development and application. As the manufacturing process approaches the yield-monitoring phase of mature production, random defects become the dominant source of yield loss. In general, large particles ($>1\mu\text{m}$) indicate mechanical problems while small particles ($<0.5\mu\text{m}$) indicate process problems [1]. Table 4.2 summarizes the number of added-in particles measured for films deposited using the two different recipes in the four sets of experiments.

		Experiment 1		Experiment 2	Experiment 3	Experiment 4
Process recipe		Recipe CVD1	Recipe CVD2	Recipe CVD1 with different thickness	Recipe CVD2 with different thickness	Recipe CVD2 with different $\text{O}_2/3\text{MS}$ flow ratios
Wafer number	1	11	2	70002	11	8
	2	2710	6	6799	51	18
	3	2340	1	3125	34	14
	4	2670	1	12	21	11
	5	2847	4	13	5	13
	6					16
	7					46

Table 4.2: The number of added-in particles on film surfaces. In experiments 2 and 3, wafer 1 to 5 corresponds to films deposited with nominal thickness from $1000\text{\AA}$ to $5000\text{\AA}$. In experiment 4, wafers 1 to 7 correspond to films deposited with $\text{O}_2/3\text{MS}$ flow ratios from 1/6 to 7/6.

Chapter 4: Optimization of process steps and the effects of oxygen in the growth process

As can be seen, the number of added-in particles is quite high when using recipe CVD1, and is beyond the specification that requires the count of particles greater than 0.2 μm not to exceed 0.1 particles per square centimeter. To illustrate, the pre and post-deposition maps of wafer 3 in experiment 2, which has a large post particle count, are shown in Figs. 4.1(a) and (b) respectively. Figure 4.2(a) shows a SEM picture of a particle embedded in the film, which is commonly seen, while Fig. 4.2 (b) shows a typical EDX spectrum of the particles, revealing the presence of Si, O and C. As these are the same elements found in the reactant precursors $\text{C}_3\text{H}_{10}\text{Si}$ and O_2 , therefore, it can be deduced that the particles are a byproduct of the deposition process itself.

Figure 4.1: The pre (a) and post-deposition (b) maps of wafer 3 in experiment 2 deposited using recipe CVD1 with a thickness of 3000 Å.

Chapter 4: Optimization of process steps and the effects of oxygen in the growth process

Figure 4.2: (a) SEM image showing a particle embedded in the carbon doped silicon oxide low dielectric films. (b) A typical EDX spectrum of the particles revealing the presence of Si, O and C.

The large number of particles incorporated when using recipe CVD1 is likely to originate from the gas-phase chemistry during the oxygen (O_2) treatment (step B). Pure oxygen is reactive, and upon reacting with and possibly sputtering the chamber wall, which inevitably has a very thin layer of film coating arising from previous growths, can result in a large amount of particles formed in the O_2 plasma environment during step B. When the RF power is turned off in the pump down step (step C) in recipe CVD1, the sudden absence of the plasma precludes gas-phase reaction, but the particles formed in the previous step (step B) still remain and are likely to drop onto the wafer surface due to gravity and effect of static electricity. This will lead to the presence of a very large number of particles during the following film

Chapter 4: Optimization of process steps and the effects of oxygen in the growth process

deposition step (step D), and account for the many embedded particles seen [see Fig. 4.2(a)]. However, when using recipe CVD2 that omitted the pump down step, there is no interruption to the RF power and O₂ plasma environment, and the particles formed in the previous oxygen (O₂) treatment (step B) continue to float and drift inside the plasma boundary while the film deposition process is ongoing. These particles will finally drop onto the wafer surface at the end of film deposition step (step D) when the rf power is turned off. They are then most likely sputtered away by the following helium treatment step (step F). To confirm the origin of the particles in recipe CVD1 as being due to the sputtering of carbon doped silicon oxide film coated on the chamber wall, we have performed an extended over-etched of the chamber using C₂F₆ and NF₃ for 400 seconds, in comparison to standard etching time of 100 seconds, to thoroughly clean the chamber. Indeed, it was found that films deposited using recipe CVD1 immediately after the extended over-etched have particle counts reduced to levels comparable to those achieved in recipe CVD2. Nevertheless, such over-etched is not recommended as it will shorten the operational lifetime of the PECVD system, and hence the large particle-count problem can only be resolved through using recipe CVD2.

4.3.3 Deposition rates

For the films deposited in experiment 2 using recipe CVD1, the actual film thickness matches the expected thickness from 1000 Å to 5000 Å very closely, which suggests that the deposition rate is stable and uniform, as shown in Fig. 4.3(a). On the other hand, for films deposited using recipe CVD2 in experiment 3, the deposition

Chapter 4: Optimization of process steps and the effects of oxygen in the growth process

rate is much higher for thinner films than for thicker films, and for the latter, the deposition rate approaches that obtained using recipe CVD1 [see Fig. 4.3(a)]. This result is interesting given that the actual deposition conditions are identical in the two recipes.

(a)

(b)

Figure 4.3: (a) Deposition rates of films with different thickness using recipe CVD1 and CVD2 in experiments 2 and 3 respectively, and (b) deposition rates of films with different O₂/3MS flow ratios in experiment 4.

Chapter 4: Optimization of process steps and the effects of oxygen in the growth process

For recipe CVD2, due to the omission of the pump down step (step C), it is expected that a certain amount of oxygen will remain in the chamber during the next step of film deposition. The residual oxygen can lead to a higher initial partial pressure of oxygen as compared to that of 3MS, and is believed to be responsible for the larger initial deposition rates seen. As the film deposition process progresses, the effect of residual oxygen diminishes and the concentration of oxygen species is then only determined by the inlet oxygen gas flow. This accounts for the decreasing growth rate for thicker samples grown over a longer period of time that ultimately approaches that obtained using recipe CVD1, which is as expected given the identical deposition conditions.

The proposed effect of oxygen on the deposition rate can be verified by studying the series of films deposited using recipe CVD2 with different $O_2/3MS$ flow ratios in experiment 4. The deposition rates for the films are shown in Fig. 4.3(b), which indeed confirm that the deposition rates of the carbon doped silicon oxide low k films are sensitive to the partial pressure of oxygen, being larger at a higher oxygen partial pressure.

4.3.4 Refractive index and dielectric constant

The refractive indices and dielectric constants of the films deposited in experiments 2 and 3 are shown in Figs. 4.4(a) and 4.4(b) respectively. The corresponding parameters for the films deposited in experiment 4 are shown in Fig. 4.5.

Chapter 4: Optimization of process steps and the effects of oxygen in the growth process

(a)

(b)

Figure 4.4: (a) Refractive indices and (b) k values of the films deposited with different thickness using recipe CVD1 and CVD2 in experiments 2 and 3 respectively.

Chapter 4: Optimization of process steps and the effects of oxygen in the growth process

Figure 4.5: Refractive indices and k values of the films deposited with different O₂/3MS flow ratios in experiment 4

From Fig. 4.4(a), it can be seen that the refractive index is nearly uniform to within ± 0.015 and ± 0.005 for films deposited with different thickness using recipes CVD1 and CVD2 respectively. The refractive indices of the films deposited using recipe CVD1 are slightly larger than those deposited by recipe CVD2 by about 0.015 on average, which is not significant. From Fig. 4.4(b), it can be seen that the k values are slightly less than 3.00 for films deposited using recipe CVD1 and show a very slight increase when using recipe CVD2. As both the refractive indices and k values show no correlation with the thickness of the films, therefore it can be concluded that the plasma environment is very stable for these processes and the residual oxygen in recipe CVD2 due to the treatment step (step B) affects only the growth rate but does not have much impact on these parameters.

Chapter 4: Optimization of process steps and the effects of oxygen in the growth process

From Fig. 4.5, it can be seen that the refractive index shows a slight decrease when the $O_2/3MS$ flow ratio increases from 1/6 to 3/6, and remains constant at higher flow ratios. On the other hand, there is a continuous and more significant increase in the k value from 3.02 to 3.95 with increasing $O_2/3MS$ flow ratio. This increase is attributed to the lower number of Si-CH₃ bonds resulting in reduced polarizability [2], as shall be seen shortly. From the above and the deposition rate results presented earlier, it can be concluded that oxygen has a significant impact on the growth rates of the carbon doped silicon oxide low dielectric and their k values, but relatively less effect on their refractive indices.

4.3.5 FTIR spectra

Figures 4.6, 4.7 and 4.8 show the FTIR spectra of the films deposited in experiments 2, 3 and 4 respectively. The peaks observed at 780cm^{-1} and 1270cm^{-1} are assigned to the symmetric deformation vibration of CH₃ in the Si-CH₃ group, while the peak at 1040cm^{-1} is assigned to the Si-O structure. The absorption at 2890 to 2990cm^{-1} , on the other hand, is assigned to the C-H_m, $m=1-3$ stretching mode [3, 4].

To investigate the effects of oxygen incorporation on the dielectric constants of the films, the FTIR spectra around the Si-CH₃ and Si-O groups absorption are fitted with several Gaussian lineshape functions, and the integrated absorption area ratio (Si-CH₃/Si-O ratio) of the Si-CH₃ group at 1270cm^{-1} and the Si-O group at 1040cm^{-1} are determined.

Chapter 4: Optimization of process steps and the effects of oxygen in the growth process

Figure 4.6: FTIR spectra of the films deposited using recipe CVD1 in experiment 2 with different film thickness.

Figure 4.7: FTIR spectra of the films deposited using recipe CVD2 in experiment 3 with different film thickness.

Chapter 4: Optimization of process steps and the effects of oxygen in the growth process

(a)

(b)

Figure 4.8: (a) FTIR spectra of the films deposited with different $O_2/3MS$ flow ratios in experiment 4. (b) Enlarged FTIR spectra showing the main absorption bands.

Chapter 4: Optimization of process steps and the effects of oxygen in the growth process

For the films deposited in experiments 2 and 3, besides the increased absorption seen for thicker films, there is also a slight increase in the Si-CH₃/Si-O ratio with film thickness, as shown in Fig. 4.9(a). As this trend is observed for both series of films deposited using recipe CVD1 and CVD2, it is not attributed to the residual oxygen, but rather to the oxygen treatment step prior to film growth. Oxygen treatment involves a surface modification process, which includes surface contamination removal and surface activation. The former uses oxygen plasma to remove micron-level contamination, while the latter employs oxygen plasma to react with the silicon surface and create the Si-O bonds as chemical function groups on the surface. The presence of these bonds is more significant for thinner samples, thus giving rise to the lower Si-CH₃/Si-O ratio shown in Fig. 4.9(a). For the films deposited in experiment 4, there is a decrease in the Si-CH₃/Si-O ratio from 4.17% to 2.27% with increasing O₂/3MS flow ratio as shown in Fig. 4.9(b), suggesting an increased incorporation of oxygen in the films.

Figure 4.10 shows the k values versus the Si-CH₃/Si-O ratios for all the films deposited in experiments 2, 3 and 4. A common trend can be seen among the three sets of data, suggesting that a correlation exists between the parameters. The sharp increase in the dielectric constant with increased oxygen incorporation (for Si-CH₃/Si-O ratio < 3.25%) is attributed to the stronger polarizability of Si-O bond as compared to Si-CH₃ bonds. However, for Si-CH₃/Si-O ratio > 3.25%, the dielectric constant stays nearly constant at around 3.0. This result suggests that any increase in the carbon doping beyond this point does not help in lowering the dielectric constant.

Chapter 4: Optimization of process steps and the effects of oxygen in the growth process

(a)

(b)

Figure 4.9: The integrated absorption area ratio of Si-CH₃ and Si-O bonds plotted (a) as a function of thickness for films deposited in experiment 2 and 3, and (b) as a function of O₂/3MS flow ratio for films deposited in experiment 4.

Chapter 4: Optimization of process steps and the effects of oxygen in the growth process

Figure 4.10: The k values versus the Si-CH₃/Si-O integrated absorption area ratio for films deposited in experiments 2, 3 and 4.

There is an obvious shoulder at about 1130 cm^{-1} in all the FTIR absorption spectra, associated with the broad Si-O-Si peak. It was suggested that this shoulder corresponds to Si-O-Si in a cage structure [5] which can lead to micro pores and consequently a lower film density and dielectric constant. To investigate the effect of the cage structure on the dielectric constant, we compared the integrated absorption area ratio of the Si-O main peak at 1040 cm^{-1} and the shoulder at 1130 cm^{-1} for films having a wide range of k values. However, no correlation has been observed.

Chapter 4: Optimization of process steps and the effects of oxygen in the growth process

4.4. Conclusion

Carbon doped silicon oxide $\text{SiO}(\text{C}, \text{H})$ low k thin films ($k \sim 2.9$) deposited by the plasma enhanced chemical vapor deposition (PECVD) technique from trimethylsilane (3MS) and oxygen (O_2) have been studied. Two types of process recipes, namely CVD1 and CVD2 were applied for film deposition. CVD1 is an initial recipe that resulted in films with a uniform deposition rate irrespective of film thickness and a low dielectric constant of about 2.9. However, it suffers from extraordinarily high post particle counts. CVD2 is a modified recipe adopted to address this issue. The main difference between the two recipes is that a pump down step immediately before the film deposition has been omitted in recipe CVD2, and this has successfully reduced the particle counts to a satisfactory level. However when using recipe CVD2, the deposition rate is non-uniform and the dielectric constant is slightly above 3.0, attributed to the residual oxygen in the process step prior to film deposition.

Chapter 4: Optimization of process steps and the effects of oxygen in the growth process

4.5. References

1. Novellus concept one / concept two, Dielectric PECVD process guide / introduction to CVD processing, Volume 1, 73-10093-01, Rev. A, 12 December 1997, p 3-8.
2. Byung Keun Hwang, Mark J. Loboda, Glenn A. Cerny, Ryan F. Schneider, Jeff A. Seifferly, and Tom Washer, Interconnect Technology Conference 2000, Proceedings of the IEEE 2000 International, 5-7 June 2000, Page(s): 52 –54
3. Shiuh-Ko JangJean, Ying-Lang Wang, Chuan-Pu Liu, Weng-Sing Hwang, and Wei-Tsu Tseng, Chi-Wen Liu, In situ fluorine-modified organosilicate glass prepared by plasma enhanced chemical vapor deposition, Journal of Applied Physics, Volume 94, Issue 1, pp. 732-737
4. G. Socrates, Infrared characteristic group frequencies, John Willy & Sons, New York, (1994).
5. Keith Buchanan, The evolution of interconnect technology for silicon integrated circuitry, 2002 GaAsMANTECH Conference.

Chapter 5: Effects of Annealing on Low Dielectric Constant Carbon Doped Silicon Oxide Films

5.1 Introduction

In chapter four, we have optimized the growth of carbon doped silicon oxide (SiO(C,H)) films. Using oxygen to trimethylsilane (3MS) flow ratio of 100sccm:600sccm, SiO(C,H) films with a dielectric constant of 2.9 have been achieved. In the chapter, we aim to study the thermal stability of the films by annealing them at different temperatures from 400 °C to 700 °C in a N₂ atmosphere for 30 minutes. Currently, 400 °C is the highest processing temperature for the back end of line structure, therefore, the stability of the dielectric material at this temperature and possibly high temperatures is a critical issue [1]. This study will provide us with a better understanding of SiO(C, H) films and their thermal stability, and how their dielectric properties can be optimized for use in deep submicron integrated circuit technology.

5.2 Experimental details

The films were deposited on p-type <100> orientation bare silicon 8 inches wafers, with a deposition temperature of 350°C, process pressure of 4.0Torr and rf power of 600W. In this work, we have adopted a simplified version of the recipes discussed in chapter three. The process sequence comprised only gas stabilization, film deposition for a period of 45 seconds and pump down. The flow rates of O₂ and

Chapter 5: Effects of annealing on low dielectric constant carbon doped silicon oxide films

3MS were set at optimized conditions of 100sccm and 600sccm respectively. Post-annealing of the films was performed at 400 °C, 500 °C, 600 °C and 700 °C in a N₂ atmosphere at 7.0Torr for a duration of 30 minutes.

5.3 Results and discussion

The percentage of thickness shrinkage of the films upon annealing at different temperatures is shown in Fig. 5.1. As can be seen, the shrinkage is small and around 1% after annealing at 400 °C and 500 °C, which is within the uncertainty of the measurement technique. However, a more obvious thickness shrinkage of about 4% is observed when annealed at 600 °C, which is further increased sharply to 16% when annealed at 700 °C. The latter suggests a significant change in the bonding structure of the films and the collapse of microvoids in the as-deposited films. In fact, the low density SiO(C,H) films contain microvoids, which is closely related to the incorporation of CH₃ moieties into the films from organosilicon precursor (CH₃)₃SiH [2].

Figure 5.2 shows the refractive indices of the films as a function of the annealing temperature. There is a slight decrease in the refractive index of the films with annealing temperature up to 600 °C. Over this annealing temperature range, the films have undergone some degree of thermal decomposition, with low molecular weight components as well as methyl groups (-CH₃) evaporated, as will be seen from the FTIR results shortly. This leaves behind a more porous microstructure resulting in a slight decrease in the film density, as reflected by the decrease in the refractive

Chapter 5: Effects of annealing on low dielectric constant carbon doped silicon oxide films

index seen in Fig. 5.2 [3].

Figure 5.1: Thickness shrinkage after annealing treatment at different temperatures.

Figure 5.2: Refractive indices of the films as a function of the annealing temperature.

Chapter 5: Effects of annealing on low dielectric constant carbon doped silicon oxide films

Upon annealing at 700 °C, the collapse of the microvoids as discussed earlier resulted in a densification of the films, leading to an increase in the film density and higher refractive index, as seen in Fig. 5.2.

Figure 5.3 shows the dielectric constants of the films as a function of the annealing temperature. Compared with the as-deposited film, the dielectric constant shows a very slight decrease when annealed at 400 °C. Our previous studies of a series of SiO(C,H) films deposited at different O₂/3MS flow ratios (from 50sccm/600sccm to 900sccm/600sccm) also revealed a decrease in the dielectric constants of all the films upon annealing at 400 °C [4]. The decrease, attributed to a reduction in the moisture on the surface of the films, was only very slight for samples deposited at lower O₂/3MS flow ratios, similar to the sample investigated in this work, and progressively became more significant for samples grown at higher flow ratios [4]. When annealed at higher temperature of 500 °C, there is a further decrease in the dielectric constant, as can be seen from Fig. 5.3. However, a sharp increase in the dielectric constant is seen when the samples were annealed at 600 °C and 700 °C. This can be attributed to the lost of incorporated carbon (such as CH and CH₃) among the SiO₂ backbone structure when annealed at higher temperatures.

These proposed changes will be supported by the FTIR spectra to be presented shortly. From the results presented in Figs. 5.1, 5.2 and 5.3, it can be concluded that the chemical structures of SiO(C,H) films are thermally stable up to 500 °C, which exceeds the temperatures encountered during typical interconnect processing steps (400 °C - 450 °C) [5].

Chapter 5: Effects of annealing on low dielectric constant carbon doped silicon oxide films

Figure 5.3: Refractive index of the films as a function of the annealing temperature.

Figure 5.4(a) shows the AFM image measured over a $5\mu\text{m} \times 5\mu\text{m}$ surface area for the as-deposited film, whereas Figs. 5.4(b) to 5.4(e) show the corresponding image of the films annealed at 400°C , 500°C , 600°C and 700°C respectively.

Chapter 5: Effects of annealing on low dielectric constant carbon doped silicon oxide films

(a) Rms: 0.395nm

(b) Rms: 0.525nm

(c) Rms: 0.560nm

(d) Rms: 0.411nm

(e) Rms: 0.392nm

Figure 5.4: Surface morphology of the films (a) as deposited, (b) annealing at 400°C, (c) annealing at 500°C, (d) annealing at 600°C, (e) annealing at 700°C.

Chapter 5: Effects of annealing on low dielectric constant carbon doped silicon oxide films

The root mean square (RMS) roughness deduced from the AFM measurements of the as-deposited and annealed films are shown in Fig. 5.5. The initial increase in the RMS roughness when annealed at 400 °C and 500 °C is attributed to the loss of CH_x and SiCH_x and concurrently the creation of voids near the surface. However, at higher annealing temperatures of 600°C and 700°C, there will be a rearrangement of the amorphous covalent network, resulting in the collapse of voids and compaction of the films, leading to smoother surfaces [1, 6].

Figure 5.5: The change of root mean square roughness of the films as-deposited and annealed films

The FTIR spectra of the as-deposited and annealed films are shown in Fig. 5.6.

Chapter 5: Effects of annealing on low dielectric constant carbon doped silicon oxide films

The assignment of the main peaks observed, $3500\text{--}3600\text{cm}^{-1}$ indicates Si-OH bond, all

others are the same as the which discussed in chapter four. Upon annealing, there is a decrease in the intensity of the Si-CH₃ and C-H peaks, particularly at 700°C , indicating a loss of CH fragments from the film during annealing [7].

Figure 5.6: The FTIR spectra of as-deposited and annealed films.

To measure the changes quantitatively, we have fitted the FTIR spectra over the range of energy where the main absorption occurs with several Gaussian line shape functions, as discussed in chapter four. The relative concentrations of the two main groups in the SiO(C,H) films, Si-CH₃ and the Si-O, were determined using the integrated absorption area ratio (Si-CH₃/Si-O ratio) of the bands at 1270cm^{-1} and 1040cm^{-1} respectively, as discussed in chapter four. The results are plotted as a function of the annealing temperature as shown in Fig. 5.7. From the results, it can be seen that the Si-CH₃/Si-O ratio remains almost unchanged when annealed at 400°C ,

Chapter 5: Effects of annealing on low dielectric constant carbon doped silicon oxide films

and decreases sharply when annealed at higher temperatures. This indicates that the

annealing has eroded the carbon content through out-gassing of the low molecular weight species CH_x as well as the methyl groups SiCH_x . It suggests that the thermal decomposition of the $\text{SiO}(\text{C,H})$ films is governed by the dissociation of low molecular weight reactive species at lower annealing temperature, and the dissociation of Si-CH_3 bonds at higher annealing temperature. As can be seen from Fig. 5.6, there is no C-H peak observed from FTIR spectra when annealing temperature is up to 700°C , and the reduction in the height of Si-CH_3 peak become obvious.

Figure 5.7: The integrated absorption area ratio of the Si-CH_3 bonds to Si-O bonds for as-deposited and annealed films.

The difference in the thermal expansion coefficients of the films and substrate [8,9] can result in high stress in the films and potentially lead to film delamination and affect their long term reliability. Therefore it is crucial to investigate the stress in the

Chapter 5: Effects of annealing on low dielectric constant carbon doped silicon oxide films

SiO(C,H) films upon thermal annealing. The stresses of the film were determined by a

optical laser to measure the change in the curvature induced in the wafer upon annealing, and the results are shown in Fig. 5.8. All the films have been found to exhibit tensile stress, however, with no clear trend observed at different annealing temperatures. In general, the change in stress after annealing may be related to the creation of voids at lower temperatures, and film shrinkage, reconfiguration of the structural network and increased film compactness upon annealing. For the highest interconnect process temperature of 450°C, the stress level is within the acceptable range of 1.5×10^8 to 6×10^8 dynes-sq.cm.

Figure 5.8: The film stress for as-deposited and annealed films.

Chapter 5: Effects of annealing on low dielectric constant carbon doped silicon oxide films

5.4 Conclusion

SiO(C,H) films deposited with O₂ and 3MS flow rates of 100sccm and 600sccm respectively have been investigated. It was found that the thermal stability of this low dielectric could be as high as 500°C. The shrinkage of post cured film is less than 1%, with no obvious change in the film composition at this temperature. The SiO(C,H) low k films were also found to exhibit tensile stress.

Chapter 5: Effects of annealing on low dielectric constant carbon doped silicon oxide films

5.5 References

1. A. Grill and V. Patel, Journal of Applied Physics, Volume 85, Issue 6, Pages 3314-3318.
2. Zhen-Cheng Wu et al. J. Electrochem. Soc. 148, F127 (2001).
3. Licheng M. Han et al., June 27-29, 2000 VMIC Conference, 2000 IMIC-200/00/0401(c), Page 401.
4. M.R.Wang, Rusli, M.B.Yu, N.Babu, C.Y.Li and K. Rakesh, Thin Solid Film, Volumes 462-463, Pages 219-222 (2004).
5. Michael Morgen, E. Todd Ryan, Jie-Hua Zhao, Chuan Hu, Taiheui Cho, Paul S. Ho, Annual Review of Materials Science. Volume 30, Pages 645-680.
6. Byung Keun Hwang, Mark J. Loboda, Glenn A. Cerny, Ryan F. Schneider, Jeff A. Seifferly, and Tom Washer, Interconnect Technology Conference 2000, Proceedings of the IEEE 2000 International, 5-7 June 2000, Pages 52 – 54
7. A. Grill and V. Patel, Applied Physics Letters, August 6, 2001, Volume 79, Issue 6, Pages 803-805.
8. Masahiko Maeda and Manabu Itsumi, Physica B: Condensed Matter , Volume 324, Issues 1-4 , Pages 167-172.
9. Aboaf, J.A., Journal of the Electrochemical Society, Volume 116, Issue 12, 1969, Pages 1732-1736.

Chapter 5: Effects of annealing on low dielectric constant carbon doped silicon oxide films

Chapter 6: Effects of Changing Process Pressure

6.1 Introduction

The dielectric constants of carbon doped oxide films ($\text{SiO}(\text{C,H})$) prepared by the plasma enhanced chemical vapor deposition (PECVD) technique are strongly dependent on the deposition conditions such as temperature, process pressure, rf power and gas flow rate. In this chapter, $\text{SiO}(\text{C,H})$ films have been prepared by the PECVD technique from trimethylsilane (3MS) in an oxygen (O_2) environment with different process pressures from 1.5Torr, 2.0Torr, 4.0Torr, 6.0Torr and 8.0Torr. The effects of changing process pressure on the mechanical, optical and electrical properties of the $\text{SiO}(\text{C,H})$ films were investigated. It has been found that the refractive index decreased from 1.48 to 1.38 while dielectric constant decreased from 3.4 to 2.9 with increasing deposition pressure. FTIR spectra revealed that more -CH and - CH_3 groups were introduced into the silicon dioxide network of the films at higher deposition pressure.

6.2 Experimental details

The films were deposited on p-type <100> orientation bare silicon 8 inches wafers, with a deposition temperature of 350°C , rf power of 600W, O_2 and 3MS flow rate of 100sccm and 600sccm respectively. In this work, we have adopted a simplified version of the recipes discussed in chapter three. The process sequence comprised only gas stabilization, film deposition for a period of 45 seconds and pump down. A

Chapter 6: Effects of changing process pressure

series of films were deposited at different process pressures of 1.5Torr, 2.0Torr, 4.0Torr, 6.0Torr and 8.0Torr.

6.3 Results and discussion

Figure 6.1 shows the film deposition rate as a function of the process pressure. The deposition rate increases sharply with pressure at lower pressure range, reaches a maximum at about 4.0Torr before it decreases gradually at higher pressure.

Figure 6.1: Variation of deposition rate with changes of the deposition pressure.

At very low pressure, the growth rate is slow as there are too few collisions, and electrons traverse the chamber without causing ionization. With increasing deposition pressure, there are many possible elastic and inelastic collisions between

Chapter 6: Effects of changing process pressure

the electrons and the precursor reactants in the plasma due to a decrease in their mean free path. This leads to a high density of reactive species in the plasma, and therefore the deposition rate increases sharply. The gradual decrease in the growth rate at pressures beyond 4.0 Torr is attributed to a further decrease in the mean free path of the species, leading to a decrease in the energies of the charged species, and consequently lower activation of oxygen and decomposition of 3MS molecules [1].

Figure 6.2 shows the refractive indices of the SiO(C,H) films as a function of the deposition pressure.

Figure 6.2: Refractive indices of the SiO(C, H) films on the deposition pressure.

For the as-deposited films, the refractive index decreases from 1.48 to 1.38 with increasing deposition pressure. As higher pressure, there will be an increased incorporation of CH and CH₃ in the film from the 3MS dissociated fragments [2], as shall be seen from the FTIR results shortly. This increase will lead to more CH and

Chapter 6: Effects of changing process pressure

CH₃ bonds relative to Si-CH₃ bonds. Since the refractive index of amorphous carbon films is lower than that of amorphous SiC films, therefore, based on the effective medium theory, overall there will be a decrease in the refractive index of the films.

Figure 6.3 shows the dielectric constants of the SiO(C, H) films. The dielectric constant is observed to decrease from 3.42 to 2.86 with increasing deposition pressure. The reason is that the reactant species become less energetic at higher pressure, and there will be lower dissociation of the precursor in the plasma and reduced ion bombardment. This leads to a lower film compaction, and consequently lower dielectric constant [3]. There is a report that lowering of the plasma power density decreases the dielectric constant of SiO(C, H) films [4, 5, 6]. An increase in the process pressure produces the same effect as the lowering of the plasma power, because of the reduced mean free path of the species leading to less dissociation and bombardment [1, 7]. This is indeed what has been observed in our results.

Figure 6.3: The dielectric constants of the SiO(C, H) films on the deposition pressure.

Chapter 6: Effects of changing process pressure

The FTIR spectra of the SiO(C,H) films are shown in Fig. 6.4. The main peaks observed in the spectra are the same as those observed in chapter four. All the as-deposited films exhibit similar bonding structure. It is noted that the intensity of the C-H bond absorption decreases at lower process pressure. This is attributed to the higher energy of the ions under lower pressure impinging onto the surface of the growing films, leading to a reduced incorporation of hydrogen.

Figure 6.4: The FTIR spectra of the SiO(C, H) films.

The relative concentrations of the Si-CH₃ group and the Si-O group were determined using the integrated absorption area ratio of the bands at 1270cm⁻¹ and 1040cm⁻¹ respectively, as discussed in chapter four, and are shown in Fig. 6.5. As can be seen, there is an increase in the Si-CH₃/Si-O ratio with process pressure for the as-deposited film. Comparing Fig. 6.5 and Fig. 6.3, it can be seen that there is a correlation relation between the Si-CH₃/Si-O ratio and the k value. This conclusion is

Chapter 6: Effects of changing process pressure

consistent with the results presented in chapter four.

Figure 6.5: The Si-CH₃/Si-O ratio of the SiO(C, H) films on the deposition pressure.

Figures 6.6 show the image of the surface morphology for the SiO(C, H) films with pressure of (a) 1.5Torr, (b) 2.0Torr, (c) 4.0Torr, (d) 6.0Torr and (e) 8.0Torr. Figure 6.7 plots the root mean square (RMS) roughness of the SiO(C, H) films as a function of the process pressure.

Chapter 6: Effects of changing process pressure

(a) Rms: 0.442nm

(b) Rms: 0.511nm

(c) Rms: 0.481nm

(d) Rms: 0.445nm

(e) Rms: 0.428

Figures 6.6: Surface morphology of the SiO(C, H) films prepared with varying deposition pressure of (a)1.5Torr, (b)2.0Torr, (c)4.0Torr, (d)6.0Torr and (e)8.0Torr.

Chapter 6: Effects of changing process pressure

Figure 6.7: The root mean square (RMS) roughness of the SiO(C,H) films on the deposition pressure.

All the as-deposited films have a smooth surface with root mean square surface roughness in the range of 0.422 – 0.511nm. The slight increase in the RMS roughness at decreasing pressure from 8Torr to 2Torr can be attributed to the higher energy of the ions resulting in an enhanced bombardment of the growing film, leading to rougher surfaces. On the other hand, the decrease in the roughness of the film deposited at 1.5 Torr may be due to its slower growth rate, which allows the ions and radicals time to locate energetically favourable sites. A more compact film, which is supported by the higher refractive index seen, with smoother surface will be formed.

Chapter 6: Effects of changing process pressure

6.4 Conclusion

The effects of process pressure on the properties of SiO(C,H) film deposited by PECVD technique from trimethylsilane have been investigated. An increase in the deposition pressure will result in films with low dielectric constant and low index. Dielectric constant as low as 2.86 has been obtained from the prepared film at 8.0Torr. Deposition rate as high as 5120Å/minutes has been obtained for the film deposited at 4.0Torr.

Chapter 6: Effects of changing process pressure

6.5 References

1. Yong Chun Quan, Jongryang Joo, Sanghak Yeo and Donggeun Jung, Jpn. J. Appl. Phys. Vol.39 (2000) 1325-1326, Part 1, No. 3A, 15 March 2000
2. Yi Xu et al., Optimization of baking for flare organic low k dielectric material, June 27-29, 2000 VMIC Conference, 2000 IMIC – 200/00/0393(c), Page 393.
3. Alfred Grill, Journal of Applied Physics, Volume 93, Issue 3, Pages 1785-1790 (2003).
4. P. Gonon, A. Sylvestre, H. Meynen, and L. Van Cotthem, J. Electrochem. Soc.150, F47 (2003).
5. AGrill, Thin Solid Films, Volumes 398-399, Pages 527-532.
6. Takeshi Furusawa, Daisuke Ryuzaki, Ryo Yoneyama, Yoshio Homma, and Kenji Hinode, Journal of The Electrochemical Society, Volume 148, Issue 9, Pages F175-F179.
7. Yong Chun Quan, Jongryang Joo and Donggeun Jung, Jpn. J. Appl. Phys. Vol.38 (1999) 1356-1358, Part 1, No. 3A, 15 March 1999.
8. Aboaf, J.A., Journal of the Electrochemical Society, Volume 116, Issue 12, 1969, Pages 1732-1736.
9. Masahiko Maeda and Manabu Itsumi, Physica B: Condensed Matter , Volume 324, Issues 1-4 , Pages 167-172.

Chapter 7: Optical Properties of the Carbon Doped Oxide Film

7.1. Introduction

In this chapter, we have characterized the optical properties of carbon doped oxide films ($\text{SiO}(\text{C}, \text{H})$) by measuring their reflectivity under normal incident and at 70° incident angle with polarized light. These measurements were carried out over a range of wavelengths from 200nm to 1700nm to determine the optical constants (n and k) and thickness of the films.

From the optical results obtained, it is found that the growth of $\text{SiO}(\text{C}, \text{H})$ films involves a two-layer process, in which a layer of thin SiC:H film is first formed, which is then followed by the growth of $\text{SiO}(\text{C}, \text{H})$ film. For example, a $\text{SiO}(\text{C}, \text{H})$ film of 525nm prepared with a $\text{O}_2/3\text{MS}$ flow ratio of 100/600 was found to consist of 25nm of SiC:H followed by 500nm of $\text{SiO}(\text{C}, \text{H})$ film.

In this work, we have investigated the deposition process and proposed a growth mechanism for the $\text{SiO}(\text{C}, \text{H})$ films to explain the two-layer growth process. Though the thin layer of SiC:H does not have much influence on the dielectric constants of the $\text{SiO}(\text{C}, \text{H})$ films, however, it may pose a potential challenge for these low k films in terms of advanced integration, such as acting as an unexpected etch stop layer.

Chapter 7: Optical properties of the carbon doped oxide film

7.2. Experiment details

The SiO(C,H) films were deposited using the Applied Materials CENTURA 5200 D×Z CVD system, as described in chapter four. The SiO(C,H) films were deposited on p-type <100> orientation bare silicon 8 inches wafers, with a deposition temperature of 350°C, process pressure of 4.0Torr and RF power of 600W. The O₂ flow rate was set at 50sccm, 100sccm, 300sccm, 600sccm and 900sccm, while keeping the 3MS flow rate constant at 600sccm. These conditions are similar to those used in chapter four, except that the range of O₂ flow rate has been increased. The process sequence comprised gas stabilization, film deposition for a period of 45 seconds and pump down.

The spectrophotometer used for the optical characterization is FilmTek™ 4000, an optical thin film measurement system from Scientific Computing International (SCI). It combines fiber-optic spectrophotometry with material modeling software for the simultaneous measurement of film thickness, index of refraction, and extinction coefficient [1]. During the measurement, normal incident and polarized 70 degree reflectance data were collected and used to calculate thickness and index of refraction of the measured film. Absolute reflection data is obtained by comparing sample data to the measured reflection of reference sample. The software then performs a regression on the unknown parameters to fit the simulated and experimental reflectance spectra.

The optical constants n and k are modelled using the SCI model, which is a

Chapter 7: Optical properties of the carbon doped oxide film

generalization of the Lorentz Oscillator model given by [1],

$$\varepsilon = \varepsilon_{\infty} \left(1 + \frac{A^2}{E_{center}^2 - E(E - iv)} \right) \quad (7.1)$$

where ε is dielectric constant and E is the photon energy. ε_{∞} is the high frequency dielectric constant, E_{center} is the center energy, A is the amplitude (strength), and v is the vibration frequency of the oscillator. In the Lorentz oscillator model, all oscillators are independent. The SCI model allows for coupling between the oscillators and in the limit that the damping coefficient goes to zero, the SCI model converges to the Lorentz Oscillator Model. The SCI model is well-suited for the modeling of dielectric materials [1], and has been found to accurately describe the optical constants of our films in the measured wavelength range.

7.3. Results and discussion

7.3.1 FTIR spectra and dielectric constants of the SiO(C, H) film

The FTIR spectra of the SiO(C,H) low k films deposited at different O₂/3MS flow ratios are shown in Fig. 7.1. The assignment of the various peaks observed have been discussed in chapter four.

Figure 7.2 shows the dielectric constants of the films as a function of the O₂/3MS flow ratio. The lowest dielectric constant of 2.96 is obtained for the film deposited at a O₂/3MS flow ratio of 100/600. The k values of the as-deposited films

Chapter 7: Optical properties of the carbon doped oxide film

have a slight variation at lower $O_2/3MS$ flow ratio, and increase sharply once the ratio exceeds 100/600. These results are similar to what have been observed in chapter four.

Figure 7.1: FTIR spectra of the $SiO(C,H)$ films deposited at different $O_2/3MS$ flow ratios.

Figure 7.2: Dielectric constants of the $SiO(C,H)$ films as a function of the $O_2/3MS$ flow ratio.

Chapter 7: Optical properties of the carbon doped oxide film

Figure 7.3 plots the integrated FTIR absorption area ratio of the Si-CH₃ bonds to Si-O bonds as a function of the O₂/3MS flow ratio. Similar to the results presented in chapter four, an inverse relation exists between the dielectric constant of the films and the integrated absorption area of the Si-CH₃ bonds to Si-O bonds.

Figure 7.3: The integrated FTIR absorption area ratio of the Si-CH₃ bonds to Si-O bonds for SiO(C,H) films as a function of O₂/3MS flow ratio.

7.3.2 Two-layer growth of the SiO(C, H) film

To ensure that the SCI model used for the modelling can accurately describe the optical dispersion of the films, the measurements were carried out over a wide range of wavelength from 200nm to 1700nm (UV measurement capability is only available for normal incident). A crucial test of the validity of the model will be whether a good fit between the simulated and experimental data can be achieved over the entire range of wavelength investigated. Indeed as shall be seen, a very good fit

Chapter 7: Optical properties of the carbon doped oxide film

can be obtained concurrently at both incident angles for all the films using the SCI model.

Initially, a one-layer optical model was assumed in fitting the experimental reflectance data. However, this simple model fails to provide a good fit to the reflectance spectra of the films. A two-layer model was then adopted to account for possible inhomogeneous growth during the deposition process. To compare the fitting using the two different models, the simulated and the experimental reflectance spectra of the film deposited at a $O_2/3MS$ flow ratio of 100/600 are shown in Fig. 7.4(a) and 7.4(b) using the one-layer and two layer models respectively.

The best fitted coefficients based on the two different models are shown in Table 7.1.

	One layer model coefficients	Two layer model - layer 1 coefficients	Two layer model - layer 2 coefficients
No. of Oscillators	1	1	1
ϵ_{∞}	1.00	1.00	1.00
Damping Coef. (eV)	0.97	0.97	1.28
Amplitude A (eV)	10.86	10.86	13.75
E_{center} (eV)	11.35	11.35	12.48
ν (eV)	0.67	0.67	0.045

Table 7.1: SCI material model coefficients.

As can be seen, the two-layer model gives a much better fit compared to the one-layer model. Indeed, the two-layer model has been found to consistently provide better fitting for all the other films as well. To check for the uniformity of the optical

Chapter 7: Optical properties of the carbon doped oxide film

properties of the SiO(C,H) films, and to ensure the repeatability of the results, the reflectance spectra for all the samples were measured at five different points on the 8-inch wafers. We found consistent best-fitted parameters in the SCI model across the different points, and hence deduced that the optical properties are very uniform across the films.

Figure 7.4: The measured and simulated reflectance spectra of the SiO(C, H) film deposited with a O₂/3MS flow ratio of 100/600 using (a) one layer model and (b) two layer model.

Chapter 7: Optical properties of the carbon doped oxide film

Based on the two-layer model fitting, it was found that the lower layer next to the substrate has consistently higher refractive indices compared to the upper layer. We illustrate this by considering the sample deposited at a $O_2/3MS$ flow ratio of 100/600. The refractive indices and extinction coefficients for the lower layer and upper layer are shown in Fig. 7.5(a) and Fig. 7.5(b) respectively.

Figure 7.5: The refractive indices and extinction coefficients of the (a) lower layer and (b) upper layer of the $SiO(C,H)$ film deposited with a $O_2/3MS$ flow ratio of 100/600.

Chapter 7: Optical properties of the carbon doped oxide film

The thickness of these layers for the films deposited at different $O_2/3MS$ flow ratios are plotted in Fig. 7.6. The lower layer is also found to be consistently much thinner compared to the upper layer. Based on the growth time of 45 seconds and assuming uniform growth rate, it can be estimated that the growth of the first layer occurred over a very short initial period of around 1 to 2 seconds.

Figure 7.6: The thickness of the lower and upper layers of the SiO(C,H) films deposited at different $O_2/3MS$ flow ratios.

As 3MS does not have oxygen in its chemical composition, an oxidant is required in the deposition process to provide low k films based on a Si-O network. The network formation occurs through the replacement of Si-C bonds in 3MS with Si-O bonds [2]. The oxygen radicals also help in the decomposition of 3MS in the plasma [3]. Oxygen radicals activate and dissociate 3MS molecules into highly reactive species through elastic and inelastic collisions that bring Si-C bonds to the substrate. Subsequently, a large amount of dissociated oxygen radicals produced

Chapter 7: Optical properties of the carbon doped oxide film

selectively oxidize Si-C bonds at the surface to form a complex containing Si-O bonds. These complexes are then absorbed on the depositing surface to form the film. Therefore, upon the initial growth of a thin layer of Si-C rich film with higher refractive indices, the subsequent growth involves bulk material of SiO(C,H) film with lower refractive indices. This will give rise to two optically distinct layers, and is believed to account for the optical measurement results observed.

7.4 Conclusion

A detailed investigation of the optical properties of SiO(C,H) films using reflectance spectrophotometry revealed a two-layer growth process for these films. The results are attributed to the initial growth of a thin layer of Si-C rich film, before the growth of the subsequent SiO(C,H) bulk material.

Chapter 7: Optical properties of the carbon doped oxide film

7.5 References

1. “FilmTek 4000™ operations manual”, by Scientific Computing International, 2002.
2. Mark O'Neill, Aaron Lukas, Raymond Vrtis, Jean Vincent, Brian Peterson, Mark Bitner and Eugene Karwacki, Low-k Materials by Design, Semiconductor International, 6/1/2002.
3. M.R.Wang, Rusli, M.B.Yu, N.Babu, C.Y.Li and K. Rakesh, Thin Solid Film, Volumes 462-463, Pages 219-222 (2004).

Chapter 8: Conclusion and Recommendations

8.1 Conclusion

This thesis reports on the growth and characterization of carbon doped silicon oxide ($\text{SiO}(\text{C}, \text{H})$) low k dielectric thin films for multilevel interconnect applications. The films were deposited using the plasma enhanced chemical vapour deposition (PECVD) technique, with source gases of linear organosilicate trimethylsilane (3MS) and oxygen. The films are hybrid materials consist of both organic and inorganic contents. They therefore hold some unique properties such as low dielectric constant, good thermal and mechanical stability. Their properties can also be tuned through changing the process condition as well as process sequence.

In this work, we have first studied $\text{SiO}(\text{C}, \text{H})$ films deposited using two recipes CVD1 and CVD2. The recipe CVD1 is an initial recipe that suffers from extraordinarily high post particle counts. To address this issue, a modified recipe CVD2 has been adopted. The main difference between the two recipes is that a pump down step immediately before the film deposition has been omitted in recipe CVD2, and this has successfully reduced the particle counts to a satisfactory level. However this compromises the other properties of the film in terms of a slight increase in the dielectric constant and non-uniform deposition rate as a function of film thickness.

Chapter 8: Conclusion and recommendations

The thermal stability of the SiO(C, H) films was next investigated by annealing them at different temperatures from 400 °C to 700 °C in a N₂ atmosphere for 30 minutes. It was found that the thermal stability of this SiO(C, H) films could be as high as 500°C. Up to this temperature, the thickness shrinkage of the annealed film is less than 1% and there is no obvious change in their chemical composition.

The effects of process pressure on the mechanical, optical and electrical properties of the SiO(C, H) films have also been studied. The process pressure was tuned from 1.5Torr to 8.0Torr while keeping the other growth parameters identical. It has been found that the refractive index decreased from 1.48 to 1.38 while the dielectric constant decreased from 3.4 to 2.9 with increasing deposition pressure. Dielectric constant as low as 2.9 has been obtained for the film deposited at 8.0Torr and deposition rate as high as 5120Å/minutes has been obtained for the film deposited at 4.0Torr. The FTIR results revealed that more -CH and -CH₃ groups were introduced into the silicon dioxide network of the films at higher deposition pressure.

In this work, we have also investigated the deposition of SiO(C, H) films, and proposed a growth mechanism to explain the observed two-layer growth process. We have characterized the optical properties of SiO(C, H) films by measuring their reflectivity under normal incident and at 70° incident angle with polarized light. From the optical results obtained, it is found that the growth of SiO(C, H) films involves a

Chapter 8: Conclusion and recommendations

two-layer process, in which a thin layer of SiC:H film is first formed, which is then followed by the growth of SiO(C,H) film.

8.2 Recommendations for further research

The properties of the PECVD deposited SiO(C, H) films are not only dependent on the deposition conditions such as process pressure and gas flow rate, but also on the process temperature, rf power and other parameters. Therefore the effects of the process temperature and rf power on the properties of the SiO(C, H) film need to be further investigated. The integration of SiO(C, H) low k film as multilevel interconnect dielectric using damascene structure need to be intensively studied in the future work to assess its suitability as the next generation low k material.

Author's publication

Author's Publications

Journal paper

1. M. R. Wang, Rusli, J. L. Xie, N. Babu, C. Y. Li and K. Rakesh, Study of oxygen influences on carbon doped Silicon oxide low k thin films deposited by plasma enhanced chemical vapor deposition, Journal of Applied Physics, Volume 96, Issue1, pp.829-834.
2. M. R. Wang, Rusli, M. B. Yu, N. Babu, C. Y. Li and K. Rakesh, Low dielectric constant films prepared by plasma-enhanced chemical vapor deposition from trimethylsilane, Thin Solid Films, Volumes 462-463, Pages 219-222 (2004).
3. Rusli, M. R. Wang, M. B. Yu, and C. Y. Li, Process pressure effect on properties of carbon doped silicon oxide low dielectric constant films prepared by PECVD using trimethylsilane, Journal of Applied Physics, to be submitted.
4. Rusli, M. R. Wang, M. B. Yu, and C. Y. Li, Effects of annealing on low dielectric constant carbon doped silicon oxide films, Diamond and Related Materials, to be submitted.

Conference paper

1. M. R. Wang, Rusli, M. B. Yu, N. Babu, C. Y. Li and K. Rakesh, Low dielectric constant films prepared by plasma enhanced chemical vapor deposition from trimethylsilane, ICMAT2003, Singapore, p551.
2. Rusli, M. R. Wang, B. K. Tay, M. B. Yu, N. Babu, C. Y. Li and SH.R.Wang, Two-layer growth of carbon doped silicon oxide low dielectric constant films prepared by PECVD using trimethylsilane, ThinFilm2004, Singapore.