Plasma assisted deposition of Ti-Si-N and Ti-Si-N-O diffusion barrier films

Ee, Elden Yong Chiang

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PLASMA ASSISTED DEPOSITION OF TI-SI-N AND TI-SI-N-O DIFFUSION BARREIR FILMS

Ee Yong Chiang, Elden

School of Materials Science and Engineering

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TERMINOLOGY

AFM	-	Atomic Force Microscopy
BTS	-	Bias Temperature Stressing
BE	-	Binding Energy
BOE	-	Buffered Oxide Etch
CCP	-	Capacitively Coupled Plasma
EL	-	Electroless
EEDF	-	Electron Energy Distribution Functions
EDX	-	Energy Dispersive X-ray
EDTA	-	Ethylene Diamine Tetraacetic Acid
FESEM	-	Field Emission Scanning Electron Microscopy
ICP	-	Inductively Coupled Plasma
ITRS	-	International Technology Roadmap for Semiconductors
ILDs	-	Interlayer Dielectrics
IC	-	Integrated Circuit
KE	-	Kinetic Energy
MPU	-	Micro Processor Unit
MOCVD	-	Metalorganic Chemical Vapor Deposition
MOALD	-	Metalorganic Atomic Layer Deposition
MSQ	-	Methyl Silsesquioxane
MOS	-	Metal Oxide Semiconductor
MIS	-	Metal Insulator Semiconductor

OMCVS	-	Organo Metallic Chemical Vapor Deposition
PECVD	-	Plasma Enhanced Chemical Vapor Deposition
PVD	-	Physical Vapor Deposition
RMS	-	Root Mean Square
RTA	-	Rapid Thermal Annealing
R.F	-	Radio Frequency
RBS	-	Rutherford Backscattering Spectrometry
SPM	-	Scanning Probe Microscopy
SC1	-	Standard Cleaning 1
SC2	-	Standard Cleaning 2
HRTEM	-	High Resolution Transmission Electron Microscopy
TOF-SIMS	-	Time-of-Flight Secondary Ion Mass Spectrometry
TDMAT	-	Tetrakis Dimethyl Amino Titanium
TDEAT	-	Tetrakis Diethylamido Titanium
ULSI	-	Ultra Large Scale Integration
VLSI	-	Very Large Scale Integration
XPS	-	X-ray Photoelectron Spectroscopy
XRD	-	X-ray Diffraction

ABSTRACT

In the sub-quarter-micron generation integrated circuits (ICs), Cu has completely replaced aluminum as the interconnect material due to its favorable electrical conductivity ($1.67 \mu\Omega\cdot\text{cm}$) and resistance to electromigration. In order to prevent Cu contamination in the silicon device layer, diffusion barriers such as tantalum (Ta) and tantalum nitride (Ta₂N₃) have to be used to fully contain the Cu interconnects. It is a challenging issue to develop a new generation of more effective diffusion barriers with further down-scaling of transistor dimensions.

This work explores the processing and properties of Ti-Si-N and Ti-Si-N-O material systems to be used as the new generation barrier materials. The novelty of this research work is the development of plasma assisted deposition processes for the growth of Ti-Si-N and Ti-Si-N-O barrier films by low frequency, high density inductively coupled plasma (ICP) assisted nitrogen implantation into an existing titanium silicide substrate, and physical-chemical vapor deposition (P-CVD) employing silane/nitrogen gas and titanium sputtering target, respectively. Film properties were characterized by time-of-flight secondary ion mass spectrometry (SIMS), field emission scanning electron microscopy (FESEM), high resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectrometry (RBS), X-ray diffraction (XRD), four-point resistivity probe, and atomic force microscopy (AFM).

In the work of ICP processed Ti-Si-N, 2 – 67 at% of nitrogen were successfully introduced into Ti_xSi_y structure. This proved the feasibility of ICP process for the formation of ternary barrier films. In addition, unfavorable columnar structure of Ti_xSi_y was damaged by ion bombardment and formed nanostructured TiN and Si₃N₄ phases. Furthermore, the work finds that the external bias plays an important role in controlling the sheet resistance of Ti-Si-N films, but has less effect on the implantation depth of nitrogen. Increasing argon plasma activation time improves the penetration

depth of nitrogen into Ti_xSi_y structure. Copper diffusion studies showed that higher external bias and longer nitrogen plasma treatment time led to degradation of the barrier performance due to higher density of defects by the plasma treatment. A 15-nm thick barrier showed no Cu diffusion at 650°C for 30 minutes. With the diffusion of copper into Ti-Si-N film at high annealing temperatures, Cu-Ti and Cu-N compounds formation were detected. From the analysis of compound formation, the current work suggests that it is the Si that contributes to the improvement in the diffusion barrier performance. Based on the overall requirements, a 15-nm Ti-Si-N layer formed by low frequency, high density inductively coupled plasma process in the current study produces an effective barrier against copper diffusion.

This work also explores electroless copper seed layer deposition on the ICP Ti-Si-N barrier films. To the knowledge of the author, there has been little work on the deposition of electroless copper seed layer on TiSiN barrier film. The results showed that the required palladium activation time was generally shorter on the Ti-Si-N as compared to TiN. Several important properties for the seed layer, such as surface coverage, grain size, texture formation, and electrical resistivity were studied.

The physical-chemical vapor deposition presents another novel process for the formation of Ti-Si-N-O barrier at very low temperatures between 35 to 40°C. This process produced films containing 2 – 15 nm Ti-N, Si-N and Ti-Si nanocrystals embedded in Ti-O, Si-O and Si-N-O amorphous matrix. Several unique features of this process were identified. This process is found capable of producing films with very smooth surface. In addition, the film possesses very good electrical stability against copper ion diffusion. Thorough investigation on the electrical stability was carried out by bias temperature stress (BTS) test. All the Ti-Si-N-O films have shown good BTS stability up to 150°C and 1 MV/cm, 200°C and 0.5 MV/cm, which far exceeds the requirements for industrial applications. Besides that, the mechanism of electrical instability was also carefully clarified.

Chapter 1

Introduction

This chapter will outline the motivation of this research, the objectives and work plan, followed by the summary of novelty of the work. The organization of this thesis will also be introduced in this chapter.

1.1 Background and motivation

As we enter the twenty-first century, rapidly evolving market-driven needs are accelerating the development of integrated circuitry (IC) with increasingly higher speed and more diverse functionality. Emerging performance specifications are being met through a combination of new IC designs and innovative material and process solutions. IC designs almost universally share a common trend in increasing the density of devices per chip, which thus requires shrinking the feature size of individual devices and enhancing the overall number of metallization layers that exploit the third spatial dimension in order to minimize the overall interconnect wire-length distribution.

The achievement of maximum signal transmission in emerging chip and system architectures requires minimizing the resistance times capacitance (RC) time delay. RC delay has replaced intrinsic device delay as the major speed limiter in sub-quarter-micron device nodes. This replacement is due primarily to the increasingly higher RC time constant in the ever narrower, more-closely spaced interconnect lines [ITRS 2004]. Minimizing RC delay has forced a transition from aluminum-copper (Al-Cu), tungsten (W), and silicon dioxide (SiO₂)-based interconnects to Cu and low-dielectric constant (k) metallization schemes. This transition results in significant reduction in RC time delay because of the higher conductance of Cu and lower capacitance of low- k materials.

The shift to copper-based interconnects for sub-quarter-micron device technologies has generated significant challenges in the identification and development of the robust material and process technologies required to form reliable multilevel metallization interconnects. Copper, is a well known fast diffuser and a triple acceptor in silicon that generates deep levels at 0.24, 0.37 and 0.52 eV, which act as recombination centers in the band gap of silicon [Milnes, 1973]. Thus, the objective is to identify and develop diffusion barrier materials that are excellent in preventing the diffusion and intermixing of copper with the adjacent dielectric and semiconductor regions of the computer chip.

A reliable diffusion barrier should possess several features, which include the following [Grovenor, 1989; Nicolet, 1978]:

- (1) Thermodynamical stability when in contact with materials: A viable barrier material must not react with copper or underlying substrate under the thermal, mechanical and electrical stress conditions encountered in subsequent processing steps or normal operating conditions
- (2) High density so as to eliminate diffusion across voids, defects or loosely packed grain boundaries
- (3) Microstructure which minimizes grain boundaries as diffusion paths
- (4) Low contact resistance and a reasonable thermal conductivity
- (5) Excellent adhesion to all materials used in the metallization scheme
- (6) Electrochemical potential close to that of surrounding materials in order to avoid the formation of galvanic corrosion cells with the metallization layers
- (7) Low film stresses [Baluffi, 1975] and enhanced resistance to thermal and mechanical stresses
- (8) Excellent step coverage in aggressive device structures

- (9) Acceptable thermal and electrical conductivities
- (10) Suitable texture to drive the nucleation and growth of subsequent Cu conductor layers with the desirable morphology
- (11) High thermal and structural stabilities against surrounding insulator and conductor materials
- (12) Good chemical mechanical polishing (CMP) compatibility
- (13) Excellent compatibility with integrated circuitry fabrication flows, including the ability to be deposited within the thermal budget limitations of microelectronics processing, capability of selective patterning
- (14) Non-contamination to device & equipment
- (15) Ability to accommodate the surface roughness created by dielectric materials on an atomic scale

From the list of requirements, compromises are often needed and some contradictions cannot be avoided. Thus, careful design of the functionality of barrier layer is essential. According to the 2005 international technology roadmap for semiconductors (ITRS), beyond the current 70 nm technology node, diffusion barrier thickness requirements for copper are anticipated to be less than 5.6 nm [ITRS 2005] as shown in Table 1-1.

Table 1-1: Micro-processor unit (MPU) interconnect technology requirement – near term 2005.

Year of Production	2005	2006	2007	2008	2009	2010	2011	2012	2013
Technology node (nm)	80	70	65	57	50	45	40	36	32
Number of metal level	11	11	11	12	12	12	12	12	13
Barrier thickness (nm)	6.5	5.6	4.8	4.3	3.7	3.3	2.9	2.6	2.4

Various refractory metals and their nitrides were heavily examined as barrier materials. For example, TaN was used as diffusion barrier for copper, due to its high thermal stability and chemical inactivity with Cu [Kaloyeros, 1999]. However, Hara [Hara, 2001] reported that a high stress developed at the Cu/TaN interface in thin copper seed layers. Besides that, copper layer peeled easily during chemical-mechanical polishing process, [Toida, 2001] due to poor adhesion between TaN and Cu layer. In addition, polycrystalline TaN barrier layer was found to provide fast diffusion paths; as a result, a thick barrier layer had to be used. But, according to Hara [Hara, 2001], such copper interconnections with thick barrier layers would lead to undesirable higher sheet resistance interconnection layers.

Besides TaN, extensive work in the deposition of TiN by both sputtering [Kumar, 1988; Kanamori, 1986] and chemical vapor deposition [Yuokoyama, 1991; Ishihara, 1990] has been reported. Unfortunately, TiN has not been able to provide adequate copper barrier performance for thickness at or below 20 nm [Chang, 1990]. A common denominator underlying many of the above references is the columnar structure of TiN, typically with a (111) or (200) preferred orientation. Such a structure can lead to short-circuit diffusion paths via grain boundaries and result in the failure of the devices. Besides that, binary alloy barriers are inferior to the ternary alloy barriers in thermal stability, because the reaction of binary alloy barriers with the metal overlayers and/or the Si substrate takes place far below the crystallization temperature of the alloy [Mayumi, 1996]. Thus, with the down-scaling of devices and more stringent reliability requirements, there is a need for more effective barrier materials. The diffusion barriers can be further improved by alloying the binary barrier materials with silicon or oxygen, leading to a high diffusion-resisting quasiamorphous structure [Chen, 2000].

In this respect, ternary refractory metal barriers such as titanium-silicon-nitrides (Ti-Si-N), tantalum-silicon-nitrides (Ta-Si-N) and tungsten-silicon-nitrides (W-Si-N) systems, are potential candidates as the next generation diffusion barrier in copper/low- k dielectric back-end-of-line device fabrication, because of their favorable chemical, structural, and thermal properties. A proven barrier solution [Ding, 2001] is TDMAT (tetrakis dimethyl amino titanium)-based CVD Ti-Si-N, which has demonstrated more than 90% conformal step coverage and copper diffusion properties equivalent to PVD TaN. By introducing Si into Ti-N matrix, the diffusion properties can be improved. From XPS analysis, Si is bonded to the N which significantly improved barrier properties compared with CVD TiN [Ding, 2001]. The existing CVD TiN based hardware can be easily modified to deposit Ti-Si-N by adding a SiH₄ gas line. In addition, as reported by Ryu *et al* [Ryu, 1999] and Sun *et al* [Sun, 1997], Ti-Si-N films are stable against crystallization at temperatures as high as 900°C – 1000°C. Ti-Si-N has the additional advantage of good wettability to copper. The wetting characteristics of copper to the underlying barrier layer correlated with the improved electromigration resistance [Ding, 1994].

Existing work in developing Ti-Si-N barrier films includes physical vapor deposition (PVD) [Reid, 1994; Reid, 1993; Reid, 1996; Shacham, 1997] and chemical vapor deposition (CVD) techniques [Eric, 2000; Edward, 2001; Prindle, 2002]. In the PVD studies, most of the diffusion barriers were more than 100 nm thick, which made the resulting conclusions less applicable to subquarter-micron device structure [Reid, 1993; Reid, 1996; Shacham, 1997]. In addition, tantalum-based ionized PVD diffusion barriers used across the semiconductor industry might begin to show marginality and devices failures as the interconnect feature sizes continue to scale down with each new technology generation [Prindle, 2002]. More conformal barriers become necessary for

adequate step coverage in high aspect ratio vias and trenches. For good step coverage, CVD process is usually preferred. Custer *et al* used a MOCVD process, in which the reaction of tetrakis diethylamido titanium (TDEAT), silane (SiH_4), and NH_3 took place to deposit Ti-Si-N films over the temperature ranging from 300°C to 450°C [Custer, 1996]. More recently, metalorganic atomic layer deposition (MOALD) was employed to deposit conformal Ti-Si-N layers at low substrate temperature (180°C) [Min, 1999]. Good step coverage was reported; however, information about film purity, resistivity and barrier properties was not provided.

The work is focused on the development of low frequency, high density inductively coupled plasma process (ICP) for the growth of Ti-Si-N diffusion barrier films. The ICP featuring high ion densities: 10^{11} - 10^{13} ions/cm³, (convention plasma density: 10^9 - 10^{11} ions/cm³) and low plasma potentials have advantages in the generation of large-area and large volume plasma for fabrication and processing of unique materials and ultra-fine selective etching of semiconductor wafers. In addition, low frequency ~ 0.5 MHz was applied for plasma production, which increased the number of turns in a planar coil. A higher number of turns increased the degree of the radial uniformity of plasma.

The ICP process implants N into existing Ti_xSi_y to form Ti-Si-N films. The implantation process has destroyed the columnar structure and formed a dense microstructure. Process temperatures below 400°C, which is compatible with current back-end-of-line processes. By employing a low frequency, high density inductively coupled plasma process, very good control in Ti-Si-N thickness can be achieved by controlling the process parameters. Thus, in short, the inductively coupled plasma process provides the competitive advantages over other processes in the formation of Ti-Si-N barrier films.

Besides the ICP process, physical-chemical vapor deposition process was also used to grow Ti-Si-N-O films. Many studies on ternary films deposited by PVD have been reported [Sun, 1997; Vaz, 1998; Diserens, 1999; Vaz, 2000; Vaz, 2001; Ribeiro, 2004]. Deposition temperatures of these existing works range from 150°C to 600°C. Although most of them used r.f.- or d.c.-reactive sputtering in an Ar/N₂ gas mixture, the results were not always consistent with each other. The structure and the properties of films depended sensitively on the depositing conditions [Jehn, 2000].

The current work aims to use r.f. reactive magnetron sputtering of Ti target together with silane and nitrogen gases to form Ti-Si-N-O films. In this process, silane gas is decomposed at temperature as low as 40°C, which is not achievable in the CVD process (to decompose silane gas through CVD, the required temperature is between 800°C – 1050°C for atmospheric pressure CVD (APCVD); 500°C for low pressure CVD (LPCVD) [Badih, 1997; Murarka, 1989]). It should be noted that for back-end-of-line process, the temperature cannot exceed 425°C because of the dielectric used. In the current P-CVD process, the reacting gases can be broken down to create plasma using a RF field. This lowers the chemical reaction activation barrier, which results in a lower deposition temperature. Low-temperature processing is attractive because it creates less diffusion spreading.

After the formation of Ti-Si-N and Ti-Si-N-O films, investigation on the thermal and electrical stability was carried out. In thermal stability studies, Shin *et al* [Shin, 2004] and Olowolafe *et al* [Olowolafe, 1991] found that Cu diffusion occurred at temperature above 425°C. This was mainly due to columnar structure of TiN films. On the other hand, Ti-Si-N films consist of crystalline structures and amorphous structure which can reduce the grain boundaries density and thus improve the barrier performance against copper diffusion. Research reports on thermal diffusion barrier

performance vary, ranging from 600°C to 850°C [Reid, 1994; Eric, 2000; Shalish, 1999; No, 2000]. Thus, this research work will focus on the effect of plasma process parameters and annealing temperatures on the diffusion performance of Ti-Si-N films.

It should be noted that, as in the case of most diffusion barrier studies, simple thermal stressing was employed. A more accurate test of interconnect reliability is bias temperature stress (BTS) testing, where the stacks are subjected to low temperature stressing under actual voltage bias.

For BTS studies, Angyal *et al* applied bias temperature stressing to Cu/PVD TaSi_xN_y/SiO₂/Si capacitor structures to examine the diffusion barrier performance of 10 nm thick Ta₃₆Si₁₄N₅₀ liners [Angyal, 1995]. The capacitor structures were stressed at 1.1 MV/cm and 300°C for 80 h. The authors observed the occurrence of shifts in the flatband voltages of the resulting C-V curves. However, they concluded that barrier failure had not happened and attributed the voltage behavior to unrelated effects [Kolawa, 1990]. On the other hand, Smith *et al* reported BTS testing at 50 V and 200°C on 10 nm thick MOCVD TiSi_xN_y samples. In particular, they found that the MTTF of an MOCVD Ti₂₃Si₁₄N₄₅O₃C₃H₁₂ sample deposited at 400°C was approximately 10 -100 times better than that of PVD TiN [Smith, 1996]. In the work by Kizil and Steinbrüchel [Kizil, 2004], 90% barrier failure was evident for amorphous TiN after 90 minutes bias-temperature stressed (BTS) at 150°C, 2 MV/cm. Although amorphous TaN performed better than TiN, a 40% barrier failure was still observed after the same BTS condition. In addition, all barriers failed more rapidly at the higher temperature, such as at 200°C and 250°C. In the current work, the barrier films can prevent copper diffusion up to 200°C and 0.5 MV/cm.

Besides diffusion studies, electroless copper deposition on Ti-Si-N films was investigated. Before electrolytic Cu plating, a thin Cu is needed as the seed layer.

Electroless deposition of copper as a seeding technology has been proposed due to its uniform deposition, complete surface coverage, and better corrosion resistance [Ding, 2001]. In addition, power supplies, electrical contacts and other apparatus necessary for electroplating are not required.

The ITRS 2005 roadmap [ITRS, 2005] proposed several alternative seeding alternatives such as CVD Cu seed, seedless electro-deposition and electroless (EL) Cu seed. CVD Cu seed has excellent step coverage in sub-micron features but suffers from high cost [Lee, 2000; Jackson, online; Park, 2000]. Seedless electrodeposition cannot provide the throughput necessary for production [Takahashi, 1999]. Electroless copper seed is a low-cost process and it is expected to deliver conformal step coverage down to an aspect ratio of $\sim 8:1$ for $0.1\ \mu\text{m}$ dimensions [Shacham, 1997; Morand, 2000]. To date, there is no research work on electroless copper deposition on Ti-Si-N barrier layers. This work, for the first time, provides guidelines for electroless Cu plating on Ti-Si-N surface.

1.2 Objectives and scopes

Based on the above, this thesis reports ternary barrier formation and characterization. In order to improve the binary barrier system, a third element is added. The study covers the formation of Ti-Si-N and Ti-Si-N-O barrier films via the two process routes, namely low frequency, high density inductively coupled plasma process and physical-chemical vapor deposition process. In addition, the effect of processing parameters on the properties of Ti-Si-N and Ti-Si-N-O films; thermal and electrical properties of Ti-Si-N/Ti-Si-N-O against copper diffusion are investigated. Electroless copper deposition on Ti-Si-N films is studied in detail too. The thesis aims

to provide a systematic understanding of the correlation of the processing parameters, microstructure and the properties of the Ti-Si-N and Ti-Si-N-O films.

The objectives and scope of the work are described below.

A) **Formation of Ti-Si-N and Ti-Si-N-O barrier films**

This work explores the processing and properties of Ti-Si-N and Ti-Si-N-O material systems to be used as the new generation barrier materials. Two plasma assisted deposition processes were developed for the growth of Ti-Si-N and Ti-Si-N-O barrier films; namely:

1) Low frequency, high density inductively coupled plasma (ICP) process:

The objective of this part is to study the formation of Ti-Si-N barrier films using ICP process that involves the following reaction:

This work aims to (1) understand the implantation mechanism of N into Ti_xSi_y matrix; (2) investigate the implantation depth of nitrogen and chemical bonding states of implanted N; (3) characterize the properties of Ti-Si-N films including uniformity, microstructure, phase composition, resistivity, surface roughness and surface morphology of Ti-Si-N barrier films; (4) study the relationship between plasma processing parameters and the properties of Ti-Si-N films.

2) Physical-chemical vapor deposition (P-CVD) process for the formation of Ti-Si-N-O barrier at very low temperatures between 35 to 40°C, that involved the following reaction

Ti plasma (from Ti target) + Silicon plasma (from SiH_4) + nitrogen plasma + O (from vacuum chamber) $\rightarrow$ Ti-Si-N-O

This work aims to (1) investigate low temperature process in the formation of Ti-Si-N-O films; (2) characterize the properties of Ti-Si-N-O films including

uniformity, microstructure, phase composition, resistivity, surface roughness and surface morphology of Ti-Si-N-O barrier films; (3) study the effects of plasma processing parameters on the properties of Ti-Si-N-O films.

(B) Thermal diffusion studies of Ti-Si-N barrier films

In this part of the study, the relationship between plasma process parameters and diffusion performance of ICP Ti-Si-N films is evaluated. Besides that, ICP Ti-Si-N diffusion performance at various temperatures from 350°C to 850°C is investigated. Furthermore, mechanisms of being a good barrier material are discussed. Finally, the relationship between the barrier performance and the film structures is studied in an attempt to elucidate the controlling factor for Cu diffusion in Ti-Si-N films.

(C) Electrical stability of P-CVD Ti-Si-N-O barrier films

This work aims to evaluate the barrier properties of Ti-Si-N-O films against metal ionic diffusion using bias temperature stressing (BTS) technique at different temperatures and biasing conditions. Besides that, this work also investigates the mechanism of electrical instability in Ti-Si-N-O films and the mechanisms of being a good barrier material. Furthermore, an understanding the correlation between Ti-Si-N-O barrier performance, processing issues and film properties is provided.

(D) Deposition of Electroless Cu on Ti-Si-N films

This work investigated the mechanisms of palladium seed distribution on Ti-Si-N films and Ti-N films. In addition, the effect of plasma processing parameters on palladium seed distribution and electroless copper film properties are studied. Finally,

the relationship between plasma process parameters and the properties of electroless copper on Ti-Si-N films are evaluated.

1.3 Novelty of the work

This work explores the processing and properties of Ti-Si-N material systems to be used as barrier materials in advanced interconnect systems. The novelty of this research work can be classified as following:

A) Low frequency, high density inductively coupled plasma (ICP) process has been successfully developed for the formation of Ti-Si-N films. Through this process, unfavorable columnar structure of Ti_xSi_y was damaged by ion bombardment and formed nanostructured TiN and Si_3N_4 phases, which showed no Cu diffusion at 650°C for 30 minutes.

B) Electroless copper seed layer deposition on the ICP Ti-Si-N barrier films, for the first time, provides guidelines for Cu seeding technology on ternary barrier surface. The results showed that the required palladium activation time was generally shorter on the Ti-Si-N as compared to TiN.

C) Physical-chemical vapor deposition presents another novel process for the formation of Ti-Si-N-O barrier at very low temperatures between 35 to 40°C. This process produced films containing 2 – 15 nm Ti-N, Si-N and Ti-Si nanocrystals embedded in Ti-O, Si-O and Si-N-O amorphous matrix. All the Ti-Si-N-O films have shown good BTS stability up to 150°C and 1 MV/cm, 200°C and 0.5 MV/cm, which far exceeds the requirements for industrial applications. These works have been published in *Electrochemical Solid-State Letters*, 9, G100 (2006) and *Journal of The Electrochemical Society*, 153, G470 (2006), which also has been selected for

publication in Virtual Journal of Nanoscale Science and Technology, 13, Issue 14 (10 April, 2006), which covering a focused area of frontier research.

1.4 Organization of thesis

This thesis is organized into five chapters. Chapter 1 focuses on the project background, motivation, objectives and scope, the novelty of the work and the organization of the thesis. Chapter 2 reviews contemporary and relevant research findings in copper barriers. These topics include current issues of binary and ternary barriers, such as deposition methods, films properties, diffusion properties and mechanisms. Comparisons are also made between binary barriers and ternary barriers in terms of deposition methods, film composition, microstructure, diffusion performance and barrier failure mechanisms. In addition, reviews on the low frequency, high density inductively coupled plasma process, physical-chemical vapor deposition process; mechanistics of deposition and plasma nitriding process are also presented in this chapter. Furthermore, this chapter also describes the analytical techniques used in this thesis and its working principles. The methodologies to achieve the objectives of these works are presented in each individual experiment section in chapter 3 and 4.

Chapter 3 is divided into three sections. The first section is devoted to detailed experimental investigation on the formation of Ti-Si-N films by low frequency, high density inductively coupled plasma process. Implantation mechanisms of N into Ti_xSi_y matrix are studied. Besides that, implantation depth of nitrogen and chemical bonding states of implanted N are determined. In addition, the effect of processing parameters on the properties of Ti-Si-N films, such as surface morphology, stoichiometric composition, microstructure, electrical resistivity, film uniformity and phase composition are investigated. Section two discusses the effect of plasma processing

parameters on the diffusion performance of Ti-Si-N films. Besides that, investigation on the thermal stability of Ti-Si-N films against copper diffusion at various temperatures is carried out. The relationship between the barrier performance and the film structures is studied in an attempt to elucidate the controlling factor for Cu diffusion in Ti-Si-N films. The last section in this chapter examines the deposition of Cu as a seed layer on Ti-Si-N films, using electroless deposition technique. This work, for the first time, provides guidelines for electroless Cu plating on Ti-Si-N surface. The mechanisms of palladium seed distribution on Ti-Si-N films and Ti-N films are studied. The effect of plasma process parameters on the properties of electroless copper will also be presented in this section.

Chapter 4 focuses on the formation of Ti-Si-N-O barrier films using physical-chemical vapor deposition process. The formation of Ti-Si-N-O films at this low temperature process is studied. Extensive discussions on the film properties and comparison with other research findings are made. On top of that, electrical stability of Ti-Si-N-O films against metal ions diffusion at various temperature and bias conditions is investigated in-depth using bias temperature stressing (BTS) technique. Thorough investigation of the mechanism of electrical instability of Ti-Si-N-O films has been carried out.

Finally, chapter 5 wraps up the thesis with conclusions and proposal for future work related to Ti-Si-N and Ti-Si-N-O barrier films. The citations used and referred to this thesis are provided in the bibliography.

Chapter 2

Literature Review

The transition to copper-based interconnects in back-end-of-line fabrication process has generated significant challenges in the identification and development of the robust material and process technologies required to form reliable multilevel metal interconnects. In particular, a critical need exists for the identification and development of a diffusion barrier that is excellent in preventing the diffusion and intermixing of copper with the adjacent dielectric and semiconductor regions of the computer chip. This chapter introduces the concept of diffusion barrier, the predominant diffusion mechanisms in barrier materials and the candidate diffusion barrier for copper metallization. Focus will be given on Ti-N and Ti-Si-N barrier films. A discussion of other research works on both Ti-N and Ti-Si-N barrier films properties is also presented in this chapter. From this chapter, it can be seen how the objectives and scope of this work are being developed. Besides that, two deposition processes will be introduced which will be used to produce the Ti-Si-N and Ti-Si-N-O barrier films. Finally, analytical techniques used in this thesis are briefly presented.

2.1 DIFFUSION BARRIERS IN CU METALLIZATIONS

2.1.1 The concept of diffusion barriers

The concept of the use of barrier layers in metallization systems is simple: two materials that have favorable chemical interactions are kept separate by an intermediate layer. Practical diffusion barriers are generally divided into (i) sacrificial barriers, (ii) stuffed barriers, and (iii) amorphous diffusion barriers [Nicolet, 1978] as shown in Figure 2-1. The idea of the sacrificial barrier is that the intermediate layer X reacts either with one or both of the materials A and B in a laterally uniform manner

with characterized reaction rates. The effectiveness of the barrier is determined by the reaction rate. As long as the intermediate layer is not completely consumed in the reactions, the separation between the materials A and B is still effective. Therefore, reaction rate between X and A or/and B should not be too high in order to have an effective barrier layer. This finite lifetime is also the major limitation of sacrificial barriers. For a more permanent protection the barrier layer X should be thermodynamically stable against A and B. This means that there are no driving forces for reactions at the interfaces A/X and X/B. This is necessary but not sufficient for a stable diffusion barrier. It is also necessary to stop or reduce diffusion of A and B across X via short-circuit paths, since there is still a driving force for A to diffuse into B and vice versa. This can be achieved either by (1) eliminating the short-circuit paths or (2) filling the easy paths with appropriate atoms/molecules and thereby preventing the short-circuit diffusion of A and B [Nicolet, 1978].

Fig. 2-1: Schematic illustration of the three classes of diffusion barriers [Nicolet, 1978].

The second approach leads to the concept of stuffed barrier. When atoms of A and B cannot use the short-circuit paths (they are now occupied by the atoms or molecules introduced there on purpose), diffusion is slowed down generally by several orders of magnitude. The elimination of short-circuit paths can also be achieved by

making the structure of the barrier amorphous, which reduce the easy paths (*i.e.* grain boundaries). It is emphasized that amorphous layers are metastable and will eventually crystallize. When crystallization takes place, grain boundaries are again present in the barrier. Thus, the crystallization temperature of an amorphous layer is of critical importance.

2.1.2 Predominant diffusion mechanisms in barrier materials

The identification of a viable barrier material for Cu metallization requires establishing a fundamental understanding of the underlying mechanisms that drive atomic mobility and associated interdiffusion phenomena. It is well known that the placement of chemically different atoms in close proximity leads to atomic migration in order to lower the overall free energy and establish equilibrium [Ho, 1982]. Atomic migration is typically driven by the presence of concentration differences, existence of a negative free energy of reaction, application of an electric field, availability of thermal energy, generation of a strain gradient, or a combination of some or all of these factors [Ho, 1982]

Atomic migration could result in a diffusion flux, with the net flow of atoms being characterized by a diffusion coefficient D . The latter is described by Fick's First law [Kirkaldy, 1987]:

$$J = -D(dC/dx),$$

where C is the atomic concentration, J the atomic flux per unit area per second, and x the distance. The temperature dependence of the diffusion coefficient D takes on the form of an Arrhenius relationship [Gupta, 1993]:

$$D = D_0 \exp(-Q/kT),$$

where D_0 is a constant, Q the activation energy for diffusion, k Boltzmann's constant, and T the temperature in degrees Kelvin. The diffusion parameters D_0 and Q implicitly contain information on the thermodynamic and kinetic properties of the defects responsible for diffusion.

In the case of the Cu/barrier material system, three mechanisms typically dominate diffusion barrier failure [Park, 1996; Stavrev, 1999]: (a) diffusion of copper or substrate atoms through bulk defects in the barrier, (b) diffusion of copper along grain boundaries, and (c) loss of barrier integrity due to a metallurgical or chemical reaction with the copper and/or substrate. Two types of bulk defects tend to contribute to diffusion: vacancies and dislocations. Diffusion through vacancies, defects, and grain boundaries occurs at significantly different rates [Gjostein, 1973]. It was experimentally observed that lattice diffusion rates are proportional to the absolute melting temperature T_m of the host material, with the corresponding behavior being given by the following empirical relationship [Gjostein, 1973]:

$$D \sim AT_m,$$

where A is a proportionality constant that depends on a variety of factors, including lattice structure and type of material. Diffusion rates due to atom-vacancy exchange tend to be the lowest (smallest A), thus corresponding to the slowest diffusion. Dissociated dislocations exhibit intermediate rates, whereas high-angle grain boundaries, which result from a large misfit between adjoining grains, have the highest diffusion rates (largest A). Although significant uncertainty exists in the estimated values of A , the empirical relationship above provides a reasonable estimate of diffusion rates in different materials systems. Therefore, it represents a reasonable guideline in the selection of appropriate materials for diffusion barrier applications. In

particular, it indicates that materials with elevated melting points could act as better barriers.

In this respect, microstructure plays a critical role in the resultant barrier performance. Film microstructure can be categorized as single crystal, polycrystalline, nano-crystalline and amorphous (no long range ionic periodicity), as shown schematically in Figure 2-2 [Kaloyeros, 2000]. Polycrystalline barriers tend to yield the poorest barrier performance and are thus the least desirable for diffusion barrier applications. This assessment is especially true for barriers with grain sizes on the order of film thickness or films with columnar structure. The latter exhibit grain boundaries that extend through the entire thickness and are mostly normal to the substrate surface, as shown in Figure 2-2c, thus providing an effective pathway for copper diffusion.

Fig. 2-2: Barrier microstructure can be categorized as (a) single crystal, (b) polycrystalline, (c) polycrystalline columnar, (d) nano-crystalline, and (e) amorphous. [Kaloyeros, 2000].

Single crystal diffusion barriers are ideal for diffusion barriers. However, material and process constraints, including lattice mismatch with the underlying substrate and thermal budget limitations, make it unlikely to deposit barriers in single crystal forms [Movchan, 1969]. Therefore, stable nano-crystalline and/or amorphous materials are the most desirable for diffusion barrier applications, especially in the light of material and process limitations. From this aspect, Ti-Si-N diffusion barrier possess the above- mentioned properties and with the combination of these properties, Ti-Si-N film is a potential candidate for copper diffusion barrier. A review of Ti-Si-N films is presented in the following section.

2.1.3 Candidate diffusion barrier for copper metallization

The dependence of diffusion processes on the melting temperature of the host lattice makes it desirable to select barrier materials with a high melting point. This selection can help to ensure that even the fastest diffusion mechanism, namely, grain boundary diffusion, is negligible at the typical thermal budgets encountered during fabrication and operation of the IC. Accordingly, refractory metallic systems with characteristically high melting points and chemical inertness serve as viable candidates for diffusion barrier applications in Cu-based metallization schemes. Various refractory transition metals and their binary and ternary compounds have been suggested for such applications [Wang, 1994]. The corresponding materials systems are classified into seven groups:

1. Refractory metals such as Cr, Ti, Ta, W, Mo, Co, Pd, and Nb.
2. Refractory metallic alloys, including Ti_xW_{1-x} , Fe_xW_{1-x} , Ni_xNb_{1-x} , Ni_xMo_{1-x} , Ir_xTa_{1-x} , and Ir_xZr_{1-x} .

3. Polycrystalline or amorphous refractory metal-silicon alloys or compounds, such as TiSi_2 , CoSi_2 , $\text{Mo}_x\text{Si}_{1-x}$, $\text{W}_x\text{Si}_{1-x}$, TaSi_2 , $\text{Ta}_{74}\text{Si}_{26}$, and CrSi_2 .
4. Polycrystalline or amorphous refractory metal-nitrogen, metal-oxygen, metal-carbon, and metal-boron compounds, such as TiN_x , HfN , W_2N , TiC , TaC , Ta_xN_x , Mo-O , and TiB_2 ;
5. Polycrystalline or amorphous silicon-nitrogen and silicon-carbon compounds, such as SiN_x , SiC , Si_3N_4 , and SiC_xN_y ;
6. Amorphous ternary barriers that include $\text{Ti}_x\text{Si}_y\text{N}_{1-x-y}$, $\text{Mo}_x\text{Si}_y\text{N}_{1-x-y}$, $\text{W}_x\text{Si}_y\text{N}_{1-x-y}$, $\text{Ta}_x\text{Si}_y\text{N}_{1-x-y}$ and $\text{W}_x\text{B}_y\text{N}_{1-x-y}$;
7. Polycrystalline or amorphous carbon-based alloys and compounds, such as diamond-like carbon coatings.

Of all these, W-, Ta-, and Ti-based binary and ternary compounds are the most studied owing to their desirable physical, chemical, and electrical properties. The following section will only present key results pertaining to the Ti-N and Ti-Si-N performance as Cu diffusion barriers.

2.1.4 Titanium nitride

TiN has been widely employed in aluminum- and tungsten-based interconnect systems. As such, the possibility of extending their applicability to copper-based interconnects represents a highly attractive option, both technically and economically. Unfortunately, TiN has not been able to provide adequate copper barrier performance for thickness at or below 20 nm [Change, 1990]. A TiN barrier typically failed through grain boundary diffusion. In this respect, TiN deposited by physical vapor deposition (PVD) [Wang, 1990; Kumar, 1988; Hibbs, 1983; Kanamori, 1986; Wu, 1991] and chemical vapor deposition (CVD) [Sherman, 1991; Yuokoyama, 1991; Kurtz, 1986;

Ishihara, 1990; Faltermeier, 1997; Faltermeier, 1998; Hu, 1997] techniques exhibited mostly columnar type morphology (Figure 2-3), with grain boundaries running along the entire thickness of the TiN film. This morphology provided a fast diffusion pathway for copper migration across the barrier to the underlying substrate [Olowolafe, 1992] and leads to a device failure. Table 2-1 summarizes some of the research works on TiN as copper diffusion barrier.

Fig. 2-3: TiN deposited by inorganic CVD techniques exhibits typically a columnar type morphology [Faltermeier, 1998].

Table 2-1: Summary of research work on TiN barrier film properties.

Deposition Method	Flow-Modulation CVD using TiCl ₄ and NH ₃ as reactants			Ion beam assisted deposition TiN			Reactively sputtered TiN			
Composition	TiN			TiN _{0.95}			TiN			
Diffusion Properties	No evidence of Cu diffusion was observed for annealing at 400°C.			50 nm TiN _x stables for temperatures below 425°C			Barrier failure temperature: 500°C			
Microstructure & Texture	Columnar structure			Columnar grains			Columnar structure			
Barrier failure Mechanisms	Cu diffusion might occur through the grain boundaries of TiN films			The reaction of Cu with Ti leads to the formation of Cu ₃ Ti			Pinholes and white spots on the copper surface			
Any evidence to show TiN	TEM	XRD	Other	TEM	XRD	Other	TEM	XRD	Other	
	Yes	No	No	No	No	No	No	No	No	

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structure?
Resistivity	-	350 $\mu\Omega\cdot\text{cm}$	65 to 72 $\mu\Omega\cdot\text{cm}$
Roughness	-	-	-
Reference	[Shin, 2004]	[Olowolafe, 1991]	[Rha, 1998]

Deposition Method	Organo-metallic chemical vapor deposition (OMCVD)	CVD process using $\text{TiCl}_4+\text{NH}_3$	Reactively sputter Ti targets. N_2 was used as the reactive gas which was mixed with Ar																		
Composition	TiN	TiN	TiN																		
Diffusion Properties	-	-	-																		
Microstructure & Texture	<p>TiN film exhibits a columnar character that increases with plasma parameters.</p> <p>No plasma treatment: Nanocrystallites with no texture Short time plasma treatment: $\langle 100 \rangle$ Long time plasma treatment: $\langle 110 \rangle$</p>	Columnar crystals	<ul style="list-style-type: none">Columnar grain structure started to evolve in the region which is further away from the interface.The diffraction spectrum shows (111), (200) and (220) peaks																		
Barrier failure Mechanisms	Poorer barrier performance resulting of high plasma parameter application	-	-																		
Any evidence to show TiN structure?	<table><tr><td>TEM</td><td>XRD</td><td>Other</td></tr><tr><td>Yes</td><td>No</td><td>No</td></tr></table> <div> </div>	TEM	XRD	Other	Yes	No	No	<table><tr><td>TEM</td><td>XRD</td><td>Other</td></tr><tr><td>Yes</td><td>No</td><td>No</td></tr></table>	TEM	XRD	Other	Yes	No	No	<table><tr><td>TEM</td><td>XRD</td><td>Other</td></tr><tr><td>Yes</td><td>Yes</td><td>No</td></tr></table>	TEM	XRD	Other	Yes	Yes	No
TEM	XRD	Other																			
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TEM	XRD	Other																			
Yes	Yes	No																			

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Resistivity	-	80 $\mu\Omega\cdot\text{cm}$ for 50 nm film	-
Roughness	-	-	-
Reference	[Ikeda, 1999]	[Yuokoyama, 1991]	[Wu, 1991]

It can be observed that a common denominator underlying many of the above references is the columnar structure of TiN, typically with a (111) or (200) preferred orientation. Such a structure can lead to short circuit diffusion paths via grain boundaries and voiding at the corners of vias. The problem becomes compounded as the thickness of barrier layers shrinks to meet the demands of future ULSI circuits. Besides that, there are limited reports on the thermal and electrical diffusion properties of TiN films. In the work of Shin *et al* [Shin, 2004] and Olowolafe *et al* [Olowolafe, 1991], the TiN films were stable at temperature up to 425°C, compared to Ti-Si-N films, copper diffusion was not observed at 600°C to 850°C because of different film microstructures and deposition methods [Reid, 1994; Eric, 2000; Shalish, 1999; No, 2000]. From Table 2-1, there is no report on TiN surface roughness, which is an important property for subsequence copper deposition process. Copper film properties such as adhesion, uniformity and resistivity will be affected by TiN surface roughness. For example, a rough TiN surface will result in a high electrical field developed at sharp regions during copper plating process, resulting in non-uniform copper film.

Thus, many efforts have been made to improve TiN barrier properties. It was observed that TiN exposure to air prior to the aluminum deposition step led to improved barrier performance for Al interconnects, compared with the case where no vacuum break was implemented [Sinke, 1994]. This finding was attributed to the diffusion of oxygen to grain boundaries in the TiN matrix upon air exposure, leading to what is known as oxygen stuffing. The oxygen subsequently reacted with Al to form

an aluminum oxide phase, which blocked any further material transport through the TiN liner. Similar oxygen stuffing mechanism was found by Olowolafe *et al* [Olowolafe, 1991], they reported that $\text{TiN}_{1.3}\text{O}_{0.75}$ was a more effective diffusion barrier than $\text{TiN}_{0.95}$.

TiN films grown by metalorganic CVD (MOCVD) techniques, on the other hand, displayed an amorphous microstructure [Jackson, 1995; Katz, 1991; Kin, 1996] and were thus thought to provide improved barrier performance due to the absence of grain boundary pathways for fast Cu diffusion. Unfortunately, the presence of high levels of carbon, oxygen, and hydrogen contaminants for films deposited below 450°C led to the formation of a low-density, high-resistivity, and porous TiN microstructure that acted as a poor barrier to Cu diffusion [Paranjpe, 1995]. Efforts to remedy this problem included the use of plasma-assisted MOCVD growth [Yun, 1998; Weber, 1995] and the application of post-deposition annealing treatments, in the presence or absence of a plasma environment [Lu, 1997; Danek, 1996]. However, these attempts did not yield the optimized TiN barrier performance.

Other efforts included the implementation of a cycled deposition approach, whereby multiple deposition and plasma treatment cycles were sequentially performed. This approach was successful at enhancing the stability, lowering the resistivity, and improving the barrier properties of MOCVD TiN. The resulting performance of the post-treated MOCVD TiN films was equivalent to that of their PVD analogs, with both sets of barriers surviving thermal stressing at temperatures up to 650°C. Unfortunately, the TiN thickness used in this study was 50 nm and was thus too thick to be considered for sub-quarter-micron device applications [Kim, 1996].

Another strategy used to improve the barrier performance of ultrathin MOCVD TiN involved the application of a hybrid barrier approach. In the case shown by Jain *et*

al [Jain, 1998], a patterned SiO₂ via was selectively nitrided in a nitrogen plasma, followed by the growth of a ~ 5 nm thick MOCVD TiN film with plasma densification, then a copper deposition step. The resulting copper interconnect stack demonstrated improved electrical performance compared with a similar stack with a 20 nm thick TiN liner without nitridation. This result was attributed to the presence of larger effective Cu volume in the case of the thinner TiN [Jain, 1998]. However, this strategy required the use of a CVD Si flash layer over the TiN in order to avoid de-wetting of the copper, and no Cu texture or stack reliability data were provided. In addition, the extendibility of this approach from SiO₂-based interconnects to their low-*k* dielectric analogs is yet to be demonstrated.

2.1.5 Titanium-silicon-nitride

As pointed out by Nicolet *et al* [Nicolet, 1983], the addition of a third element into a transition metal nitride matrix disrupts the crystal lattice, which leads to the formation of a stable amorphous ternary phase with significantly higher recrystallization temperature than its binary counterpart. In addition, another advantage of ternary metal-silicon-nitrides is due to their increased diffusion activation energy which is related to their high inter-atomic binding energies [Reid, 1993; Reid, 1994]. These properties are essential to provide adequate performance in 100 nm device generation.

As a result, a class of refractory ternary nitrides, such as Ti-Si-N, Ta-Si-N and W-Si-N were proposed as candidates for the next generation diffusion barrier in copper/low-*k* dielectric back-end-of-line device fabrication [Marcadal, 2002; ITRS, 2004]. Various research groups explored the formation of ternary nitride films by physical vapor deposition (PVD) [Reid, 1994; Shalish, 1999; No, 2000], chemical vapor deposition (CVD) [Marcadal, 2002; Eric, 2000; Edward, 2001; Prindle, 2002;

Joseph, 2002], atomic layer deposition (ALD) techniques [Min, 1998; Min, 1999] and documented their resulting electrical, structural and thermal properties.

Recently, Ti-Si-N film as a diffusion barrier has been shown to possess the required electrical, chemical, structural, and thermal properties and has been successfully integrated in sub-130 nm copper/low-*k* semiconductor device technology nodes [Marcadal, 2002]. Table 2-2 shows the literature survey on Ti-Si-N films formed by different research groups using different approaches. The special features, finding and films properties are also summarized in the table.

Table 2-2: Summary of other research works on Ti-Si-N barrier film properties.

Deposition Method	Reactively sputtered from a Ti ₅ Si ₃ target	Low temperature inorganic thermal chemical vapor deposition process (TiI ₄ +SiI ₄ +NH ₃)	Metalorganic chemical deposition (MOCVD) (TDMAT+SiH ₄)
Composition	Ti _{34±2} Si _{123±2} N _{43±3}	Ti ₃₃ Si ₁₅ N ₅₁	-
Diffusion Properties	<ul style="list-style-type: none">➤ 100 nm Ti₃₄Si₁₂₃N₄₃ barrier prevent copper from reaching the Si substrate during 850°C/30 min anneal in vacuum.➤ 10 nm film prevents diffusion up to 650°C/30min.	<ul style="list-style-type: none">✓ RBS results indicated the absence of any diffused Cu in the CVD TiSiN liner or underlying Si substrate after annealing at 600°C.✓ Onset of copper diffusion for the same film after annealing at 700°C.	Depth profile elemental composition of TiSiN film measured by XPS. No evidence of Si diffusion through the TiSiN & Cu films at various sites across the wafer as determined by both depth profile & intensity plots.
Microstructure & Texture	Ti ₃₄ Si ₁₂₃ N ₄₃ consists of nanophase TiN grains roughly 2nm in size.	Nanocrystalline TiN phase within an amorphous SiN matrix	Small grains close to the amorphous structure formed by a mixture of TiN & Si-N.
Diffusion Mechanisms/ Advantages of the micro-structure	* The random arrangement of nanophase TiN eliminates straight grain boundary paths associated with most columnar TiN films.	TiN phase within an amorphous SiN matrix. It was suggested that this Ti-Si-N microstructure is desirable from a diffusion barrier	-

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	* Integranular Si components may be viewed as severely “stuffing” the grain boundaries of TiN.			performance perspective, especially in view of the absence of grain boundaries.					
Any evidence to show TiSiN structure?	TEM Yes	XRD No	Other No	TEM No	XRD Yes	Other No	TEM Yes	XRD No	Other No
Resistivity	680 $\mu\Omega\cdot\text{cm}$ for 100 nm thick			800 $\mu\Omega\cdot\text{cm}$ for 25 nm thick			Via resistance is lower for thinner CVD TiSiN barrier films.		
Step Coverage	-			50% in 130 nm wide, 10:1 aspect ratio trenches.			TiSiN deposits as a conformal & continuous film within the via, with 100% sidewall & 75% bottom step coverage.		
Roughness	-			-			As-deposited TiSiN = 0.45 nm		
Reference	[Reid, 1994]			[Eric, 2000]			[Prindle, 2002]		

Deposition Method	Deposited from a Ti_5Si_3 target in Ar/N_2 gas mixture discharges.	CVD TiSiN (TDMAT-based)	Reactively sputtered from a Ti_5Si_3 target
Composition	$\text{Ti}_{27}\text{Si}_{20}\text{N}_{53}$ (100 nm thick)	-	$\text{Ti}_{29}\text{Si}_{25}\text{N}_{46}$
Diffusion Properties	<ul style="list-style-type: none"> □ No significant change after annealing at 500°C □ A redistribution of the N_2 is observed starting at 600°C & increasing with the annealing temperature. □ Prevent the interdiffusion of Cu & SiO_2 up to 30min of annealing at 850°C 	Cu diffusion barrier properties equivalent to PVD Ta (N)	<ul style="list-style-type: none"> ➤ 20 nm $\text{Ti}_{29}\text{Si}_{25}\text{N}_{46}$ barrier prevent copper from reaching the Si substrate during 650°C/30 min anneal in vacuum. ➤ 65 nm film prevents diffusion up to 700°C/30min.
Microstructure & Texture	✓ A cross-sectional micrograph of the annealed sample reveals a columnar structure of the TiSiN layer with a	-	$\text{Ti}_{29}\text{Si}_{25}\text{N}_{46}$ is amorphous structure even after annealing at 800°C.

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	lateral period of about 60 nm. ✓ Polycrystalline TiN is observed in the (111) preferred orientation. A high flow of N ₂ during growth is known to switch the orientation to (200)																				
Diffusion Mechanisms/ Advantages of the micro-structure	-	By introducing Si into TiN matrix, the Si is bonded to the N, significantly improving barrier properties compared to with CVD TiN.	* Diffusion of Cu into the Si substrate to form Cu ₃ Si. * Interfacial reaction between the barrier layer and the Si substrate. These are the two possible mechanisms for the barrier failure.																		
Any evidence to show TiSiN structure?	<table><tr><td>TEM</td><td>XRD</td><td>Other</td></tr><tr><td>No</td><td>No</td><td>SEM</td></tr></table>	TEM	XRD	Other	No	No	SEM	<table><tr><td>TEM</td><td>XRD</td><td>Other</td></tr><tr><td>No</td><td>No</td><td>No</td></tr></table>	TEM	XRD	Other	No	No	No	<table><tr><td>TEM</td><td>XRD</td><td>Other</td></tr><tr><td>No</td><td>Yes</td><td>No</td></tr></table>	TEM	XRD	Other	No	Yes	No
TEM	XRD	Other																			
No	No	SEM																			
TEM	XRD	Other																			
No	No	No																			
TEM	XRD	Other																			
No	Yes	No																			
Resistivity	Sheet resistance = 11- 180 Ω/sq Resistivity of TiSiN = 110 — 1800 μΩ•cm	350 μΩ•cm for 5 nm TiSiN	The sheet resistance slightly drops at annealing temperature below 500°C, which thought to be caused by a decrease of the defect density and the grain growth of the Cu film. After annealed at 700°C, the sheet resistance of Ti ₂₉ Si ₂₅ N ₄₆ increases significantly to 3 Ω/Sq. (~20 μΩ•cm for 65 nm)																		
Step Coverage	-	> 90% conformal step coverage	Local defects observed sparsely after annealing at 700°C. The defects formed only at a small fraction of the total surface area.																		

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			<p>A: Cu B: Ti, Si</p> <p>The density and size of the region B significantly increased with increasing annealing temperature up to 750°C.</p> <p>The increase of region B as well as the formation of Cu₃Si seems to be the main reason for an abrupt increase in sheet resistance.</p>
Roughness	-	-	-
Reference	[Shalish, 1999]	[Chin, 2001]	[No, 2000]

Deposition Method	MOCVD formation of TiN followed by plasma treatment with a gas mixture of nitrogen and hydrogen and in situ exposed to Silane	MOCVD formation of TiN followed by plasma treatment with a gas mixture of nitrogen and hydrogen for 30s and exposed to Silane for 10s	Thermal nitridation of thin amorphous Ti-silicide films using N ₂ H ₄ gas at 500°C for 10 min.
Composition	Ti ₂₉ Si ₇ N ₂₁ C ₂₉ O ₁₄	-	Ti:Si:N = 1.0: 1.4: 1.0
Diffusion Properties	<ul style="list-style-type: none">➤ 50 nm thick PVD Cu on TiSiN, annealed for 30 min at 350°C. SIMS results that barrier performance is apparently improved by Silane exposure of TiN layer.➤ SiH₄ exposure to a TiN film without N₂/H₂ plasma treatment yields the best barrier.	-	<ul style="list-style-type: none">➤ The film structures were stable at least up to an annealing temperature of 750°C. This feature is considered to be related to the simultaneous formation of both Ti-N and Si-N bonds. These bonds in the films are thought to retard the atomic rearrangement of the

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			<p>constituent elements to form nucleation sites of sufficiently large size.</p> <p>➤ Ultra thin barrier film (5 nm) is an effective barrier between Al & Si, against 550°C annealing.</p>
Microstructure & Texture	<p>➤ Two weak and broad peaks corresponding to TiN (111) and TiN (200). This can be explained by the nanosize of the crystallites and the broad peak corresponds to the close packing distance in the material.</p> <p>➤ TiN film without plasma treatment consists of nanocrystallites of TiN embedded in an amorphous matrix. The Si-N bonding takes place in this matrix improving its barrier performance.</p>	<p>Nanocrystalline TiN phase within an amorphous Si_3N_4 matrix.</p>	<p>◆ Amorphous-like structure is stabilized by nitridation of the amorphous silicide.</p> <p>◆ Amorphous-like structure consisting of fine grains with diameter less than 1nm from TEM picture.</p>
Diffusion Mechanisms /Advantages of the micro-structure	<p>*The TiN film without the plasma treatment consists of nanocrystallites of TiN embedded in an amorphous matrix. The Si-N bonding takes place in this matrix improving its barrier performance; fast diffusion channels are absent since there is no percolation via grain boundaries in this microstructure.</p>	<p>* The main factor improving the barriers integrity is the plasma treatment and only a slight improvement by SiH_4 exposure.</p> <p>* Plasma treatment causes crystallization of as-deposited TiN amorphous film. This process increases the films density, thus improving barrier properties. They believed that the film which was not plasma treated has low density and a porous structure, and copper permeates through the film just as water penetrates a porous sponge. The crystallization of the film during the plasma</p>	-

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		<p>treatment results in a polycrystalline film of grains about 5 nm in diameter. This film has a higher density in the plasma treated region than the film which was not plasma treated at all, and although copper could diffuse through the grain boundaries, this film is a better diffusion barrier since it does not allow copper to penetrate through the entire low-density film which is covered by a plasma treated layer.</p> <p>* Exposure of films to SiH₄ was introduced to block the grain boundaries through the incorporation of Si. Si reacts with the N₂ to form Si₃N₄ which has a tight amorphous structure.</p>																			
Any evidence to show TiSiN microstructure ?	<table><tr><td>TEM</td><td>XRD</td><td>Other</td></tr><tr><td>Yes</td><td>Yes</td><td>No</td></tr></table>	TEM	XRD	Other	Yes	Yes	No	<table><tr><td>TEM</td><td>XRD</td><td>Other</td></tr><tr><td>No</td><td>No</td><td>No</td></tr></table>	TEM	XRD	Other	No	No	No	<table><tr><td>TEM</td><td>XRD</td><td>Other</td></tr><tr><td>Yes</td><td>No</td><td>No</td></tr></table>	TEM	XRD	Other	Yes	No	No
TEM	XRD	Other																			
Yes	Yes	No																			
TEM	XRD	Other																			
No	No	No																			
TEM	XRD	Other																			
Yes	No	No																			
Resistivity	TiSiN= 275μΩ•cm for 52Å thick.	-	-																		
Step Coverage	Step coverage (bottom & top) is 88%. Sidewall thickness is 54Å is slightly higher than the top field thickness (52Å)	-	-																		
Roughness	-	-	-																		
Reference	[Marcadal, 2002]	[Joseph, 2002]	[Dauksheer, 2000]																		

It can be seen from the above references that the composition of Ti-Si-N films varies with different process approaches as well as the initial materials used. As a result, the reported diffusion barrier performance differs among researchers, ranging from 600°C to 850°C. The difference might be due to the difference in film thickness,

annealing time, and the failure criteria used by the researchers. Despite that, a common feature underlying many of the above references as reported is the microstructure of Ti-Si-N films, which consists of nanocrystalline Ti-N phase embedded in an amorphous Si-N matrix [Reid, 1994; Marcadal, 2002; Eric, 2000; Prindle, 2002; Joseph, 2002; Dauksher, 2000]. However, little concrete evidence was provided by most of the researchers to show the microstructure of Ti-Si-N films.

Marcadal *et al* [Marcadal, 2002], prepared Ti-Si-N film by CVD using a metallorganic precursor (MOCVD-TiN) by thermal decomposition of tetrakis(dimethylamino) titanium (TDMAT). The deposition was followed by plasma treatment with a gas mixture of nitrogen and hydrogen. Finally, the films were *in situ* exposed to silane. The formed Ti-Si-N film contained nanocrystalline phase (Ti-N) embedded in an amorphous matrix (Si-N) as shown in Figure 2-4. Unfortunately, no further investigation of this structure was reported. They also reported that $\text{Ti}_{29}\text{Si}_7\text{N}_{21}\text{C}_{29}\text{O}_{14}$ film provided the best barrier performance. However, this conclusion which was given based on the annealing result at 350°C for 30 minutes, is premature as copper may diffuse at higher temperatures. In addition, the film contains an undesirable high amount of carbon element which will degrade the adhesion performance.

Fig. 2-4: High resolution TEM micrograph of a $6 \times 50 \text{ \AA}$ TiSiN sample treated by N_2/H_2 plasma. [Marcadal, 2002]

Smith *et al* employed the MOCVD reaction of tetrakis-diethylamido titanium (TDEAT), silane (SiH_4), and NH_3 to deposit TiSi_xN_y over the temperatures ranging from 300 to 450°C. The authors also reported BTS testing at 50 V and 200°C on 10 nm thick MOCVD TiSi_xN_y samples. In particular, they found that the MTTF of an MOCVD $\text{Ti}_{23}\text{Si}_{14}\text{N}_{45}\text{O}_3\text{C}_3\text{H}_{12}$ sample deposited at 400°C was approximately 10–100 times better than that of PVD TiN [Smith, 1996]. In addition, Reid *et al* [Reid, 1994], using PVD to produce Ti-Si-N film, found that 100 nm $\text{Ti}_{34}\text{Si}_{23}\text{N}_{43}$ film was stable up to 850°C for 30 minutes vacuum annealing. In comparison, TiN was reported to be effective only up to around 650°C [Olowolafe, 1991; Wang, 1990]. As such, the addition of silicon components to TiN represents a prodigious improvement in barrier performance. But, this work did not provide X-ray spectroscopic analysis of Ti-Si-N film and surface roughness data, which are important for subsequent back-end-of-line processes.

In the work by Nose *et al* [Nose, 2003], Ti-Si-N films were prepared by r.f. reactive sputtering process. They investigated the influence of Si content and sputtering conditions on the microstructure and properties of Ti-Si-N films. They found that the tendency to grow columnar grains was strongest at approximately 5 at. % of Si with grains larger than 20 nm in length. They also reported that the films consisted of TiN nanocrystals embedded in Si_3N_4 amorphous phase. However, this work did not provide (i) concrete evidence showing the mixed microstructure of their Ti-Si-N film, (ii) thermal or electrical diffusion properties of Ti-Si-N film.

In summary, the characterization of copper diffusion is a current technological issue receiving maximum attention from several researchers and from the semiconductor industry. The process approaches and conditions are quite different; hence a direct comparison of the data cannot be attempted. Thus, it is important to

have a reproducible process to grow Ti-Si-N barrier films and to understand its diffusion barrier performance. In this sense, the characterization of the basic properties such as microstructure, surface morphology, phase composition and texture, surface roughness will play an important role in the study. Also, the mixed microstructure of Ti-Si-N film were reported but did not received detailed attention. From the discussion in the above papers, it appears to be an implicit assumption that nanocrystal Ti-N phase is embedded in an amorphous Si-N matrix. As will be seen later, results in this thesis question this assumption. From some copper thermal and electrical diffusion experiments, Ti-Si-N materials seem to exhibit good diffusion barrier properties. Similar results were obtained in this thesis. It is interesting to note that the incorporation of oxygen into Ti-Si-N films provides good copper barrier properties.

The next section will introduce the two processes that have been used to grow Ti-Si-N and Ti-Si-N-O films, namely the low frequency, high density inductively coupled plasma process, and the physical-chemical vapor deposition process, respectively. Besides that, techniques used for analysis are described.

2.2 LOW FREQUENCY, HIGH DENSITY INDUCTIVELY COUPLED PLASMA PROCESS

2.2.1 Introduction

The thin film deposition process, in which condensable radicals are created by the decomposition of precursor gases in non-equilibrium plasma, is known as plasma-assisted deposition.

A wide variety of materials have been deposited by the plasma process and referenced lists can be found in several reviews [Hollahan, 1974; Rand, 1979; Reinberg, 1979]. Plasma deposition and etching processes have for many years been

widely used for film patterning and deposition steps in the fabrication of microelectronics components [Reid, 1993]. The fact that insulating films for diffusion masks, interlayer dielectrics, and passivation layers can be deposited and be removed at low temperatures, so that previous process steps are not affected, is extremely important for this industry. The plasma deposition of silicon nitride, particularly, has been extensively studied in certain reactor designs [Rosler, 1976; Rosler, 1981]. Silicon compounds emerged as one of the most important materials and have become the most widely used in semiconductors. The most promising among those are silicon nitride deposited at about 300°C.

The most important raw material for these films is silane. By reaction with nitrogen, it forms silicon nitride. Of particular interest and importance is the plasma deposition of amorphous and nanocrystalline materials. The highest quality electronic and doping efficiency is obtained from plasma induced decomposition of silane, i.e.,

More generally, plasma-assisted deposition techniques have opened up possibilities for other potentially important products such as Ti-Si-N, Ta-Si-N, a-C, a-P and a-P₃N₅ with unique properties. Other important amorphous and crystalline materials are the III-V and II-VI compounds [Mort, 1986].

The importance of plasma technology in these films is based on features such as considerably reduced deposition temperature, thus permitting the polymerization of solids with superior short-range order, which is not attainable by using conventional techniques. Such non-crystalline materials of excellent short-range order are most desirable for a number of important applications since it is the short-range order that determines important physical and chemical properties.

2.2.2 Nature of the deposition process

At the heart of any physical vapor deposition process is the creation of a flux of condensable species. In the case of evaporation and sputtering processes, these species originate from a spatially constrained source such as a solid or an intermediate liquid. The work piece, or substrate, is required to be in direct line-of-sight with this source in order to be covered with a thin film of the source material [Mort, 1986]. Plasma processes are significantly different from other vapor deposition processes in that the depositing species are created from precursor gases which, without energy input, are not in themselves condensable. These deposition processes are therefore not in direct line-of-sight in the sense that the precursor materials surround the substrate, irrespective of its shape or its position in the deposition chamber. This, in principle, enables the substrate to be densely packed during the deposition process.

In a plasma deposition process [Mort, 1986], electrical energy is supplied to the gas through the mediation of electrons which are accelerated in an applied electric field. A non-equilibrium plasma, in which the electrons have a much higher effective temperature than the ions and uncharged species, is created through the action of the electric field. The extent of the electric field defines approximately the deposition area. The substrate is commonly close to an electrode or can also function as an electrode.

Different methods can be used to couple the electrical energy into the plasma. Low frequency electric power can be coupled into the discharge through the capacitance of a dielectric wall of a vacuum chamber by the use of a coil, and this method is referred to as “inductive coupling” [Mort, 1986].

The use of gaseous precursor materials has significant priority advantages over the use of solid or liquid sources. These latter sources are not only spatially but also compositionally constrained. This is a serious limitation for the demanding materials

requirements of microelectronics devices. Controlled doping, alloying, and multilayering are very hard to accomplish with solid sources of material of fixed composition, but this flexibility is easily obtained by the variable flow control of gaseous precursors [Mort, 1986]. Therefore plasma process in practical is favored over other methods.

The most important phenomena in the plasma excitation process is which condensable species are created from the precursor gases. Precursor gases are always molecular compounds and a wide variety of species are created by the electron impact dissociation, excitation, and ionization of the gas molecules. The electrons are accelerated in the electric field applied between two electrodes, and their velocity distribution is determined by frequent collisions with gas molecules.

The important point is that ions do not measurably contribute to the deposition process [Jansen, 1985; Drevillon, 1983] although the ionic bombardment during film growth can have a significant effect on the physical properties of the film. The fact that the species which contribute predominantly to film growth are electrically neutral and have to find their way to the surface of the growing film by diffusion has important practical consequences. The diffusing radicals have a relatively low density and the plasma deposition process is therefore inherently inefficient materials. The deposition on a flat surface is isotropic in nature, i.e.; the vapor at any point of a flat surface originates from a hemisphere with a radius of about the mean free path of the radicals. Step coverage of surface features depends on the size of the surface feature relative to the radical mean free path [Ross, 1984] and is subjected to electric field distortion. Furthermore, columnar structures and nodular film defects, resulting from self-shadowing or macroscopic shadowing during film growth [Geunther, 1982] are prevalent defect patterns in plasma deposited films [Knights, 1980].

Compositional gradients of the deposited film are frequently observed in the direction of the gas flow and are due to the relative depletion of one of the precursor gases. Non-uniformity of the film properties on stationary substrates can sometimes be adequately minimized by the proper selection of the operating parameters [Rand, 1979; Sabin, 1983]. In practice, substrates are frequently translated or rotated through the reaction zone in such a way that film non-uniformities due to depletion are averaged.

2.2.3 Low frequency inductively coupled plasma

Highly efficient sources of low-temperature plasma have recently been of great interest because of their numerous applications for fabrication of microelectronic circuits and devices, material surface structuring and modification, thin films deposition and etching, and plasma-assisted synthesis of novel materials [Auciello, 1990]. In a number of modern plasma processing technologies, high uniformity of ions and active species, high product yield with low damage, process selectivity, and reproducibility are common requirements. Inductively coupled plasma (ICP) process is a good candidate to satisfy all the above requirements [Hopwood, 1992; Keller, 1997].

Typically, plasma densities of $10^{10} - 10^{12} \text{ cm}^{-3}$ are normally achieved with inductively coupled plasma sources. Inductively coupled plasma is produced by external or internal currents driven by coils of various configurations. ICP featuring high ion densities and low plasma potentials have advantages in generation of large-area and large volume plasma for fabrication and processing of unique materials and ultra-fine selective etching of semiconductor wafers [Tsakadze, 2001]. Low frequency $\sim 0.5 \text{ MHz}$ has been applied for plasma production. Low operation frequency allows one to increase the number of turns in a planar coil. This will increase the degree of the radial uniformity of plasma.

For the current work, the plasma is generated in a cylindrical, stainless steel double-walled (with water cooling) vacuum chamber (see Figures 2-5 and 2-6) with the inner diameter $2R = 32$ cm and length $L = 20$ cm. The top plate of the chamber is a fused silica disk, 35 cm in diameter and 1.2 cm thick. The typical base pressure of $\sim 2 \times 10^{-4}$ torr is routinely achieved. The operating pressure is typically maintained in the range of $P_o = 2 \times 10^{-2}$ torr. The r.f. field is generated by means of a 17 turn, flat spiral coil, made of 6.35 mm diameter copper tube fixed 3 mm above the quartz window atop of the vacuum chamber. A low frequency (~ 500 kHz) r.f. generator is used to drive the flat spiral coil through a matching network. The r.f. magnetic fields are measured using two miniature magnetic probes each consisting of 12 turn windings on the end of 5 mm diameter fused silica tubes. One of them senses the radial component whereas the other senses both axial and azimuthal components, with appropriate orientation. The probe is inserted either horizontally or vertically through the holes in the side port or bottom of the chamber. The electron energy distribution functions (EEDF), electron density, temperature and plasma potential can be measured using an r.f. compensated single cylindrical Langmuir probe. The probe can be moved radially and axially through one of the four port windows or holes in the bottom plate.

Fig. 2-5: Schematic cross-section of low frequency, high density inductively coupled plasma chamber.

Fig. 2-6: Low frequency, high density inductively coupled plasma chamber.

2.2.4 Comparison between conventional plasma (Capacitive Plasma) and inductively coupled plasma

Plasma is a quasineutral gas of charged and neutral particles exhibiting collective behavior [Chapman, 1980]. The term “quasineutral” means that, except for localized regions in space, overall charge density in the plasma is zero. That is, on average the densities of positively and negatively charged particles compensate each other. The term “collective behavior” refers to the fact that charged particles interact with each other via long range Coulomb forces [Chapman, 1980].

In conventional plasma, radio frequency of 13.56 MHz is used. Because ions cannot respond to this frequency in the plasma, their behavior on the substrate tends to be time-independent. In other words, the r.f.-powered electrode behaves as if it were a DC-powered cathode. According to the experimental analysis [Chapman, 1980], both ion current and electron current are out of phase with the applied r.f. voltage, showing capacitive nature rather than resistive nature. In particular, the r.f. current in the vicinity of the 13.56 MHz frequency shows a typical capacitive behavior. This is the reason we call it “Capacitive Coupled Plasma” (CCP).

On the other hand, in inductively coupled plasma (ICP), low frequency of 0.5 MHz is used. Low frequency electric power is coupled into the discharge through the capacitance of a dielectric wall of a vacuum chamber by the use of a coil, and this method is referred to as “inductive coupling” [Mort, 1986]. That is, non-capacitive power transfer is the key to achieving low voltage, normally 20 – 40 V, across the sheath at the dielectric or the wall. In inductively coupled plasma processes, high utilization of power for high ionization efficiency (capacitively coupled plasma: 1 – 3%, partially for ionization) [Chapman, 1980]. Mostly power is spent in sheath for CCP, but for ICP, it is spent in bulk). In addition, due to the low bias applied in ICP,

there will be little damage to the devices. Furthermore, high processing rates, high etching rates and high deposition rates are the additional advantages of using ICP. Table 2-3 shows the charged particles density of CCP and ICP.

Table 2-3: Comparison between conventional plasma and inductively couple plasma [Chapman, 1980].

	Particle Density (particles/cm ³)	Charged Particle Density (ions/cm ³)	Pressure
Conventional Plasma	10 ¹⁴ – 10 ¹⁶	10 ⁹ – 10 ¹¹	High
Inductively Coupled Plasma	10 ¹³ – 10 ¹⁴	10 ¹¹ – 10 ¹³	low

2.2.5 Mechanistics of deposition

When a particle from the plasma arrives on a surface and does not return to the gas phase, i.e., when it is absorbed to the surface, it is deposited and becomes part of film. The arriving particles may be ions, ion-radicals, free radicals, excited molecules or neutral species. Any or all of these adsorbates can react with molecules or atoms of the substrate surface which, due to exposure to the glow discharge, may be in one form or another of activated state. The adsorbed species also react with each other via an ionic or free radical mechanism in the film forming process. The first particles to arrive at the surface will also be able to enter the smallest crevices in the substrate surface. By participating in the subsequent film forming process, these particles will be anchored within the minute surface pores and in this way contribute to the firm film adherence of the growing film [Boenig, 1988].

Thus, in plasma film deposition distinction is made among three processes, [Boenig, 1988] which are (1) the formation of plasma monomers, i.e., ions, free radicals, excited species, neutral and other interactions in the gas phase; (2) the

interaction of impacting species with surface molecules, and (3) the film-forming polymerization on the substrate surface.

A further complication in this film forming mechanism arises from the fact that the newly formed absorbed and reacted species are further subjected to the energetic components of the plasma environment, including the highly energetic photons. This is a continuing process which imposes additional changes in the newly arrived particles and thus causing additional or changed reactions, including cross-linking in the growing film. It is because of these reactions that films formed in a glow-discharge environment are generally amorphous in nature and usually possess very little short-range structural order [Boenig, 1988]. The latter is also due to the systematic packing of particles arriving on the newly-forming surface. This, combined with the multifunctional reaction mechanisms, causes the growing film to be generally of high integrity with no, or very few, pinholes.

It must be realized that virtually any species in vapor form can be made to polymerize and to deposit under plasma conditions. In deposition, sticking coefficient (which makes an impacting species stay on the substrate surface instead of bouncing off), is better known as the deposition coefficient [Boenig, 1988]. It is related to the nature and condition of the impacting particle (mass, kinetic energy, reactivity, charge, etc) as well as the surface temperature.

2.2.6 Plasma nitriding

Plasma nitriding is a process of ion implantation. Implantation of ions into metal surface has become an important technology in modern metallurgy for producing vast improvement in such properties as friction, wear, hardness, corrosion,

resistance, fatigue life, bonding, electrochemical behavior as well as improvement in the surfaces of optical elements and novel optical components.

Ion implantation is a process by which alloying elements are introduced into a host material by accelerating them to a sufficiently high energy and permitting them to impact on the surface of the substrate. Depending on the atomic number and the energy, the impinging ions may penetrate into the substrate surface to a depth of 0.01 to 1 micron to form a dense, alloyed surface layer on the substrate [Boenig, 1988]. Through ion implantation, one can modify the composition, structure, and the very nature of metallic surfaces. The bulk properties of the component are unaffected; there are no significant dimensional changes.

Plasma nitriding has been studied for a variety of materials including Ti, Zr, steel, Si, GaAs and GaSb. Most ion implantation work has been done on nitriding and practically all large-scale production plants are nitriding units. For plasma nitriding in r.f. discharges, the elementary process scheme has been described by Matsumoto [Matsumoto, 1984], as follows:

- (1) Active species can be formed in the gas phase by the collision of energetic free electrons with nitrogen and hydrogen molecules.
- (2) Adsorption of these active species is expected to occur at the surface in contact with the plasma.
- (3) Adsorption of the species on the surface is followed by a chemical reaction with the metal lattice. This appears to be the first step in the formation of the bulk metal nitride phase, with the chemical reaction being the rate determining step at the beginning of the reaction.
- (4) After the formation of the nitride layer on the surface, the near-surface nitride layer becomes supersaturated with nitrogen across the nitride-metal phase

boundary. Diffusion of nitrogen from nitride to metal is the rate-determining step after nitride formation. Since the kinetics is represented by a parabolic relationship for longer nitriding times, the diffusing is the rate-determining step after nitride layer formation.

In nitriding process, the positive nitrogen ions in the glow discharge are attracted towards the negatively connected work pieces. They impinge upon the surfaces, are thus occluded, and they heat up the pieces to the required diffusion temperature at which time, the nitrogen diffuses into the work pieces in its atomic form. Nitriding process is controlled by the exchange of energy between the gas phase and the solid matter. In the case of transition metals, the vibration energy of the plasma, which is transferred to the solid surface, makes it possible to go beyond the activation barrier [Matsumoto, 1984]. The result is a solid surface N bond. On the other hand, the energy of the plasma transferred to the Si surface, is converted into heat. In the case of metal, the energy release beyond the activation barrier facilitates either the diffusion of N atoms into the solid surface or recombination of N atoms and desorption of N₂ molecules.

Four advantages have been cited for plasma nitriding. First, treatment time is reduced because of more rapid saturation of the surface owing to the enhanced mass transfer through the plasma. Second, energy consumption is also reduced. This is due to reduced treatment time and reduced heat loss (only the cathode is heated; heat loss occurs only by radiation through the vacuum to be cold chamber wall). Next, gas consumption is reduced with claimed 95% savings. Finally, there are no environmental hazards, such as toxic wastes and risks of explosion [Staines, 1981].

2.2.7 Deposition variables

There are many variables for the plasma-assisted deposition of thin film that must be carefully controlled. Several of these deposition variables interact with each other; consequently, the individual contribution of a specific variable on the deposition and film properties are difficult to determine.

a) Power

In general, the deposition rate appears to increase and eventually saturate as the power density increases. At low power density, the reaction is limited by the number of active species created in the discharge. Increasing the power increases the number of species and consequently the deposition rate. At high power densities, the reaction is limited by transport of the active species. The deposition rate is now independent of power density but strongly dependent on gas flow and reactor geometry. [Mort, 1986]

b) Pressure

Increasing the total pressure decreases the electron temperature and the number of active species formed in the discharge, thus causing a fall in deposition rate. Increasing pressure also increases the possibility of gas-phase reactions which enhance the deposition rate but degrade the film properties. [Mort, 1986]

c) Other variables

The increase in reactive gas concentration increases the number of active species in the discharge and results in high deposition rate. The deposition rate increases when the total gas flow increases, especially at high power densities [Rosler, 1976; Sinha, 1978; Catherine, 1977]. Low gas flow often cause depletion of reactants and non-uniform deposition [Sabin, 1983]. The frequency of the discharge also affects the deposition rate. As the frequency increases from 50 KHz to 13.56 MHz, the deposition rate decreases to a minimum at about 2 MHz and then increases [Koyama,

1982]. The condition of the electrodes also affects the deposition rate and uniformity [Blaauw, 1984; Ramiller, 1982]. The deposition rate slowly decreases as material deposits on the electrodes.

2.3 PHYSICAL-CHEMICAL VAPOR DEPOSITION PROCESS

2.3.1 Introduction

Low pressure electrical glow discharge processes are used widely in the fabrication of thin films devices and passive components. The technique commonly known, as physical vapor deposition (PVD) is such a process; it is also frequently referred to as sputtering. Sputtering process involves the removal of material from a solid cathode. This is accomplished by bombarding the cathode with positive ions emitted from a rare gas discharge. When ions with high kinetic energy are incident on the cathode, the subsequent collisions sputter atoms from the material. The process of transferring momentum from impacting ions to surface atoms forms the basis of sputter coating [Elshabini, 1998].

Sputter deposition can occur in several environments [Donald, 1998]. First, it occurs in a good vacuum ($<10^{-5}$ torr) using ion beams, second, in a low pressure gas environment where sputtered particles are transported from the target to the substrate without gas phase collisions (i.e., pressure less than about 5 mtorr), using a plasma as the ion source of ions. Finally, a higher pressure gas where gas phase collisions and “thermalization” of the ejected particles occurs but the pressure is low enough so that gas phase nucleation is not important (i.e., pressure greater than about 5 mtorr but less than about 50 mtorr).

Sputter deposition can be used to deposit films of compound materials either by sputtering from a compound target or by sputtering from an elemental target in a

partial pressure of a reactive gas (i.e., “reactive sputter deposition”). There are various detailed forms of PVD and these include: diode dc, diode r.f., magnetron dc and magnetron r.f. R.f. reactive magnetron sputtering process, which has been successfully used to produce Ti-Si-N barrier films in the current work, will be discussed here. Physical vapor deposition occurs when sputtered titanium plasma reacts with nitrogen plasma and silicon plasma (from silane gas), while chemical vapor deposition occurs when nitrogen plasma reacts with silicon plasma, thus, we named it as physical-chemical vapor deposition process (P-CVD).

Briefly, magnetron sputtering requires a magnetic field B to be perpendicular to the electric field E , i.e. $B \perp E$, and parallel to the cathode surface. For a planar magnetron sputtering configuration, a permanent magnet is placed behind a target (an electromagnet can also be used, but it will add complexity to the system) to provide the required magnetic field B (see Figure 2-7 a) [Li, 1999]. These magnetic field lines are predominantly parallel to the top face of the cathode (target) (see Figure 2-7 b). A strong electric field E perpendicular to the top of the cathode (i.e. to the magnetic field B) exists in the ion sheath region near the target, but not in the glow discharge plasma region, because there the electric potential is almost the same. Thus the magnetic field B is perpendicular to the electric field E , and parallel to the top face of the cathode, thus meeting the necessary requirements for the magnetron sputtering source. The magnetic field close to the surface of the sputtering target permits an enhancement in efficiency of the process, typically by a factor of up to four times.

Fig. 2-7: Electron motion near planar magnetron electrode. (a) Profile of magnetron electrode, (b) Magnetic field on the target surface. [Li, 1999]

Figure 2-8 shows the cross-section of r.f. reactive magnetron sputtering chamber. On the application of r.f. power to the cathode (target), the working gas is ionized into plasma. The plasma produced by r.f. discharge in the above system is an open (dissipative) system. The plasma energy can be lost by means of thermal conduction, emission and outflow of thermal energy carried by pumping, and is determined by the balance between the input r.f. power and these dissipative approaches. The energy dissipated through these means largely depends on the discharge condition. Specifically, when input r.f. power is fixed, the plasma energy depends on the pressure; when the pressure is fixed, the plasma energy varies with the input r.f. power. The resulting magnetic field confines the electrons to a circular path on the surface of the target disk. These energized electrons further ionize the gas molecules through collision, resulting in a large increase in plasma density at the target surface and an increase in sputtering rate from the target, with reduced irradiation of the substrate and chamber walls. Because the sputtered target atoms are relatively massive and neutrally charged, they are not affected by the magnetic field, and they migrate to coat the substrate and exposed chamber surfaces.

Fig. 2-8: Schematic cross-section of r.f. reactive magnetron sputtering chamber.

The key advantages of magnetron source as shown in Figure 2-9 are first a vast improvement in efficiency over conventional sources, sputter deposition rates are improved because of the increased plasma density, and a reduction in substrate bombardment by energetic electrons occurs. However, the primary problems of magnetron sources are because these sources are more complex and therefore more expensive. Moreover, uneven consumption of the target material results from the confinement of the electrons around a ring at the center of the target, and this is expensive for precious metal deposition.

Fig. 2-9: Cross-sectional view of a magnetron sputter source [Li, 1999].

R.f. sputtering uses a 13.56 MHz sinusoidal voltage to drive the source. The substrate and chamber walls are held at ground potential. Using this approach, the charge that builds up on a dielectric target is dissipated through the second half of the cycle. R.f. sputtering is perhaps the most versatile technique and can be used to deposit virtually any material. The key difference between an r.f. system and a DC deposition system is the need for a matching network. The matching network is needed to match the impedance of the source to the chamber in order to maximize the power transfer from source to load. A bias can also be applied to the substrate to increase irradiation, causing resputtering of the deposited films [Elshabini, 1998]. This process is selective such that material at elevated locations on the substrate is selectively removed.

2.3.2 Deposition variables

In r.f. reactive magnetron sputtering deposition, a number of process parameters must be controlled in order to have a reproducible process and product. These include the sputtering system, pressure, gas flow, target power and voltage. Each is discussed in the following paragraphs.

a) Sputtering system

A good sputtering system should first of all a good vacuum system. The vacuum capability is very important since it allows a reproducible plasma environment to be established. The plasma causes ion scrubbing of the system's surfaces which desorbs contaminants into the plasma where they are activated and can react in a detrimental manner with the target or depositing material. Contamination in the system can be reduced by preconditioning the system using a plasma and then flushing the contamination from the system. Adequate gas throughput should be maintained during deposition to prevent the buildup of contamination in the deposition chamber.

b) Pressure

The properties of sputter deposited films can be very dependent on the gas pressure. For example, the film stress can vary dramatically with pressure [Cuthrell, 1988; Hoffman, 1994; Windischmann, 1992]. If the pressure is low, the deposited film can have a high compressive stress whereas if the pressure is higher, the stress can be tensile. One method of controlling the film stress is to periodically cycle the pressure from high to a low value during the deposition [Cuthrell, 1988]. The pressure determines the thermalization of energetic particles in the system. Therefore it is very important to have precise pressure measurements from run-to-run.

c) Gas flow

In reactive sputter deposition, the gas flow is an important processing variable and in non-reactive deposition, gas flow is important in sweeping contaminants from the processing chamber. A typical gas flow rate is 200 sccm or higher.

d) Target power and voltage

Reproducible sputtering parameters call for monitoring the target power (watts/cm²) and voltage. In the case of r.f. sputtering, the reflected power from the target is measured and controlled by the impedance matching circuit. In reactive deposition, there can be hysteresis on target power due to reaction of the target surface with the reactive gas. In the work of Zhang *et al* [Zhang, 2004], they reported that different target powers will produce different film compositions, size, amount and distribution of the nanocrystalline TiN phase.

2.3.3 Advantages and disadvantages

Sputter deposition has several advantages [Donald, 1998]. In this process, any material can be sputtered and deposited, such as element, alloy or compound. In

addition, the sputtering target provides a stable, long lived vaporization source and vaporization is from a solid surface and can be up, down or sideways. Besides that, the sputtering target can be made conformal to a substrate surface such as a cone or sphere and sputtering conditions can easily be reproduced from run-to-run. Moreover, in reactive deposition, the reactive species can be activated in plasma. When using chemical vapor precursors, the molecules can be dissociated or partially dissociated in the plasma. In addition, the utilization of sputtered material can be high in this process and in situ surface preparation is easily incorporated into the processing.

However, there are some disadvantages [Donald, 1998] for sputter deposition process. In this process, most of the sputtering energy goes into heat in the target and the targets must be cooled. In addition, sputter vaporization rates are low compared to those that can be achieved by thermal vaporization. Besides that, sputtering is not energy efficient and sputtering targets are often expensive. Furthermore, substrate heating from electron bombardment can be high in some configurations; substrates and films may be bombarded by short wavelength radiation and high energy particles that are detrimental to their performance. Moreover, contaminants on surfaces in the deposition chamber are easily desorbed in plasma-based sputtering due to heating and ion scrubbing. Gaseous contaminants are “activated” in plasma-based sputtering and become more effective in contaminating the deposited film.

2.4 **CHARACTERIZATION OF THIN FILMS AND SURFACES**

2.4.1 **Introduction**

Scientific disciplines are identified and differentiated by the experimental equipment and measurement techniques employed. The same is true of thin-film science and technology. With the explosive growth of thin film utilization in microelectronics, there is an important need to understand the intrinsic nature of films in more complex material environments. Increasingly, the benefits of multilayer film structures have been realized in an assortment of high technology applications. Examples include multilayer metal and insulating films in microelectronics, compound semiconductor films in optoelectronics, dielectric film stacks for optical coatings, and ceramic film layers in hard coatings.

A list of the modern techniques employed in the characterization of Ti-Si-N films is shown in Table 2-4 [On-line, eaglabs.com]. Figure 2-10 [On-line, eaglabs.com] is a chart of detection sensitivity versus analytical spot size for a variety of analytical techniques. This chart, along with Table 2-4 which summarizes crucial parameters for a number of techniques, allows us to begin the process of selecting the appropriate technique for a given problem. Among their characteristics are the unprecedented structural resolution and chemical analysis capabilities over both small lateral and transverse dimensions. Some techniques only sense and provide information on the first few atom layers of the surface. Others probe more deeply, but in most cases, depths of a micron or less are analyzed. Virtually all of these techniques require a high or ultrahigh vacuum ambient. Some are nondestructive while others are not. All of them utilize incident electron, or ion, or photon beams. These interact with the surface and excite it in such a way that some combinations of secondary beams of electrons,

ions, or photons are emitted, carrying off valuable structural and chemical information in the process.

This section will briefly presented the analytical techniques such as field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), time-of-flight secondary ion mass spectrometry (ToF-SIMS), x-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectrometry (RBS), x-ray diffraction (XRD), atomic force microscopy (AFM) and four-point resistivity probe that have been used to characterize the properties of Ti-Si-N and Ti-Si-N-O films and electroless copper seed layer in the current work.

Fig. 2-10: Detection sensitivity versus analytical spot size. [On-line, eagles.com]

Table 2-4: Analytical techniques employed in thin film science and technology.

Analytical Technique	Typical Applications	Signal detected	Elements Detected	Organic Information	Detection Limits	Depth Resolution	Imaging /mapping	Lateral Resolution (probe size)
FESEM	High resolution imaging of polished precision cross sections	Secondary and backscattered electrons	-	-	-	-	Yes	1.5 nm
TEM	High resolution imaging of thinned cross sections and planar samples	Transmitted electrons	-	-	-	-	Yes	0.1 nm
ToF-SIMS	Surface microanalysis of polymers, plastics and organics	Secondary ions, atoms, molecules	H – U	Molecular ions to mass 10,000	< 1 ppma, $1E8$ at/cm ²	1 mono-layer	Yes	0.10 micron
XPS	Surface analysis of organic and inorganic molecules	Photo-electrons	Li – U	Chemical bonding	0.01 – 1 at%	1 – 10 nm	Yes	10 micron – 2 mm
RBS	Quantitative thin film composition and thickness	backscattered He atoms	Li – U	-	~5 at% (Z<20) ~0.1 at% (20<Z<70) ~0.005at% (Z>70)	2 – 20 nm	Yes	2 mm
XRD	Crystal phase identification, orientation and crystallite size	Diffracted X-rays	-	-	-	-	No	20 micron
AFM	Surface imaging with near atomic resolution	Atomic scale roughness	-	-	-	0.01 nm	Yes	1.5 – 5 nm

2.4.2 Field emission scanning electron microscopy (FESEM)

FESEM (Figure 2-11) is similar to an SEM with the exception of how the electrons are emitted from the source. In a field emission gun, there is an extraction anode held at a very high potential relative to the source. This high potential causes electrons to stream from the source which can be W or a LaB₆ crystal to form the electron beam. Electrons are accelerated in a field gradient. The beam passes through Electromagnetic Lenses, focusing onto the specimen. As result of this bombardment different types of electrons are emitted from the specimen. A detector catches the secondary electrons and an image of the sample surface is constructed by comparing the intensity of these secondary electrons to the scanning primary electron beam. Finally the image is displayed on a monitor. The advantage of an FESEM is that a very small spot size is obtained at the gun and the optics of the column are designed to maintain the initial cross over size as opposed to demagnifying which is performed in the typical SEM.

Fig. 2-11: Schematic of the field emission scanning electron microscope [On-line: <http://infohost.nmt.edu>]

Applications of FESEM include semiconductor device cross-section analyses for gate lengths, gate oxides, film thicknesses, and construction details. Besides that, FESEM can be used to determine advanced coating thickness and structural uniformity. In addition, small contamination feature geometry and elemental composition can be measured by FESEM too.

FESEM produces clearer, less electrostatically distorted images with spatial resolution down to 1.5 nm. This is 3 to 6 times better than conventional SEM. Besides that, high quality, low voltage images are obtained with negligible electrical charging of samples. (Accelerating voltages range from 0.5 to 30 kV.). In addition, there is no need to coat a conducting layer on insulating materials if FESEM is used. Moreover, FESEM can provide ultra-high magnification imaging. Thus, FESEM is used in this work to study the surface morphology of the Ti-Si-N and Ti-Si-N-O barrier films.

2.4.3 Transmission electron microscopy (TEM)

TEM (Figure 2-12) [On-line, www.unl.edu] is a tool that can provide images at high magnification and images with information about the atomic structure of a material that is thin enough (50 to 100nm) to transmit electrons. In operation, electrons are thermionically emitted from the gun and typically accelerated to anywhere from 125 to 300 keV, or higher (e.g., 1 MeV) in some microscopes. High magnification in TEM methods is a result of the small effective wavelengths (λ) employed. According to the deBroglie relationship [Milton, 2002],

$$\lambda = h / (2mqV)^{1/2} \text{ ----- (2.1)}$$

where m and q are the electron mass and charge respectively, and V is the potential difference. Electrons of 100 keV energy have wavelengths of 0.037 Å and are capable of effectively transmitting through about 0.6 μm of Si.

Fig. 2-12: Schematic of transmission electron microscopy [On-line, www.unl.edu]

In operation, electrons are projected onto the specimen by the condenser lens system. The scattering processes experienced during their passage through the specimen determine the kind of information obtained. Elastic scattering, involving no energy loss when electrons interact with the potential field of the ion cores, gives rise to diffraction patterns. Inelastic interactions between beam and matrix electrons at heterogeneities such as grain boundaries, dislocations, second phase particles, defects, and density variations cause complex absorption and scattering effects leading to a spatial variation in the intensity of the transmitted beam.

In the current work, two types of TEM samples were prepared to observe the Ti-Si-N and Ti-Si-N-O barrier films microstructure: (1) cross-section (2) plan view samples. The preparation steps for cross-section samples are as follows:

- (i) Cleaving a number of wafer specimens transversely.
- (ii) Bonding these slivers using epoxy.
- (iii) Thinning the samples by grinding and polishing.

(iv) Finally, the resulting disk is ion milled until a hole appears at the center.

On the other hand, plan view TEM samples are prepared by dissolving the substrate (KBr in the current work) in distilled water. The films are thin enough for direct observation.

2.4.4 Time-of-flight secondary ion mass spectrometry (ToF-SIMS)

ToF-SIMS (Figure 2-13) is useful to verify low concentration of impurities introduced during processing. It uses a pulsed ion beam (microfocused Ga) to remove molecules from the very outermost surface of the sample. It is done at sufficiently low intensity to ensure that the molecule chains are not broken into their constituent pieces. The particles removed from the surface (secondary ions) are accelerated into a "flight tube" and their mass is determined by measuring the exact time at which they reach the detector. The exact masses can be calculated with such accuracy that particles with the same nominal mass (e.g. Si and C₂H₄) are easily distinguished from one another. Mass resolution to 0.00x amu and mass range 0-10,000 amu (e.g. polymers and organic components) can be obtained [Rivière, 1990]. The ToF-SIMS can detect trace elements and image the chemical distribution on surfaces with lateral resolutions near 0.1 micron.

Fig. 2-13: Schematic of time of flight secondary ions mass spectrometry.

In this work, the depth profile of Cu, Ti, Si and N after annealing is characterized by time-of-flight secondary ion mass spectrometry (ToF-SIMS) with 3 keV Ar⁺ ion primary beam at a beam current of 50 nA. The purpose of this experiment is to see if there is any metal that has diffused into the Ti-Si-N films, induced by the thermal anneal.

ToF-SIMS analysis can provide chemical compound identification; elemental and chemical mapping; surface sensitivity; trace element sensitivity (ppm or ppb); retrospective analysis; analysis of insulating and conducting samples, and depth profiling of the elements in the films.

2.4.5 X-ray photoelectron spectroscopy (XPS)

XPS is currently the most widely used surface analytical technique. In the basic processes of XPS analysis, the surface to be analyzed is irradiated with soft X-ray photons. Al K α (1486.6eV) or Mg K α (1253.6eV) is often the photon energies of choice. Other X-ray lines can also be chosen such as Ti K α (2040eV). When a photon of energy $h\nu$ interacts with an electron in a level with binding energy BE, the entire photon energy is transferred to the electron, with the result that a photoelectron is ejected with kinetic energy KE [Helmut, 2001] (see Figure 2-14).

$$KE = h\nu - BE - \phi \quad \text{-----} \quad (2.2)$$

where $h\nu$ is the energy of the exciting radiation, BE is the binding energy of the emitted electron in the solid and ϕ is the spectrometer work function.

Obviously $h\nu$ must be greater than BE. The ejected electron may come from a core level or from the occupied portion of the valence band, but in XPS most attention is focused on electrons in core levels. Since no two elements share the same set of electronic binding energies, measurement of the photoelectron kinetic energies

provides an elemental analysis. In addition, equation (2.2) indicates that any changes in BE are reflected in KE, which means that changes in the chemical environment of an atom can be followed by monitoring changes in the photoelectron energies, leading to the provision of chemical information. The energy of the photoelectrons leaving the sample gives a spectrum with a series of photoelectron peaks. The binding energy of the peaks is characteristic of each element. The peak areas can be used (with appropriate sensitivity factors) to determine the composition of the materials surface. The shape of each peak and the binding energy can be slightly altered by the chemical state of the emitting atom. XPS is not sensitive to hydrogen or helium, but can detect all other elements.

In this work, XPS analysis is carried out using Al K α radiation to determine the chemical bonding between the elements in Ti-Si-N and ti-Si-n-o films. With the combination of XRD data, the compounds in Ti-Si-N and Ti-Si-N-O films can be accurately determined.

Fig. 2-14: (a) Schematic of the basic apparatus used in XPS. X-rays are produced at the Al anode by bombardment of electrons created at the filament. (b) The X-rays impinge on a sample producing photoelectrons, which are detected after analysis in the electron energy analyzer [Leonard, 1986].

2.4.6 Rutherford backscattering spectrometry (RBS)

Elemental compositional analysis is achieved by measuring the energy losses suffered by light primary ions in single binary collisions. RBS utilizes a beam of mono-energetic (typically 1 – 2 MeV) and collimated ions of either H^+ or He^+ directed at near normal angle to the surface being analyzed, as shown in Figure 2-15. Backscattered ions, from the sample, are then analyzed. The energy of the backscattered particle is dependent on the location (depth) of the collision, mass of the target atom, and the concentration of atoms/cm² on the cross sectional area being analyzed. A depth profile is obtained by plotting the number of counts as a function of the energy of the backscattered particles.

This technique is very useful for analyzing heavy atoms but not very useful for analyzing lighter atoms. The limitation arises from the fact that collisions between similar masses result in small changes in energy. The resolution of such small changes in energy depends on the sensitivity of the detector. The limited sensitivity of the

detector at present leads to the limitation associated with the use of RBS in distinguishing atoms with similar mass [Helmut, 2001; Leonard, 1986]

Fig. 2-15: The working principle of RBS.

In this work, RBS is used to determine the atomic concentration of Ti, Si, N and O in the barrier films. Besides that, atomic concentration of implanted N in Ti-Si-N film as a function of depth is also investigated using RBS.

2.4.7 X-ray diffraction (XRD)

X-ray diffraction can be explained in simple terms by the "reflection" of an X-ray beam from a stack of parallel equidistant atomic planes. At each atomic plane a small portion of the beam can be considered to be reflected. If those reflected beams, which are not absorbed on their way through a crystal, emerge from the crystal in such a way that they do not cancel each other by interference, a diffracted beam can be observed. The condition where the reflected beams interferes positively (add up in phase) to give a strong diffracted beam is given by *Bragg's law* (Eqn 2.3) [Leonard, 1986] and can be derived by simple trigonometry as

$$n\lambda=2d\sin \theta \text{ ----- (2.3)}$$

where n is an integral number describing the order of reflection, λ is the wavelength of the X-rays, d is the spacing between the lattice planes and θ is the *Bragg angle* where a maximum in the diffracted intensity occurs. At other angles there is little or no diffracted intensity, because of negative interference.

XRD is used in the current work to determine the phase formation of Ti-Si-N and Ti-Si-N-O films and the data are coupled with other analyses to obtain the necessary information on the properties of Ti-Si-N and Ti-Si-N-O films.

2.4.8 Atomic force microscopy (AFM)

Atomic force microscopy (Figure 2-16) and scanning probe microscopy (AFM/SPM) provide topographic information down to the angstrom level. Additional properties of the sample, such as thermal and electrical conductivity, magnetic and electric field strength, and sample compliance can simultaneously be obtained using a specialty probe. Many applications require little or no sample preparation.

Fig. 2-16: Schematic working principle of AFM-9500J2.

AFM uses a physical probe raster scanning across the sample using piezoelectric ceramics. The forces between the tip of the probe and the sample surface cause the cantilever to bend or deflect. This small deflection on the cantilever will create a significant change in reflective laser light. This change will be detected by photodetector and then amplified by the amplifier and the position of the probe and the feedback signals are electronically recorded to produce a three dimensional map of the surface or other information depending on the specialty probe used.

Data output is either a three dimensional image of the surface or a line profile with height measurements. The surface roughness parameters of R_a or RMS are also available with either of the above outputs. Other types of feature analysis include particle grain size analysis, bearing ratio, fractal dimension and power spectrum analysis.

Applications of AFM include materials evaluation, failure analysis and quality control. Examples in materials evaluation, include surface roughness on implanted silicon wafers, thermal properties such as thermal conductivity, glass transition temperature (T_g), and melting temperature of various phases of a blended polymer measured down to the nanometer scale, magnetic field mapping of recording media or reading heads, and nanomechanical testing. Examples in failure analysis include rapid hot-spot analysis of powered electronic devices and defect analysis of compact disk stampers. For quality control, examples such as surface profiles of thin film and coatings, metrology of semiconductor devices and compact disks, and surface finish of substrates for thin film deposition can be analyzed by AFM.

In this work, RMS surface roughness of as-deposited Ti-Si-N and Ti-Si-N-O is evaluated by AFM.

2.4.9 Four-point resistivity probe

The purpose of the four-point probe is to measure the resistivity of a semiconductor material. It can measure either bulk or thin film specimen, each of which consists of a different expression.

The four-point probe setup consists of four equally spaced tungsten metal tips with finite radius. Each tip is supported by springs on the other end to minimize sample damage during probing. The four metal tips are part of an auto-mechanical stage which travels up and down during measurements. A high impedance current source is used to supply current through the outer two probes; a voltmeter measures the voltage across the inner two probes (Figure 2-17) to determine the sample resistivity. Typical probe spacing is approximately 1 mm.

Fig. 2-17: Schematic diagram of a four-point probe where S is the probe spacing.

The significance of the sheet resistance can be easily seen if it is refer to the end-to-end resistance of a rectangular sample. From the resistance formula:

$$R_s = \rho \ell / wt \text{ ----- (2.6)}$$

where ℓ is the length of the specimen, and if $w = \ell$ (a square), then

$$R_s = \rho / t \text{ ----- (2.7)}$$

R_s may be interpreted as the resistance of a square sample, and for this reason the units of R_s are taken to be ohms-per-square or ohm/sq. Dimensionally this is the same as ohms but this notation serves as a convenient reminder of the geometrical significance of sheet resistance. It should be noted that R_s is independent of any geometrical dimension and is therefore a function of the material alone.

2.4.10 Electrical testing

There are several methods used to investigate the diffusion of copper into interlayer dielectrics (ILDs), such as SiO_2 , SiN_x , polymers etc. In this thesis, the extent of Cu diffusion/drift into Ti-Si-N barrier films is determined at various biasing and temperature conditions using bias-temperature-stress (BTS) technique.

BTS technique is used to determine mobile charges. However, in contrast to room temperature C-V measurements, for mobile charge measurements, the measurement temperature must be sufficiently high for the charge to be mobile. In this technique, the MIS capacitor is heated to 150-250°C to make the charges mobile, and a gate bias is applied for a time sufficiently long for charges to drift to the oxide interface. The metal-insulator-semiconductor (MIS) capacitor is then rapidly cooled to room temperature under bias and a C-V curve is measured. The procedure is also repeated with opposite bias polarity. The mobile charges are determined from the negative flat-band voltage shift, given by [Schroder, 1998]

$$\Delta V_{FB} = -\gamma \frac{\Delta Q_m}{C_i} \dots\dots\dots (2.8)$$

where C_i is the accumulation capacitance and γ describes the charge distribution in the dielectric

$$\gamma = \frac{\int \rho(x) * x dx}{t \int \rho(x) dx} \dots\dots\dots (2.9)$$

where $\rho(x)$ is the charge density per unit volume, while x is measured from the metal gate interface, and t is the total thickness of the dielectric.

In these calculations, it is assumed that singly ionized Cu ions, i.e., Cu^+ are the only type of mobile ions injected and then diffuse/drift into the dielectric. This is assumed because first ionization energy of Cu (7.7 eV/atom) is about one-third of its second ionization energy (20.3 eV/atom), and ions move instantaneously under bias at high temperatures. In addition, solid solubilities of higher ionized states of most metals are much lower than that of singly ionized state [McBrayer, 1986].

Once Cu^+ ions are injected, an assumption is to be made about the distribution of ions inside the dielectric, i.e., " γ " in equation 2.9 is to be defined. $\gamma = 1$, when ions pile up at the silicon interface.

In the simplest case, there is merely a parallel shift of the two curves and ΔV_{FB} is easily read from the plot. If there is a significant change in the interface trapped charge as a result of the mobile charge drift, one of the two C-V curves may become distorted and ΔV_{FB} is more difficult to determine. The C-V curve shifts horizontally due to the change in flat-band voltage after BTS cycle. Since only relative changes are important, the exact V_{FB} was not measured in this thesis work. Instead, voltage corresponding to 95% of maximum capacitance was used in the calculations to determine mobile ion concentration.

BTS C-V measurements were made on HP 4280A 1 MHz Capacitance Meter/CV Plotter. A small a.c signal of 10 mV r.m.s was superposed on the applied dc bias. Capacitors were vacuum-held on an MS1 electronics light shield/ hot chuck and were under nitrogen purge throughout BTS (Figure 2-18). The samples were biased at high temperatures, water-cooled down rapidly to room temperature (with bias on) at

periodic intervals, and C-V measurements were conducted. Biasing voltages ranged from 0.5 MV/cm to 1 MV/cm and temperatures from 150 to 250°C.

Fig. 2-18: Schematic of BTS testing setup.

Chapter 3: Results and Discussion

Inductively Coupled Plasma Ti-Si-N Films

3.1 The Formation of Ti-Si-N Barrier Films Using Low Frequency, High Density Inductively Coupled Plasma Process

3.1.1 Introduction

As reviewed earlier, conventional barrier material includes TiN, Ta, and TaN. However, due to the down-scaling of devices and more stringent reliability requirement, more effective barrier materials have to be found. In this respect, a class of refractory, ternary nitrides, such as Ti-Si-N, has been proposed as candidates for the next generation diffusion barrier in copper/low- k dielectric back-end-of-line device fabrication [Marcadal, 2002; ITRS, 2005]. Various research groups have explored the formation of Ti-Si-N films by PVD, MOCVD, MOALD techniques, and documented their resulting electrical, structural, and thermal properties [Eric, 2000; Edward, 2001; Reid, 1994; Prindle, 2002; Goodman, 1986; Min, 1998; Smith, 1997; Min, 1999].

This work focuses on a novel approach by employing low frequency, high density inductively coupled plasma process in the formation of Ti-Si-N barrier films. Process temperatures below 400°C, which is compatible with current back-end-of-line processes. It will be shown that the nitrogen implantation into Ti_xSi_y substrate has destroyed the columnar structure. This process also enables us to have a better control of the thickness of Ti-Si-N films as well as produce a dense microstructure. The objective of this work is to investigate the effects of processing parameters on the properties of Ti-Si-N films, such as phase composition, microstructure, surface morphology, surface roughness, electrical resistivity, and film uniformity. The understanding obtained will help in the selection of appropriate processing parameters for the barrier formation in the back-end-of-line device fabrication.

3.1.2 Experimental

A 50 nm thick Ti_xSi_y film was fabricated by depositing a layer of Ti on p-type (100) silicon wafer, followed by rapid thermal annealing at 750°C (RTA1) and 850°C (RTA2). The sheet resistance of the formed Ti_xSi_y film was measured to be 6.08 Ω/Sq with a standard deviation of 1.06 %. High density nitrogen plasma implantation into the Ti_xSi_y film was conducted in a low frequency inductively coupled plasma reactor for 30 and 60 minutes. This implantation process was preceded by Ar plasma activation. The chamber was evacuated to 1×10^{-4} Torr (base pressure) before the processing gases were introduced. In addition, low frequency (~ 0.5 MHz) was applied for plasma production. During the Ar plasma activation process, the pressure was 2.4×10^{-2} Torr and 9.2×10^{-2} Torr when argon gas flow rate was set at 10 sccm and 30 sccm respectively. The total gas (Ar, N) pressure during the nitrogen plasma implantation was between 1×10^{-1} Torr to 5×10^{-2} Torr, depending on the combined gas flow rate (Table 3-1). The substrate temperature was between 200-300°C when 2 kW plasma power was used, and process parameters were external bias, plasma composition, and plasma treatment time. The bias was changed from 100 V to 300 V, argon gas flow rate from 10 sccm to 30 sccm, argon plasma activation time from 5 to 20 minutes, and nitrogen plasma treatment time from 30 to 60 minutes. Table 3-1 shows a summary of these process parameters. Stoichiometric composition was obtained by Rutherford backscattering spectrometry (RBS) using a 2.0 MeV $^4\text{He}^+$ beam. High resolution transmission electron microscopy (HRTEM) was used to characterize the nanostructure of the films. Field emission scanning electron microscope (FESEM) was used to observe surface morphology of the Ti-Si-N films, and atomic force microscope was employed to assess the roughness of the film. Electrical resistivity of Ti-Si-N films was measured using 4-point resistivity probe and phase composition was

investigated through x-ray diffraction (XRD) using a Shimadzu™ XRD 6000 diffractometer. Implanted nitrogen depth profile was characterized by time-of-flight secondary ion mass spectrometry (ToF-SIMS) with impact energy of 1 keV Ar⁺ ion primary beam. The chemical bonding states of nitrogen were analyzed by X-ray photoelectron spectroscopy (XPS) using 1486.6 eV Al K α irradiation. The X-rays and the peak positions were calibrated with respect to C 1s peak at 284.44 eV.

Table 3-1: Different plasma process conditions in producing Ti-Si-N films.

External Bias (V)	Ar flow/time sccm/min	N ₂ flow/time sccm/min	Sample label
/	/	/	Ti _x Si _y
100	10 / 5	30 / 30	A
200	10 / 5	30 / 30	B
300	10 / 5	30 / 30	C
100	10 / 20	30 / 30	I
100	20 / 20	30 / 30	K
100	30 / 20	30 / 30	M
100	10 / 20	30 / 60	J
100	20 / 20	30 / 60	L
100	30 / 20	30 / 60	N

3.1.3 Results and discussion

RBS analysis shows that there was a gradual change in the nitrogen atomic concentration through the thickness of Ti-Si-N film as shown in Figures 3-1a and b. The atomic concentration of N ranges from 2 – 67% depending on the implantation depth and nitrogen plasma treatment time. It can be seen that longer treatment time provided higher nitrogen content. RBS simulation code RUMP was used to fit a theoretical Ti-Si-N/Ti_xSi_y/Si layer structure to the experimental spectra. All spectra could be accurately fitted in this way. This procedure resulted in accurate areal densities (in atoms/cm²) and stoichiometries for the films. The limited accuracy of

these densities as given in RUMP restricted the precision of the measured film thickness to approximately 10%. Thus, ToF-SIMS was used to investigate the depth of implanted N in Ti-Si-N films, and this will be discussed in detail in section (v).

Fig. 3-1: 2.0 MeV $^4\text{He}^+$ Rutherford backscattering analysis of inductively coupled plasma Ti-Si-N thin film with varying nitrogen plasma treatment time (a) 30 min. (b) 60 min.

In addition, from XPS analysis, nitrogen was found to be bonded to titanium and silicon, forming titanium nitride and silicon nitride respectively when N_{1s} peaks were deconvoluted as shown in Figure 3-2. This result is further confirmed by XRD results as shown later. In general, these results confirmed that nitrogen ions have been successfully introduced into Ti_xSi_y lattice through the inductively coupled plasma process, forming a ternary compound of Ti-Si-N films.

Fig. 3-2: XPS analysis showing that nitrogen bonded to titanium and silicon, forming titanium nitride and silicon nitride respectively when N_{1s} peak is deconvoluted.

Further investigation was carried out using HRTEM to characterize the microstructure of the Ti-Si-N films. Figure 3-3a shows the HRTEM cross-section view of a representative Ti-Si-N/Ti_xSi_y film, indicating the successful implantation of nitrogen into Ti_xSi_y structure and the formation of nanostructure Ti-Si-N film (Figure 3-3b) on top of the columnar structure of Ti_xSi_y (Figures 3-3a and c). This clearly indicates that ion bombardment processes damaged the columnar structure of Ti_xSi_y and formed nanostructure of Ti-Si-N film. These nanostructures consisted of TiN, Si₃N₄ and Ti_xSi_y and the presence of these phases has been proved by XPS (as discussed above) and the XRD data, which will be discussed in the following section. In this section, the effects of external bias, argon plasma activation time, argon gas flow rate and nitrogen plasma treatment time on the properties of Ti-Si-N films have been discussed.

Fig. 3-3: (a) TEM micrograph showing cross-section structure of Ti-Si-N/ Ti_xSi_y /Si layers; (b) HRTEM micrograph presents the nanostructure of ICP Ti-Si-N film; (c) HRTEM micrograph of lattice spacing in Ti_xSi_y structure.

(A) THE EFFECT OF EXTERNAL BIAS ON

(i) *Surface morphology of Ti-Si-N films*

Three values of voltage: 100 V, 200 V and 300 V were used, in the growth of Ti-Si-N films. External bias serves as a purpose to attract positively charged plasma ions toward the substrate, and leads to plasma ions bombarding on the Ti_xSi_y film. As a

result, this will destroy the Ti_xSi_y structure and lead to the formation of a new film on Ti_xSi_y . Thus, it is important to investigate the effects of external voltage on the properties of this newly formed Ti-Si-N film.

Figures 3-4 and 3-5 show the surface morphology of the films before and after plasma treatment. It can be seen that the as-deposited sample has a rough surface morphology. However, the plasma process does not help in smoothening the surface morphology of the sample, and the rough surface morphology is still obtained at different external bias. This is further proven by surface roughness measurement by AFM, which will be discussed in section (iii). In comparing Figures 3-4 and 3-5, it can be seen that plasma treatment has changed the surface morphology to some extent. At the lower bias condition (100 V), as shown in Figure 3-5a, a surface morphology with clustered white dots of Ti-Si-N film is observed. But, when the voltage increases to 200 V and 300 V, those clustered white dots disappear and the surface morphology of Ti-Si-N films shows a network pattern as presented in Figures 3-5b and 3-5c. Different external bias will result in different acceleration energy of reactive ions, which will lead to different degrees of bombardment. As external bias increases, acceleration energy of reactive ions also increases. This results in severe ion bombardment on substrate surface and leads to different surface morphology of Ti-Si-N films compared to that of lower external bias.

Low Mag.

High Mag.

Fig. 3-4: FESEM surface morphology of Ti_xSi_y film without undergoing plasma process (as-deposited).

Low Mag.

High Mag.

(a)

Low Mag.

High Mag.

(b)

Fig. 3-5: FESEM surface morphology of Ti-Si-N films subjected to (a) 100 V external bias; (b) 200 V external bias; (c) 300 V external bias during intensive nitrogen plasma treatment process.

(ii) Sheet resistance of Ti-Si-N films

In copper interconnect technology, the main contributors to interconnect resistance is the barrier resistance. Thus, low resistance in the barrier material is required. The sheet resistance was measured by a four-point resistivity probe. As a reference, the sheet resistance of TiN was reported to be 17.12 Ω/Sq and 16 Ω/Sq by Yuokoyama *et al* [Yuokoyama, 1991] and Olowolafe *et al* [Olowolafe, 1991] respectively. For an inductively coupled plasma chemical vapor deposited SiN, Luís da Silva Zambom *et al* [Luís, 2002] showed that the sheet resistance was between 10^{13} Ω/Sq to 10^{17} Ω/Sq . In the current work, the sheet resistance of the Ti_xSi_y film is 6.08 Ω/Sq . As shown in Table 3-2, when the external bias is set at 100 V, the sheet resistance is 6.16 Ω/Sq with a standard deviation of 1.68 %. When the bias increases to 300 V, there is a drastic increase in sheet resistance (38.74 Ω/Sq). In other words, there is 80% increase in sheet resistance of Ti-Si-N films. Furthermore, increasing the external bias from 100 V to 300 V also produced a less uniform film as the standard deviation increased from 1.68% to 8.95%. The rise in resistance could be explained by

the increase in defect density caused by ion bombardment damage under high external bias. Thus, low external bias provides a lower resistance of barrier films.

Table 3-2: Average sheet resistance and uniformity of Ti-Si-N films at different external bias.

Sample label	Process Conditions	Sheet Resistance (ohms/Sq)	Standard deviation from sheet resistance (%)
As-deposited	Ti _x Si _y sample	6.08	1.06
A	100 V	6.16	1.68
B	200 V	8.34	2.91
C	300 V	38.74	8.95

(iii) *Surface roughness of Ti-Si-N films*

Before the plasma treatment, Ti_xSi_y film has RMS value of 18.16 nm from AFM measurement. After the plasma treatment, there was a slight increase in surface roughness as shown in Table 3-3. However, the results also show that increase in external bias did not exert significant effect on surface roughness of Ti-Si-N film. The surface roughness was within the range of 20.09 nm to 22.23 nm.

Table 3-3: Surface roughness of Ti-Si-N films for different external bias.

Process Conditions	RMS Roughness (nm)
Ti _x Si _y	18.16
100V	22.18
200V	20.09
300V	22.23

The slight increase in surface roughness of Ti-Si-N films after plasma treatment is due to the intensive bombardment of reactive ions during the processes such as activation process by argon plasma and implantation process by nitrogen

plasma. The AFM surface morphology of the samples before and after plasma treatment is shown in Figure 3-6.

Fig. 3-6: AFM surface morphology of (a) as-deposited Ti_xSi_y substrate; Ti-Si-N films under external bias of (b) 100 V; (c) 200 V; (d) 300 V.

Rough surface is desired for nitrogen plasma implantation process. With rougher surface, more areas are exposed to nitrogen plasma for subsequent implantation and diffusion process. On the other hand, a rough surface is a disadvantage for copper deposition process as a non-uniform copper film may be obtained. Thus, care must be taken in order to compromise these issues.

(iv) Phase composition of Ti-Si-N films

XRD results (Figure 3-7) show that both titanium nitride (TiN) and silicon nitride (Si_3N_4) have been formed. In comparing the XRD results with different external bias as shown in Figure 3-7, it is noticed that the intensity of TiSi_2 peak is reduced when the bias increases from 100 V to 300 V. At the same time, there is an increase in the intensity ratio between Si_3N_4 (411) peak and TiN (220) peak from 200 V to 300 V as shown in Table 3-4. The reduced presence of TiSi_2 could be due to the high bombardment energy which leads to a more thorough breakdown of the existing Ti_xSi_y structure. With the presence of nitrogen plasma and the existence of Ti and Si dangling bonds, the formation of TiN and Si_3N_4 are preferred to TiSi_2 when the substrate temperature is between 473 K to 573 K. Thermodynamic data [Barin, 1993] shows that the enthalpies of formation (ΔH_f) of TiN and Si_3N_4 are -337.45 kJ/mol and -747.56 kJ/mol respectively at 500 K, compared with that of -134.11 kJ/mol for TiSi_2 . The lower the ΔH_f , the easier the phase can be formed under the same process conditions.

Fig. 3-7: XRD measurement of as-deposited Ti_xSi_y film and Ti-Si-N films subjected to different external bias.

The diffraction intensity ratio between the strongest peak of Si_3N_4 and that of TiN is worth the attention. The atomic ratio of $\text{Si}:\text{Ti}$ in the substrate is fixed in all samples before the nitrogen plasma implantation. The variation in $I_{\text{Si}_3\text{N}_4(411)} / I_{\text{TiN}(220)}$ intensity ratio as shown in Table 3-4 may be due to a higher degree of crystallization in Si_3N_4 phase. The current implantation of N into dissociated Ti_xSi_y structure is different from vapor deposition or electrochemical deposition where the mobility of adatoms is high on a newly formed surface. However, with limited mobility of dissociated Ti and Si in the substrate, the TiN and Si_3N_4 phases are likely to form where Ti and Si meet the impinging N . Thus, it is possible that there exists a higher percentage of crystalline Si_3N_4 in some of the specimens but not in others. It is well known that Si_3N_4 formed at relatively low temperatures is in an amorphous form [Eric, 2000; Posadowski, 1988; Joseph, 2002; Miura, 1997; Ivanov, 1998; Fischer, 2000]. However the current experiment clearly shows evidence of crystalline Si_3N_4 . In the current work, we attempt to explain the reasons for the higher degree of crystallization.

Table 3-4: $I_{\text{Si}_3\text{N}_4(411)} / I_{\text{TiN}(220)}$ intensity ratio in Ti-Si-N films that subjected to different external bias.

Process conditions	$I_{\text{Si}_3\text{N}_4(411)} / I_{\text{TiN}(220)}$ ratio
100 V	0.91
200 V	0.88
300 V	1.47

In comparing samples A, B and C, it is found that when external bias increases from 100 V to 200 V, the $I_{\text{Si}_3\text{N}_4(411)} / I_{\text{TiN}(220)}$ intensity ratio remains almost the same. However, from 200 V to 300 V, the ratio increases significantly. Cu diffusion studied in these formed ternary layers also found that for the 300 V treated samples,

significant diffusion of Cu into the ternary layer occurred after 500°C annealing. On the other hand, the 100 V and 200 V samples can prevent Cu diffusion even after 650°C annealing. The details will be discussed later. Besides the reason that high external bias introduces lattice defects into the barrier, another reason could be that when more Si₃N₄ is in crystalline form, Cu diffusion becomes easier.

(v) *Depth profile of nitrogen*

ToF-SIMS has been carried out to study the depth profile of nitrogen in the Ti-Si-N films. During nitrogen plasma treatment, implantation and diffusion of nitrogen will occur with the aid of external bias and implantation time, respectively. Figure 3-8 is a ToF-SIMS depth profile showing that nitrogen has been successfully implanted to 10 nm deep into the Ti_xSi_y film. It is also found that increasing external bias from 100 V to 300 V (sample A to sample C) does not improve the implantation depth of nitrogen. This comparison is made when argon and nitrogen gas flow rate were maintained at 10 sccm and 30 sccm respectively, and nitrogen plasma treatment time was 30 minutes. An external bias does not seem to affect the N implantation depth in the current work. This indicates that kinetic energy of N atoms or ions is not a key factor for implantation depth; rather, the implantation is achieved by a time-dependant diffusion process.

According to 2005 International Technology Roadmap for Semiconductors, beyond the current 70 nm technology node, diffusion barrier thickness requirements for copper are anticipated to be less than 5.6 nm [ITRS 2005]. Thus, by employing low frequency inductively coupled plasma process, it is possible to grow a certain thickness of Ti-Si-N barrier by controlling the process parameters such as argon gas flow rate, and nitrogen gas flow rate as well as the duration of plasma treatment.

Fig. 3-8: Depth profile of Ti, Si and N in Ti-Si-N films for (a) 100 V (b) 200 V (c) 300 V external bias. Sputtering with 1 keV Ar^+ ions.

From the above experimental results and discussion, applying 300 V bias does not improve N implantation depth and will degrade the conductivity significantly. Therefore 100 V is a suitable external bias when film sheet resistance, phase composition and depth profile of nitrogen are considered. From the processing point of view, 100 V bias will not cause much damage to devices. This voltage will be employed in the following experiments.

(B) THE EFFECT OF ARGON PLASMA ACTIVATION TIME, ARGON GAS FLOW RATE, NITROGEN PLASMA TREATMENT TIME ON

(i) *Surface morphology of Ti-Si-N films*

In this experimental work, three argon gas flow rates: 10 sccm, 20 sccm and 30 sccm, were selected to investigate its effect on the properties of Ti-Si-N films. In addition, argon plasma activation time was changed to 20 minutes instead of 5 minutes. Besides that, 30 minutes and 60 minutes nitrogen plasma treatment time were used. The other process parameters such as external bias, nitrogen gas flow rate remained the same. (refer to samples I, K, M and samples J, L, N, see Table 3-1).

In order to investigate the effect of argon plasma activation time on surface morphology of Ti-Si-N films, a comparison was made between sample A and sample I, which were subjected to 5 minutes and 20 minutes argon plasma activation. Figure 3-5a shows the surface morphology of Ti-Si-N films which had been subjected to 5 minutes argon plasma activation, and clustered white dots surface morphology was observed. However, when the argon plasma activation time was increased to 20 minutes, a dense network structure was observed as shown in Figure 3-9a. The difference in surface morphology implies that surface morphology of Ti-Si-N films is affected by argon plasma activation time.

When argon plasma activation time was maintained at 20 minutes, and argon gas flow rate was changed from 10 sccm to 30 sccm, the surface morphology of Ti-Si-N films also changed from a dense network structure to a less dense network surface morphology as shown in Figures 3-9 a, b and c. When the argon gas flow rate was increased, the amount of argon plasma also increased, leading to more intensive bombardment of argon plasma on the Ti_xSi_y films and resulting in a less dense network surface morphology.

Fig. 3-9: FESEM surface morphology of Ti-Si-N films that were subjected to different argon gas flow rate of (a) 10 sccm (b) 20 sccm (c) 30 sccm. Argon plasma activation time was 20 minutes, nitrogen gas flow rate was 30 sccm and nitrogen plasma treatment time was 30 minutes.

The same phenomenon is observed when nitrogen plasma treatment time increases from 30 minutes to 60 minutes. As shown in Figures 3-9a and b are denser network surface morphology, which have been subjected to 30 minutes nitrogen plasma treatment. As the treatment time increases to 60 minutes, less dense network surface morphology is observed as shown in Figures 3-10a, b, and c.

Fig. 3-10: FESEM surface morphology of Ti-Si-N films that were subjected to different argon gas flow rate of (a) 10 sccm (b) 20 sccm (c) 30 sccm. Argon plasma activation time was 20 minutes, nitrogen gas flow rate was 30 sccm and nitrogen plasma treatment time was 60 minutes.

In conclusion, as the argon plasma activation time, argon gas flow rate, and nitrogen plasma treatment time increase, surface morphology of Ti-Si-N film will change from a clustered white dots to dense network to a less dense network surface morphology.

(ii) *Sheet resistance of Ti-Si-N films*

In the range of investigation, argon plasma activation time, argon gas flow rate, and nitrogen plasma treatment time do not have significant effects on sheet resistance. Compared with the reference sheet resistance of 6.08 Ω/Sq (Ti_xSi_y film), the measured sheet resistance at various process conditions (under fixed bias of 100 V) is within the range of 5.06 – 6.12 Ω/Sq as shown in Table 3-5. Combined with the results of the effect of external bias discussed in section A, the current work indicates that external bias plays an important role in controlling the sheet resistance of Ti-Si-N films: The higher the external bias, the higher the sheet resistance of Ti-Si-N films.

Table 3-5: Average values of sheet resistance and its standard deviation of Ti-Si-N films, at different argon plasma activation time, argon gas flow rate and nitrogen plasma treatment time.

Sample label	Activation time	Sheet Resistance (ohms/Sq)	Standard Deviation from sheet resistance (%)
A	5 minutes	6.16	1.68
I	20 minutes	5.99	1.06

30 minutes nitrogen plasma treatment, 20 minutes Ar plasma activation			
Sample label	External bias, argon gas flow rate	Sheet Resistance (ohms/Sq)	Standard deviation from sheet resistance (%)
I	100 V, 10 sccm Ar flow	5.98	1.06
K	100 V, 20 sccm Ar flow	6.12	2.23
M	100 V, 30 sccm Ar flow	5.06	1.62

60 minutes nitrogen plasma treatment, 20 minutes Ar plasma activation			
Sample label	External bias, argon gas flow rate	Sheet Resistance (ohms/Sq)	Standard deviation from sheet resistance (%)
J	100 V, 10 sccm Ar flow	5.80	2.82
L	100 V, 20 sccm Ar flow	5.94	1.36
N	100 V, 30 sccm Ar flow	5.89	1.35

(iii) Surface roughness of Ti-Si-N films

Previous studies (section A-(iii)) show that an increase in external bias does not exert significant effects on surface roughness of Ti-Si-N films. The surface roughness of the samples is shown in Figures 3-11 and 3-12. As a reference, Ti_xSi_y film has RMS value of 18.16 nm. As shown in Table 3-6, change in argon plasma activation time (sample A and I), argon gas flow rate, and nitrogen plasma treatment time do not exert significant effects on the surface roughness of Ti-Si-N films too. The surface roughness is within the value of 18.89 nm to 22.83 nm.

Fig. 3-11: AFM surface morphology of Ti-Si-N films at different argon gas flow rate of (a) 10 sccm (b) 20 sccm (c) 30 sccm. Nitrogen plasma treatment time was set to 30 minutes.

Fig. 3-12: AFM surface morphology of Ti-Si-N films at different argon gas flow rate of (a) 10 sccm (b) 20 sccm (c) 30 sccm. Nitrogen plasma treatment time was set to 60 minutes.

Table 3-6: Comparison of surface roughness of Ti-Si-N films at different argon plasma activation time, argon gas flow rate and nitrogen plasma treatment time.

Plasma Process Conditions	Sample label	RMS roughness (nm)
100V, 10 sccm Ar flow for 5 min, N ₂ flow for 30 min	A	20.54
100V, 10 sccm Ar flow for 20 min, N ₂ flow for 30 min	I	19.48
100V, 20 sccm Ar flow for 20 min, N ₂ flow for 30 min	K	18.89
100V, 30 sccm Ar flow for 20 min, N ₂ flow for 30 min	M	22.83
100V, 10 sccm Ar flow for 20 min, N ₂ flow for 60 min	J	21.63
100V, 20 sccm Ar flow for 20 min, N ₂ flow for 60 min	L	19.36
100V, 30 sccm Ar flow for 20 min, N ₂ flow for 60 min	N	19.22

(iv) *Phase composition of Ti-Si-N films*

When argon plasma activation time changes from 5 to 20 minutes with argon gas flow rate and nitrogen plasma treatment time fixed at 10 sccm and 30 minutes respectively (comparing sample A and sample I), the same phases (TiN, Si₃N₄) are detected as shown in Figure 3-13a. When argon gas flow rate increases from 10 sccm to 30 sccm, with argon plasma activation time and nitrogen plasma treatment time fixed (comparing samples I, K and M), the phase composition remains the same. However the Si₃N₄/TiN intensity ratio increases from 0.63 for sample I to 2.26 for sample M (Table 3-7 and Figure 3-13b). The trend with argon gas flow rate is much weaker when nitrogen plasma implantation time increases to 60 minutes as shown in Table 3-7 and Figure 3-13c (comparing samples J, L and N). As discussed above, this rise in the intensity ratio indicates that the higher percentage of Si₃N₄ is crystalline. The reason for the higher degree of crystallization of Si₃N₄ could be due to the high degree of ionization when argon gas flow rate increases, which in turn will raise the substrate temperature through the intensive bombardment. A high substrate temperature enhances element mobility so that a crystalline phase formation is favored. As will be shown later in the diffusion study, sample M, which has the highest I_{Si3N4(411)} / I_{TiN(220)} intensity ratio, performs the worst among samples while other parameters are fixed (I, K, M). Details will be discussed in section 3.2.

Table 3-7: I_{Si3N4(411)}/I_{TiN(220)} ratio for Ti-Si-N films under various process conditions.

Plasma Process Conditions	Sample label	I _{Si3N4(411)} / I _{TiN(220)} ratio
100V, 10 sccm Ar flow for 5 min, N ₂ flow for 30 min	A	0.91
100V, 10 sccm Ar flow for 20 min, N ₂ flow for 30 min	I	0.63
100V, 20 sccm Ar flow for 20 min, N ₂ flow for 30 min	K	/
100V, 30 sccm Ar flow for 20 min, N ₂ flow for 30 min	M	2.26
100V, 10 sccm Ar flow for 20 min, N ₂ flow for 60 min	J	1.25
100V, 20 sccm Ar flow for 20 min, N ₂ flow for 60 min	L	1.36
100V, 30 sccm Ar flow for 20 min, N ₂ flow for 60 min	N	1.39

Fig. 3-13: XRD measurement of Ti-Si-N films subjected to (a) 5 minutes and 20 minutes argon plasma activation (b) different argon gas flow rate, 30 minutes nitrogen plasma treatment. (c) different argon gas flow rate, 60 minutes nitrogen plasma treatment.

(v) *Depth profile of nitrogen*

Figure 3-8a shows the penetration depth of N of 10 nm for sample A that is subjected to 5 minutes argon plasma activation while other process parameters are fixed (100V external bias, 10 sccm argon gas flow rate and 30 minutes nitrogen plasma treatment). When the argon plasma activation time increases to 20 minutes (sample I), there is a significant rise in the penetration depth of N to 20 nm as shown in Figure 3-14a. The longer activation time will energize the substrate surface; thus, implanted nitrogen ions have better access to a deeper region. This shows that the penetration depth of nitrogen can be improved by extending argon plasma activation time.

Fig. 3-14: Depth profile of Ti, Si and N in Ti-Si-N films for 100 V external bias, 20 minutes argon plasma activation and 30 minutes nitrogen plasma treatment with (a) 10 sccm (b) 20 sccm (c) 30 sccm Ar gas flow. Sputtering with 1 keV Ar^+ ion.

The effects of argon gas flow rate and nitrogen plasma treatment time on the depth profile of N are also considered. First, for the 30 minutes of nitrogen plasma treatment, argon gas flow rate increases from 10 sccm to 30 sccm; there is a slight decrease in N depth profile as shown in Figures 3-14 a, b, and c. For 60 minutes of nitrogen plasma treatment, the argon gas flow rate increases from 10 sccm to 30 sccm, this will increase N depth profile as shown in Figures 3-15 a, b, and c.

Thus, the increase of nitrogen plasma treatment to 60 minutes at a higher argon gas flow rate (30 sccm) can improve nitrogen depth profile. For the effect of argon plasma activation time, the argon gas flow rate, and nitrogen plasma treatment time on the properties of Ti-Si-N films, the suggested process conditions are 20 minutes argon plasma activation time, 30 sccm argon gas flow rate, and 60 minutes of nitrogen plasma treatment.

Fig. 3-15: Depth profile of Ti, Si and N in Ti-Si-N films for 100 V external bias, 20 minutes argon plasma activation and 60 minutes nitrogen plasma treatment with (a) 10 sccm (b) 20 sccm (c) 30 sccm Ar gas flow. Sputtering with 1 keV Ar^+ ion.

3.1.4 Conclusions

A low frequency, high density inductively coupled plasma process has been developed for the growth of Ti-Si-N films. 2 – 67 at% of nitrogen were successfully introduced into Ti_xSi_y structure, and the atomic concentration of nitrogen is depends on the implantation depth and nitrogen plasma treatment time. The resultant nanostructure Ti-Si-N films are mainly composed of two major phases, TiN and Si_3N_4 , which proved by XRD measurement. Most importantly, the implantation has changed the unfavorable columnar Ti_xSi_y structure to nanostructure Ti-Si-N film. In this work, the effects of various process conditions on the properties of Ti-Si-N films were investigated. It was found that the external bias played an important role in controlling the sheet resistance of Ti-Si-N films, but not the implantation depth of nitrogen. The diffraction intensity ratio of Si_3N_4 and TiN could be a reflection of the degree of crystallization in the Si_3N_4 phase. Increasing argon plasma activation time, nitrogen plasma treatment time, and at higher argon gas flow rate will improve the penetration depth of nitrogen into Ti_xSi_y structure. It has been demonstrated that by controlling the process conditions, it is possible to grow Ti-Si-N films with controlled thicknesses and electrical properties. From the data presented, it is suggested that with 100 V external bias, 30 sccm argon gas flow rate, 20 minutes argon plasma activation time, and 60 minutes nitrogen plasma treatment, a 20 nm thick Ti-Si-N film with promising sheet resistance is obtainable.

Table 3-8 shows a summary of the effects of external bias, argon plasma activation time, argon gas flow rate, and nitrogen plasma treatment time on the surface morphology, sheet resistance, surface roughness, phase composition and nitrogen depth profile of inductively coupled plasma Ti-Si-N films.

Table 3-8: Summary of the effects of process parameters on the properties of Ti-Si-N films.

Process conditions/Ti-Si-N films Properties	Surface morphology	Sheet Resistance	Surface roughness	Phase composition	N depth profile
External bias	Yes	Yes	No	Yes	No
argon plasma activation	Yes	No	No	No	Yes
argon gas flow rate	Yes	No	No	Yes	Yes
nitrogen plasma treatment time	Yes	No	No	Yes	Yes

3.2 Copper Diffusion Study in Ti-Si-N Films Formed by Low Frequency, High Density Inductively Coupled Plasma Process

3.2.1 Introduction

When the electronic industries advance into nanoscale features, research and development efforts on advanced materials, and/or alternative process techniques for copper metallization increase rapidly. For the next generation of devices, the primary focus is on new materials and their process integration, such as low-*k* dielectric, copper, and barrier materials. The transition to copper interconnects in most high performance IC fabrication has been realized over the past several years. The continuous shrinking of geometrical parameters in future generation integrated circuits requires an even thinner diffusion barrier that is more effective in stopping copper diffusion.

Thermal stability is an important feature of a film that is used as a diffusion barrier in advanced technology. This section presents the results of a study to characterize the barrier performance of Ti-Si-N films formed by a new process of low frequency, high density inductively coupled plasma process. Preparation and characterization of the Ti-Si-N films were reported in section 3.1. In the current work,

the focus was on the diffusion performance of copper in the barrier films after annealing at high temperatures. The improved barrier performance compared to the conventional TiN film is contributed to the relative difficulty of forming Cu based compounds by Si. The sudden drop of the sheet resistance due to Cu compound formation provides an indication of the barrier failure.

3.2.2 Experimental

To evaluate the performance of ICP Ti-Si-N films as a copper diffusion barrier, 150 nm thick copper film was sputter deposited onto the Ti-Si-N films. The resulting stacks were annealed in nitrogen ambient at 350°C, 450°C, 550°C, 650°C, 750°C and 850°C for 30 minutes. After annealing, the unreacted copper was stripped off in a solution containing 260 g/l ammonium persulfate ((NH₄)₂S₂O₈) in H₂O. The depth profile of Cu, Ti, Si and N in the structures before and after annealing was characterized by time-of-flight secondary ion mass spectrometry (ToF-SIMS) with a 3 keV Ar⁺ ion primary beam at a beam current of 50 nA. The surface morphology of the samples was observed using field emission scanning electron microscopy (FESEM) at a voltage of 5 kV and a beam current of 12 μA. Elemental mapping was carried out using energy dispersive X-ray (EDX). The phase composition was investigated using X-ray diffraction (XRD). The sheet resistance was measured using ResMapTM four-point probe system.

3.2.3 Results and discussion

- (A) The effect of external bias, argon gas flow rate and nitrogen plasma treatment time on diffusion performance of Ti-Si-N films.

As reported in section 3.1, Ti-Si-N films consist of a mixture of TiN and Si₃N₄ phases. Figure 3-16 presents the ToF-SIMS depth profile of Cu/Ti-Si-N/Ti_xSi_y/Si structure without annealing. An abrupt gradient in copper depth profile which shows no sign of copper diffusion through the Ti-Si-N film was observed. The profile of this sample was used as a reference for the Cu diffusion study in annealed samples.

Fig. 3-16: SIMS depth profile of Cu, Ti, Si, N for as-deposited sample without annealing. No copper diffusion was observed.

Figure 3-17 shows the ToF-SIMS depth profile of Cu/Ti-Si-N/Ti_xSi_y/Si structure after 500°C annealing. The effect of external bias on the integrity of the barrier can be seen by comparing Figures 3-17a, b and c, which correspond to the Cu, Ti, Si and N profiles in samples subjected to 100 V, 200 V and 300 V respectively. In the samples subjected to 100 V and 200 V external bias, the copper profile was similar to the one without annealing, which means that the penetration of copper through the

Ti-Si-N barrier is not significant. For the sample subjected to 300 V external bias, significant Cu diffusion was observed. When these samples were annealed at 650°C, the same results were obtained, significant copper diffusion was observed only in the sample subjected to 300 V external bias as shown in Figures 3-18a, b, and c (page 101). This implies that high external bias will degrade the barrier integrity.

Fig. 3-17: SIMS depth profile of Cu, Ti, Si and N after annealing at 500°C for samples subjected to external bias of (a) 100 V; (b) 200 V; (c) 300 V.

Fig. 3-18: SIMS depth profile of Cu, Ti, Si and N after annealing at 650°C for samples subjected to external bias of (a) 100 V; (b) 200 V; (c) 300 V.

Figure 3-19 shows the ToF-SIMS depth profile of Cu/Ti-Si-N/Ti_xSi_y/Si structure after 500°C annealing for samples that were subjected to different argon gas flow rate. The effect of the argon gas flow rate on the integrity of the barrier can be seen by comparing Figures 3-19a, b and c. These samples were subjected to the same external bias (100 V) and 30 minutes nitrogen plasma treatment time. As shown in Figure 3-19, no significant copper diffusion into Ti-Si-N barrier films was detected. Similarly, as the annealing temperature was increased to 650°C, no significant copper diffusion was observed except for sample M, which was subjected to 30 sccm argon gas flow (see Figure 3-20c).

Fig. 3-19: SIMS depth profile of Cu, Ti, Si and N after annealing at 500°C for samples subjected to 100 V, 30 minutes nitrogen plasma treatment, but at different Ar gas flow rate, (a) 10 sccm; (b) 20 sccm; (c) 30 sccm.

Fig. 3-20: SIMS depth profile of Cu, Ti, Si and N after annealing at 650°C for samples subjected to 100 V, 30 minutes nitrogen plasma treatment, but at different Ar gas flow rate, (a) 10 sccm; (b) 20 sccm; (c) 30 sccm.

When the nitrogen plasma treatment time was increased to 60 minutes at fixed external bias (100 V), significant copper diffusion was observed after annealing at 650°C, regardless of argon gas flow rate as shown in Figures 3-21a, b and c. It can be clearly seen that copper penetrates through the Ti-Si-N barrier film. No significant copper diffusion was observed for samples that were annealed at 500°C as shown in Figures 3-22a, b, and c. From these results, it can be seen that the main factors that affect the barrier integrity are the external bias that applies to the substrate and the nitrogen plasma treatment time. Argon gas flow rate affects the Ti-Si-N barrier performance at higher annealing temperature.

Fig. 3-21: SIMS depth profile of Cu, Ti, Si and N after annealing at 650°C for samples subjected to 100 V, 60 minutes nitrogen plasma treatment, but at different Ar gas flow rate, (a) 10 sccm; (b) 20 sccm; (c) 30 sccm.

Fig. 3-22: SIMS depth profile of Cu, Ti, Si and N after annealing at 500°C for samples subjected to 100 V, 60 minutes nitrogen plasma treatment, but at different Ar gas flow rate, (a) 10 sccm; (b) 20 sccm; (c) 30 sccm.

It is known that below the Tammann temperature of about 50%-67% of the absolute melting temperature of a polycrystalline solid, diffusion is not controlled by the bulk mechanisms, but rather by mechanisms associated with grain boundaries, pores, pinholes and dislocations [Chamberlain, 1982]. For the samples that undergo an annealing process at a maximum temperature of 650°C, which is about 29% and 43% of the TiN (3203 K) and Si₃N₄ (2173 K) melting temperature respectively, bulk diffusion should not control the transport of copper in the Ti-Si-N films. In our Ti-Si-N samples, the plasma treatment causes crystallization of the barrier film. The Ti-Si-N barrier films are heterogeneous mixtures as proven by XRD results in section A-iv.

The dominant phases are TiN and Si₃N₄. Thus, in the polycrystalline mixture of TiN and Si₃N₄ film, diffusion through grain boundaries and other defects become dominant.

Based on the above argument, the reason that 300 V external bias leads to easy diffusion by Cu may be due to the high speed bombardment of plasma ions towards the substrate at high external bias. This will give rise to a higher density of defects in the formed film. As a result, barrier performance will be degraded. Furthermore, argon plasma treatment is used to dissociate the Ti_xSi_y bond, higher argon gas flow rate promotes the formation of TiN and Si₃N₄, but at the same time, the lattice defects may also increase.

(B) The effect of annealing temperature on diffusion performance of Ti-Si-N films.

Figure 3-16 was used as a reference for the copper diffusion study in this discussion too. Figure 3-23d shows that copper diffused into a 15 nm thick Ti-Si-N film after annealing for 30 minutes at 650°C. Below this temperature, no copper diffusion was found for the samples that were annealed at 350°C, 450°C and 550°C (see Figures 3-23a, b, and c). Figure 3-23c is the sample profile that annealed at 550°C, which is similar to the profile of as-prepared sample in Figure 3-16. However, when the samples were annealed at 750°C and 850°C for 30 minutes, significant diffusion of copper into Ti-Si-N films was observed as shown in Figures 3-23 e and f. From Figures 3-23 a to f, implanted nitrogen depth profile also changes with the annealing temperatures.

Fig. 3-23: SIMS depth profile of Cu, Ti, Si and N after annealing for 30 minutes at (a) 350°C; (b) 450°C; (c) 550°C; (d) 650°C; (e) 750°C; (f) 850°C.

Figure 3-24 shows the XRD measurement of as-deposited sample and annealed samples at various temperatures. For up to 650°C annealing, only three phases, TiN,

Ti₅Si₃ and TiSi₂, are present. No copper compounds are found in samples annealed up to 650°C. These results matched well with the SIMS results discussed above.

Fig. 3-24: XRD measurement of the samples after annealing at various temperatures. Cu-Ti and Cu-N compounds are formed at high temperature indicating the diffusion of copper into Ti-Si-N barrier films.

Careful analysis of Figure 3-24 found that when the annealing temperature increased from 350°C to 850°C, the intensities of Ti₅Si₃ (210) and TiN (111) gradually decreased. With the disappearance of Ti₅Si₃ and TiN phases at 750°C and above, several Cu-Ti phases and CuN₃ appear. The results show that the diffusion of Cu into the barrier layer is mainly driven by the reaction of Cu with Ti and N in the Ti-Si-N film.

Figure 3-25 shows the FESEM surface morphology of as-deposited sample. Regions of ridges and valleys were found on the surface and this was further

confirmed by AFM as shown in Figure 3-26. Surface roughness was found to be 22.83 nm (RMS) by AFM measurement. The surface morphology of the samples after annealing at 350°C, 450°C, and 550°C was identical to the as-deposited sample as shown in Figures 3-27a, b, and c. EDX detected only Ti, Si, N and O in samples annealed at and below 550°C as shown in Figure 3-28. The presence of oxygen was due to the exposure of the samples in environment after removing the sample from the vacuum chamber. In the work by Sinke *et al* [Sinke, 1985], oxygen was found to be homogeneously distributed through 50 nm thick TiN layer upon exposure to air. This suggests that oxygen can diffuse through the grain boundaries of crystalline TiN phase.

Fig. 3-25: FESEM surface morphology of as-deposited sample. Ridges and valleys are observed.

Fig. 3-26: AFM surface morphology showing the regions of ridges and valleys of as-deposited sample.

When the annealing temperature was increased to 650°C, the reaction products were clearly revealed by FESEM. The micrograph in Figure 3-27d shows tiny white reaction particles on the Ti-Si-N surface. The larger bright particles in Figures 3-27e and f provide clear evidence of the reaction, which appears to occur preferentially on the ridges of the film. The graphs show that with increasing annealing temperature, these reaction products grow in size and start to spread to other regions.

Fig. 3-27: FESEM surface morphology of the samples after annealing for 30 minutes at (a) 350°C; (b) 450°C; (c) 550°C; (d) 650°C; (e) 750°C; (f) 850°C. Some compounds are formed on the ridges of Ti-Si-N film after annealing at 650°C.

Fig. 3-28: EDX results showing that only Ti, Si, N and O were detected in samples annealed at and below 550°C.

Figure 3-29 presents micrographs with the element mapping of a sample annealed at 850°C for 30 minutes. It clearly shows that the compounds in the ridges consisted of mainly copper and titanium. Figure 3-29(d) shows that no silicon signal was detected on the reaction particles. The mapping indicates that compounds consist

of mainly Cu and Ti. Si did not participate in the compound formation. The results, coupled with the XRD measurement (Figure 3-24) as discussed above, enable us to conclude that the reaction products are mainly Cu-Ti and Cu-N, formed preferentially in the ridges of the Ti-Si-N barrier films.

The ridges are richer in Ti and N as sputtering proceeds, indicating preferential sputtering of silicon. The Si deficiency in the ridge region is explained by mechanism of preferential sputtering, the differences in the binding energy of Ti, N, and Si must be considered. The binding energy of Ti 2p_{2/3} is 453.9 eV, N 1s is 397 eV and Si 2p is 98.8 eV. The lower binding energy of Si means that a larger portion of the energy from Ar⁺ ions (after overcoming the binding energy and dislodging the host atoms) will be converted into kinetic energy so that the atoms will be able to leave the surface faster and more completely during the argon plasma activation process. In view of that, for the same energy of ion beam, it is easier for Si atoms to be removed. Thus, in Cu diffusion study, Cu-Ti, Cu-N reaction products are detected in the ridge areas and no Cu-Si compounds are detected.

Since the annealing temperature is well below the Tammann temperature, it is reasonable to believe that diffusion of Cu occurs preferably through the grain boundaries in ridge regions. Comparing Figures 3-27d and e, the small white particles first form in the ridge areas. The large white particles which are results of the growth of small Cu particles in Figures 3-27 e and f only appear at 750°C and 850°C annealing.

Fig. 3-29: (a) SEM surface morphology of the samples after annealing at 850°C for 30 minutes. (b) Element mapping of Cu. (c) Element mapping of Ti. (d) Element mapping of Si.

Figure 3-30 plots the sheet resistance of the samples as a function of annealing temperature. For the as-deposited sample, the sheet resistance was 5.06 Ω/Sq . This value is largely maintained up to 450°C annealing. There is a slight increase in the sheet resistance to a value of 7.3 Ω/Sq when the annealing temperature increases to 550°C and 650°C. This is probably due to the formation of high resistivity TiSi_2 phase in the samples. As shown in Figure 3-24, there was an increase in the intensity of TiSi_2 phase at annealing temperatures of 550°C and 650°C. Beyond this temperature, there

was a sudden drop of the resistance when the annealing temperature was increased to 750°C and 850°C. This corresponded to the formation of Cu-Ti and Cu-N compounds at high temperatures and also the reduction of TiSi₂ phase. The reactional diffusion of copper into the Ti-Si-N film decreased the overall sheet resistance. This result suggests that a sudden drop in the resistance could be used as an indication of Cu diffusion in Ti-based barriers, including TiN and Ti-Si-N barrier films.

Fig. 3-30: Sheet resistance of the samples after annealing at various temperatures.

Considerable effort has been spent on the barrier performance of TiN films against thermal diffusion of Cu [Wang, 1990; Olowolafe, 1991; Chang, 1990; Olowolafe, 1992; Suni, 1983; Moriyama, 2002; Ikeda, 1999; Ou, 2004; Castoldi, 2004]. It was generally acceded that the failure is caused by copper diffusion through the grain boundaries of TiN to form copper compounds [Moriyama, 2002; Ikeda, 1999; Ou, 2004; Castoldi, 2004]. However, the reported failure temperatures differ among researchers, ranging from 400 to 850°C [Olowolafe, 1991; Chang, 1990; Olowolafe, 1992; Suni, 1983]. The difference in failure temperature might be due to the difference in film microstructure, film thickness, annealing time, and the failure criteria used by the researchers. In the work by Moriyama *et al* [Moriyama, 2002], for example, Cu₃Si formation detected by XRD was used as the onset time for diffusion failure of the 25 nm TiN film deposited on Si substrate. They reported no Cu₃Si

formation at and below 850°C annealing for 30 minutes. This agrees with the current observation that no Cu-Si compounds are detected for up to 850°C annealing. However the formation of Cu-Ti and Cu-N compounds was not found in their work, which could be the reason for such a high barrier failure temperature. In most other research on different types of barrier, such as W, Ta, WN, TaN, the barriers can only prevent Cu diffusion at temperatures below 600°C (refer to the summary in reference [Moriyama, 2002]).

3.2.4 Conclusions

Copper diffusion barrier studies found that higher external bias and longer nitrogen plasma treatment time will lead to the degradation of the barrier performance. This is believed to be caused by the higher density of defects due to the plasma treatment. Besides that, copper diffusion barrier studies on 15 nm thick ternary Ti-Si-N thin film, prepared by low frequency, high density inductively coupled plasma process, indicated that barrier failure did not occur when annealed at annealing at 650°C for 30 minutes. With the diffusion of copper into Ti-Si-N film at high annealing temperatures, Cu-Ti and Cu-N compounds were formed. The formation of these compounds caused a significant reduction in sheet resistance from 5.7 Ω/Sq for as-deposited film to 1.5 Ω/Sq for the film after annealing at 850°C. FESEM and EDX results showed that the compounds formed preferably on the ridge areas. No Si-Cu was found in the current study for up to 850°C annealing temperature. This implies that the addition of Si contributes to the improvement in the diffusion barrier performance. Based on the overall requirements, the 15 nm Ti-Si-N films formed by low frequency, high density inductively coupled plasma process presents an attractive route to produce effective barrier materials against copper diffusion.

3.3 Electroless Copper as a Seed Layer on ICP Ti-Si-N Barrier Films

3.3.1 Introduction

As highlighted in chapter 2, copper has been used as a material for global interconnect in ULSI circuit because of its low resistivity, high electromigration resistance, and good electrical characteristics, compared to the commonly used aluminum-based interconnects. The damascene technique is used to pattern the Cu interconnects since Cu cannot be dry-etched easily. For filling the damascene structures, electroplating technique is the preferred method. But, a Cu seed layer is needed for subsequent electroplating process. The Cu seed is usually deposited by PVD or CVD techniques. The current Cu-seed/Ta/TaN stack configuration requires keenly monitored deposition control to avoid poor sidewall coverage and large overhang surrounding the via, which causes the Cu electrofill to close off and leave void defects in the features. Copper voids in vias have been a major device yield loss issue in adapting copper for production at the 130 nm node [Peters, 2000].

Recently, electroless deposition of copper as a seeding technology, using a chemical bath has received considerable attention [Lantosov, 2000; Joseph, 2000; Pai, 1989]. Electroless deposition possesses several characteristics not shared by other techniques, such as the uniform deposition, complete surface coverage and better corrosion resistance [Vossen, 1978]. Power supplies, electrical contacts and other apparatus necessary for electroplating are not required.

There have been some studies on the electroless Cu properties [Goh, 2002; Patterson, 1997; Patterson, 1995; Shacham, 2000]. For example, Patterson *et al* [Patterson, 1997] reported electroless copper plating on binary barrier, TiN. Various properties of the as-deposited copper such as adhesion, resistivity, grain size, and topography were examined. Besides that, Hsu *et al* [Hsu, 2002] also investigated

surface coverage, surface roughness, film thickness, electrical resistivity, and gap-filling capability of electroless copper on TaN. To the knowledge of the author, there has been little work on the deposition of electroless copper seed layer on ternary barrier films, particularly, Ti-Si-N barrier films.

In this section, the author reports the effect of plasma process parameters on electrolessly deposited copper film on Ti-Si-N barrier films formed by low frequency, high density inductively coupled plasma (ICP) process. The surface coverage, surface morphology, film resistivity, uniformity, surface roughness, crystal orientation, and copper grain size are also reported.

3.3.2 Experimental

The experimental work in the formation of ICP Ti-Si-N films have been discussed in detail in section 3.1.2. TiN barrier film prepared by chemical vapor deposition was used as a reference material. Before electroless Cu plating, samples went through standard cleaning 1 (SC1) and standard cleaning 2 (SC2) processes. Catalyzation was carried out by immersing the samples into the activating solution, which contains HF, HCl and PdCl₂. After the activation, electroless copper deposition was immediately carried out at temperature between 60°C ~ 62°C. The deposition time was kept at 8 minutes for all samples. The electroless copper bath consists mainly of copper sulphate CuSO₄ (which acts as an oxidant and provides the source of cupric ions), ethylene diamine tetraacetic acid (EDTA, as a complexing agent), and formaldehyde, HCHO (reductant). The pH level was maintained at 12.8. The experimental set up is shown in Figure 3-31.

Fig. 3-31: Schematic diagram depicts electroless copper deposition process set up.

Field emission scanning electron microscope (FESEM) was used to observe the surface coverage and surface morphology of the electroless copper film. The resistivity of the as-deposited electroless copper film was measured using the ResMapTM four-point probe system. The thickness of the electrolessly plated copper film was separately measured by TEM observation of the cross-section, and depth-profile by time-of-flight secondary ion mass spectroscopy (ToF-SIMS). The difference in copper film thickness between the two measurements is within 1.5%. Atomic force microscope was employed to assess the roughness of the film. The crystallinity, texture and grain size of the deposited film were determined by x-ray diffraction (XRD) using a ShimadzuTM XRD 6000 diffractometer.

The mean grain size, d_{mean} , of electrolessly plated copper was estimated using the (111) peak broadening according to Scherrer's equation [Takahashi, 1999]:

$$d_{\text{mean}} = \frac{0.94 \times \lambda_{\text{Cu}}}{W_{\text{eff}} \times \cos 2\theta} \quad \text{-----} \quad (3.1)$$

where λ_{Cu} = wavelength of Cu $K\alpha$ = 0.1542 nm

W_{eff} = Effective full width at half maximum

2θ = Diffraction angle

The effective full width, W_{eff} , was determined from the Gaussian distribution function of the (111) peak, curve-fitted from the experimental data. Instrumental broadening was calibrated before applying equation (3.1) for the grain size calculation. Analysis based on the data obtained in the current study shows that the error in the d_{mean} is between 7 to 11% due to curve-fitting error.

3.3.3 Results and discussion

A blanket Si wafer with Ti-Si-N/ Ti_xSi_y /Si film stack was used for the Pd activation and subsequent electroless Cu plating. The required activation time on Ti-Si-N films was found to be 1 minute or less as compared to 3 minutes on TiN. This time was determined by the amount and distribution of Pd seeds that would successfully induce copper plating [Goh, 2002; Patterson, 1995; Lau, 2004]. Figures 3-32, 3-33 a and b show the surface morphology of the films before and after Pd activation respectively. Compared Figures 3-32b and 3-33b, the density of Pd for 1 minute activation on Ti-Si-N film was much higher than the one on TiN with 3 minutes activation. For the TiN surface, 1 minute activation could not produce an effective surface for electroless Cu plating (Figure 3-33b) since there were too few Pd seeds. There are two possible reasons for the difference in Pd seed distribution. One possibility is the Pd/substrate interfacial energy between the barrier films. The activation energy for Pd nucleation is lower on the Ti-Si-N surface that leads to higher nucleation rate. Another contributing factor could be the damage on Ti-Si-N surface in the form of dangling bonds due to plasma implantation; free electrons are available to speed up the reduction of Pd from Pd^{++} . It is interesting to observe such a drastic change in Pd activation behavior on the two barrier films.

Fig. 3-32: (a) Ti-Si-N surface morphology before Pd activation. (b) Distribution of palladium seeds on Ti-Si-N film after 1 minute activation. Nitrogen plasma treatment time is 60 minutes.

Fig. 3-33: (a) TiN surface morphology before Pd activation. (b) Distribution of palladium seeds on TiN after 1 minute activation; (c) after 3 minutes activation.

Figure 3-34a shows that an average thickness of ~ 85 nm electroless copper was deposited on Ti-Si-N film with 100% surface coverage. These samples were subjected to 1 minute Pd activation. Good surface coverage is due to coalescence of the copper islands on the densely distributed Pd seeds on Ti-Si-N surface [Shacham, 2000]. Figure 3-34b shows an average thickness of ~ 85 nm electroless copper deposited on TiN film with good surface coverage, the sample was subjected to 3 minutes Pd activation for the reason mentioned before. Comparing the two cases, shorter Pd activation time is required on Ti-Si-N film in order to achieve a good surface coverage of electroless copper.

Fig. 3-34: Surface coverage of electrolessly plated copper on (a) Ti-Si-N film after 8 minutes deposition; (b) TiN film after 8 minutes deposition.

For a fixed nitrogen plasma treatment time, sheet resistance of electroless copper film was measured as a function of argon gas flow rate. Sheet resistance of the copper layer was found to be less than 1.2 ohms/sq in all cases. Besides that, changes in argon gas flow rate did not show significant effect on resistivity of electroless copper layer. A mean value of 9.6 $\mu\Omega\cdot\text{cm}$ was obtained in those samples (I, K, M) as shown in Table 3-9. These samples have undergone different argon gas flow rate at a fixed 30 minutes nitrogen plasma treatment. In addition, this result is further

confirmed by comparing samples J, L and N, which have undergone different argon gas flow rate at fixed 60 minutes nitrogen plasma treatment. The mean resistivity value of 7.6 $\mu\Omega\cdot\text{cm}$ was obtained. This shows that argon gas flow rate does not have significant effect on the resistivity of electroless copper on Ti-Si-N films. The reason for this could be related to what has been discussed in section B, where it was demonstrated that the change in argon gas flow rate does not change the surface condition of the Ti-Si-N films. Therefore the nucleation and growth of electroless copper on these Ti-Si-N films are likely to be similar.

Table 3-9: Mean grain size and surface roughness of electroless copper on Ti-Si-N.

Sample	Mean Grain Size (nm)	Average surface roughness (nm)	Resistivity ($\mu\Omega\cdot\text{cm}$)	Error associate with resistivity measurement
I	23.2	30.4	9.5	± 0.67
K	24.6	25.9	9.3	± 0.77
M	23.7	28.9	9.9	± 0.40
J	28.0	36.2	7.1	± 0.45
L	32.7	32.2	7.8	± 0.67
N	34.1	23.9	7.7	± 0.83

However, nitrogen plasma treatment time was found to affect the resistivity of electroless copper seed layer. The current work shows that there is 20% reduction in copper film resistivity as nitrogen plasma treatment time increases from 30 minutes to 60 minutes. The resistivity change could be explained by the Cu grain size difference. Table 3-9 shows that, regardless of the argon gas flow rate, Cu grain size in samples J, L, and N (60 minute N_2 treatment time), was larger than the one in samples I, K, and M (30 minute N_2 treatment time). Comparing Figure 3-32b, which shows the palladium seed distribution on sample N, and Figure 3-35b, which displays the one

from sample M, palladium seeds are smaller and more densely populated. It is clear that the palladium nuclei in sample N are larger and more sparsely populated.

Fig. 3-35: (a) Ti-Si-N surface morphology before Pd activation. (b) Distribution of palladium seeds on Ti-Si-N which has subjected to 30 minutes nitrogen plasma treatment.

The sparsely distributed palladium seeds will lead to larger copper grain size, and thus lower resistivity. Further discussion on the relationship between the grain size and the film resistivity will be provided below. Here, we focus on why a longer plasma treatment time leads to larger and less densely distributed Pd. First, it is understood that longer treatment time will lead to higher surface energy due to the damage caused by plasma bombardment. Pd nucleation rate ought to be higher on the surface of higher energy. To explain the observation made in our experiment, that in samples with longer treatment time the Pd seed density is lower, requires a full record of Pd nucleation and growth. Since the current work only compares the Pd distribution at a fixed activation time, a conclusive explanation may not be attainable. We speculate that due to the higher surface energy, the required incubation time for nucleation is shorter. Therefore although the initial nucleation density is higher, there is enough time for the Pd seeds to ripen after nucleation.

Copper grain orientation was characterized by XRD patterns shown in Figure 3-36. This work finds that there is a preferred (111) crystal orientation in all the prepared samples as for randomly oriented powdered Cu samples, $I_{(111)}/I_{(200)} = 2.17$. This factor increases to about 2.7 in all the samples obtained in this work. This implies that copper grains orientation is independent of the barrier surface condition as a result of changing the argon gas flow rate and nitrogen plasma treatment time.

Fig. 3-36: XRD measurement for different argon gas flow rate. (a) Nitrogen plasma treatment time is 30 minutes; (b) Nitrogen plasma treatment time is 60 minutes.

The texture of electroless copper is important as the Cu film is used as the seed layer for Cu electroplating in ULSI. The plated Cu film will adopt the texture of the seed layer (epitaxial effect) and the (111) texture is preferred for better electromigration performance [Ryu, 1999]. In addition, large Cu grains in the seed layer will produce large Cu grains during electroplating process, and thus a near bamboo structure, which is known to enhance the electromigration resistance and increase the lifetime of interconnects, becomes more possible.

In addition, Cu (111) planes have the lowest surface energy among all Cu planes. The relationship between the mechanical properties and the crystal structure of

copper film is influenced by the texture. For face-centre-cubic copper, the stronger the preferred orientation with (111) planes, the greater the tensile strength. The strain up to the elastic fracture will increase when (111) texture becomes stronger.

When electroless copper deposits on the Ti-Si-N film which has undergone different argon gas flow rates and 30 minutes nitrogen plasma treatment (samples I, K and M), the mean grain size of electroless copper was about 23 nm as shown in Table 3-9 (page 145). There is an increase in copper grain size when Ti-Si-N film has undergone 60 minutes nitrogen plasma treatment (samples J, L and N). The mean copper grain size increases from 28 nm to 34 nm as argon gas flow rate changes from 10 sccm to 30 sccm. This shows that larger copper grain size can be obtained by depositing copper seed layer onto Ti-Si-N barrier film which has been subjected to higher argon gas flow rate and longer nitrogen plasma treatment. As discussed previously, these conditions may lead to sparsely distributed Pd seeds on Ti-Si-N film. As a result, larger copper grains can be produced. As reported by Harper *et al.*, [Harper, 1999] the larger the copper grain size is, the lower the resistivity of copper thin film. This is believed to be related to grain boundary scattering effect. Our experiment observed the similar trend: the copper film that was deposited on Ti-Si-N subjected to 60 minutes nitrogen plasma treatment has a larger grain size of 34 nm and corresponding resistivity value $\sim 7.57 \mu\Omega\cdot\text{cm}$, while the one with 30 minutes nitrogen treatment has smaller copper grain size of 23 nm and resistivity $\sim 9.6 \mu\Omega\cdot\text{cm}$.

The root mean square (RMS) surface roughness of electroless copper deposited on Ti-Si-N film was measured by atomic force microscopy (AFM). Figure 3-37 shows one of the surface profiles of plated copper film. Prior to activation and electroless copper deposition, surface roughness of Ti-Si-N was within the range of 18 to 23 nm. After the deposition, surface roughness of plated Cu seed layer was within the range of

23 - 36 nm. The slight increase in surface roughness is largely caused by the Pd islands on Ti-Si-N surface which lead to rapid localized electroless copper growth on these nuclei at the initial stage of copper plating, leading to the increase in roughness after plating.

Fig. 3-37: 3-dimentional stereographical AFM images of electroless copper on Ti-Si-N layer.

3.3.4 Conclusions

The properties of electroless copper seed layers deposited on Ti-Si-N barrier films have been studied. With Ti-Si-N as a barrier layer, the palladium activation time is greatly reduced compared to TiN. Good surface coverage of the electroless copper seed layer on Ti-Si-N film is obtainable. In addition, larger copper grain size can be obtained by depositing copper seed layer onto Ti-Si-N barrier film which has been subjected to higher argon gas flow rate and longer nitrogen plasma treatment, as these process conditions may lead to sparsely distributed Pd seeds on Ti-Si-N film, and as a result, larger copper grains can be produced. Furthermore, larger copper grains oriented in (111) plane can be achieved when Ti-Si-N layer is subjected to longer nitrogen plasma treatment. These results indicate that electroless copper can be successfully used as a seed layer on Ti-Si-N barrier film.

Chapter 4: Results and Discussion

Low Temperature Physical-Chemical Vapor Deposition of Ti-Si-N-O Barrier Films

4.1 The Formation of Ti-Si-N-O Barrier Films

4.1.1 Introduction

Reports on ternary film properties differ a lot, depending on the deposition techniques, process conditions, and precursors used [Marcadal, 2002; Reid, 1994; Prindle; 2002; Eric, 2000; Shalish, 1999]. For example, in the work of Eric *et al* [Eric, 2000], a low temperature inorganic thermal CVD process was developed for the growth of Ti-Si-N, which involves the thermal reaction of tetraiodotitanium (TiI_4), tetraiodosilane (SiI_4), and ammonia (NH_3). The film composition was reported as $\text{Ti}_{33}\text{Si}_{15}\text{N}_{51}$, with resistivity of $800 \mu\Omega\cdot\text{cm}$. The authors claimed that the film consisted of nanocrystalline TiN phase embedded in an amorphous SiN matrix, but no evidence was shown. The surface morphology and surface roughness were also unknown. In another work, Reid *et al* [Reid, 1994] formed $680 \mu\Omega\cdot\text{cm}$ $\text{Ti}_{34}\text{Si}_{23}\text{N}_{43}$ film by reactively sputtering process using prepared Ti_5Si_3 target. The structure of $\text{Ti}_{34}\text{Si}_{23}\text{N}_{43}$ appears to be cermet-like blend of nanophase TiN with grain size around 2 nm mixed with amorphous Si_3N_4 . However, no information on the surface morphology and surface roughness of the film which are important for copper plating process in back-end-of line device fabrication was provided.

Besides that, many studies on ternary films deposited by PVD have been reported [Sun, 1997; Vaz, 1998; Diserens, 1999; Vaz, 2000; Vaz, 2001; Ribeiro, 2004]. Deposition temperatures of these existing works range from 150°C to 600°C . Although most of them used r.f.- or d.c.-reactive sputtering in an Ar/N_2 gas mixture, the results were not always consistent with each other.

In this chapter, we suggest a new process by physical-chemical vapor deposition for the formation of Ti-Si-N-O barrier films. In this process, the reacting gases can be broken down to create plasma using a RF field. This lowers the chemical reaction activation barrier, which results in a lower deposition temperature. Therefore, by using P-CVD process, silane gas can be decomposed at temperature as low as 40°C, which is not achievable in the conventional CVD process (to decompose silane gas through CVD, the required temperature is between 800°C – 1050°C for atmospheric pressure CVD (APCVD); 500°C for low pressure CVD (LPCVD) [Badih, 1997; Murarka, 1989]).

Composition, microstructure, resistivity, surface roughness, surface morphology, and chemical bonding states have been analyzed for the newly formed films. Contrary to all the reports known to us so far [Reid, 1994; Marcadal, 2002; Eric, 2000; Prindle, 2002; Joseph, 2002; Dauksher, 2000], which claim that the microstructure consists of nanocrystalline TiN embedded in amorphous Si-N. The current work finds that the nanostructures are Ti-N, Si-N and Ti-Si, and the amorphous matrix is contributed by Ti-O, Si-O and Si-N-O. The barrier films show excellent stability against copper diffusion under bias temperature stress which makes them attractive candidates as future generation barrier material.

4.1.2 Experimental

A 630 nm plasma enhanced chemical vapor deposition (PECVD) SiO₂ layer was first deposited on a p-type silicon substrate using tetraethyl orthosilicate, (Si(OC₂H₅)₄) and oxygen as precursors. The deposition temperature was between 350 – 450°C and the pressure was 4-6 Torr. This was followed by the deposition of Ti-Si-N-O films with different compositions by r.f. reactive magnetron sputtering of Ti

target in a chamber with a base pressure of 3.75×10^{-5} Torr. A processing gas such as silane as a precursor, and other gases like nitrogen and argon were introduced. The pressure was maintained at 7.5×10^{-3} Torr during the deposition process. No substrate heating and bias were provided. The substrate temperature was measured to be between $35 - 40^\circ\text{C}$ when 300 W r.f. power was applied to the titanium target. Nitrogen and argon gas flow rates were maintained at 30 sccm and 20 sccm respectively while the silane gas flow rate was changed from 20 sccm to 40 sccm to obtain different compositions of Ti-Si-N-O films.

Stoichiometric composition was obtained by Rutherford backscattering spectrometry (RBS) using a 2.0 MeV $^4\text{He}^+$ beam with the 4.0 MV Dynamitron accelerator at the Ion Beam Laboratory, Department of Physics, University at Albany. Phase composition was first investigated through X-ray diffraction (XRD) using a Shimadzu™ XRD 6000 diffractometer. The chemical states of titanium, silicon and nitrogen were then analyzed by X-ray photoelectron spectroscopy (XPS) using 1486.71 eV Al K α irradiation and the X-rays and the peak positions were calibrated with respect to C 1s peak at 284.44 eV. High resolution transmission electron microscopy (HRTEM) was used to characterize the nanostructure of the films. Electrical resistivity of Ti-Si-N-O films was measured using 4-point resistivity probe. Field emission scanning electron microscope (FESEM) was used to observe the surface morphology of the Ti-Si-N-O films, and finally the roughness of the film was assessed by atomic force microscope (AFM).

4.1.3 Results and discussion

(a) Composition and chemical bonding of Ti-Si-N-O films

Figure 4-1 shows the backscattering spectra of Ti-Si-N-O/SiO₂/Si samples at different silane gas flow rates, indicating the presence of nitrogen, oxygen, silicon and titanium. Silicon content between 12 to 15 % atomic was obtained by varying silane gas (SiH₄) flow rate from 20 sccm to 40 sccm while nitrogen and argon gas flow rate were maintained at 30 sccm and 20 sccm respectively. Si/Ti atomic ratio as a function of silane gas flow rate is reported in Table 4-1. It is observed that increased silicon levels can be incorporated in the films when silane gas flow rate increases. The film compositions determined by RBS are Ti₂₄Si₁₂N₃₅O₂₉, Ti₂₀Si₁₃N₃₅O₃₂ and Ti₁₆Si₁₅N₃₂O₃₇ and will be labeled as Si-12, Si-13 and Si-15 respectively. The presence of large amount of oxygen will be discussed later in this section. The barrier performance of these three different compositions against the metal ions diffusion will be evaluated through BTS testing in the following section.

Fig. 4-1: 2.0 MeV $^4\text{He}^+$ backscattering spectrum of the Ti-Si-N-O/ SiO_2 /Si sample. Ti-Si-N-O films were deposited at silane gas flow rate of (a) 20 sccm; (b) 30 sccm; (c) 40 sccm, while nitrogen gas flow rate and argon gas flow rate were maintained at 30 sccm and 20 sccm respectively.

Table 4-1: The film composition, thickness and Si/Ti atomic ratio as a function of silane gas flow rate.

Silane gas flow rate (sccm)	Film composition (at %)	Film label	Si/Ti atomic ratio
20	$\text{Ti}_{24}\text{Si}_{12}\text{N}_{35}\text{O}_{29}$	Si-12	0.48
30	$\text{Ti}_{20}\text{Si}_{13}\text{N}_{35}\text{O}_{32}$	Si-13	0.65
40	$\text{Ti}_{16}\text{Si}_{15}\text{N}_{32}\text{O}_{37}$	Si-15	0.91

In addition, through XPS analysis, Ti-N, Si-N, Ti-Si, Ti-O, Si-O, Si-N-O bonds were found when Ti_{2p} , Si_{2p} , N_{1s} and O_{1s} peaks were deconvoluted. The presence of crystal phases, Ti-N, Si-N and Ti-Si were further confirmed by XRD and would be discussed later. Here, we discuss the chemical bonding states of oxygen. First, Figure 4-2 is a deconvoluted O_{1s} peak, and it shows that oxygen bonds with titanium, silicon and nitrogen forming titanium oxide, silicon oxide and silicon oxynitride. Since these phases were not detected by XRD, they are likely to be in the amorphous state. In general, these results confirmed that the Ti-Si-N-O films formed by P-CVD process contain substantial amount of oxygen. Therefore, these films are subsequently addressed as Ti-Si-N-O.

Fig. 4-2: XPS analysis showing that oxygen bonded to titanium, silicon and nitrogen forming titanium oxide, silicon oxide and silicon oxynitride when O_{1s} peak is deconvoluted.

The presence of oxygen in prepared barrier films could be due to the high reactivity of titanium and silicon with residual oxygen and water in the vacuum chamber. The incorporation of oxygen in TiN or Ti-Si-N film has been reported by Olowolafe *et al* [Olowolafe, 1991], Cheung *et al* [Cheung, 1980], Lemperiere *et al* [Lemperiere, 1984], Zhang *et al* [Zhang, 2004] and Shtansky *et al* [Shtansky, 2004]. In

the work of Shtansky *et al* [Shtansky, 2004], 1 – 5 at% of O was found in Ti-Si-N film with a bias of - 250 V to 0 V during the deposition process. In the work by Olowolafe *et al* [Olowolafe, 1991], 25 at% of O was obtained in the deposition of TiN film in a base vacuum of 2×10^{-7} Torr without substrate bias. In the current work, no bias was applied to the substrate in the preparation of Ti-Si-N-O films with vacuum level of 3.75×10^{-5} Torr. We believe that bias will create a concentrated flux of sputtered species on to the substrate; such a high concentration prevents oxygen from getting close to the substrate surface due to pressure difference. Without the bias, the oxygen in the chamber has good access for the film to react with Ti and Si, and resulted Ti-O, Si-O and Si-N-O bonds.

(b) Phase composition of Ti-Si-N-O films

Figure 4-3 shows the XRD measurement of Ti-Si-N-O films obtained at different silane gas flow rates while argon gas flow rate and nitrogen gas flow rate were maintained at 20 sccm and 30 sccm respectively. Crystalline TiN, Si₃N₄ and Ti₅Si₄ phases were detected in all the samples. Si₃N₄ (411) to TiN (220) intensity ratio increased from 1.75 to 3.10 as silane gas flow rate changes from 20 sccm to 40 sccm. We believe that the rising ratio indicates an increase in the volume fraction of Si₃N₄ phase in the film. The reason is that as silane gas flow rate increases, the amount of silicon plasma also increases. In addition, the enthalpy of formation (ΔH_f°) of Si₃N₄ is - 744.79 kJ/mol is lower than that of TiN (-337.45 kJ/mol) at 300 K [Barin, 1993]. Therefore, the formation of Si₃N₄ is thermodynamically favorable compared to TiN.

However, XRD measurement did not detect any Ti-O, Si-O and Si-N-O phases. This implies that the existence of Ti-O, Si-O and Si-N-O phases as proved in XPS analysis, are amorphous. Based on the above analysis, Ti-Si-N-O barrier films consist

of a mixed crystalline and amorphous structure. Further investigation of Ti-Si-N-O microstructure was carried out using high resolution transmission electron microscopy as discussed in the next section.

Fig. 4-3: XRD measurement of Ti-Si-N-O films at different silane gas flow rates. Crystalline Ti-N, Si-N and Ti-Si phases are detected.

(c) Microstructure of Ti-Si-N-O films

Figures 4-4, 4-5 and 4-6 show the plan view high resolution TEM micrographs of a representative Ti-Si-N-O film which has a composition of $\text{Ti}_{24}\text{Si}_{12}\text{N}_{35}\text{O}_{29}$. From Figure 4-4, it is observed that crystals of 2 – 15 nm in size were formed. Further investigation was carried out to observe the microstructure of Ti-Si-N-O films. As shown in Figure 4-5, two nanocrystals were embedded in the amorphous matrix. Combining XPS, XRD results, and lattice spacing measurement from HRTEM (Figure 4-6), these nanocrystals are identified as Ti-N, Si-N and Ti-Si phases. The remaining Ti-O, Si-O and Si-N-O compounds are in amorphous state.

Fig. 4-4: High resolution transmission electron microscopy reveals that the film consists of nanocrystals embedded in amorphous matrix.

In the work by Marcadal *et al* [Marcadal, 2002], nanocrystallites of TiN was reported to be embedded in amorphous Si_xN_y matrix. In such a configuration, fast diffusion channels were said to be absent since there was no percolation via grain boundaries in this microstructure. Reid *et al* [Reid, 1994] also reported mixed microstructure of Ti-Si-N films, where random arrangement of nanophase of TiN eliminates straight grain boundary paths associated with columnar TiN films. In

addition, the intergranular silicon components may be viewed as severely “stuffing” the grain boundaries of TiN, and thus improved the barrier performance. Similar to the work by Marcadal *et al* [Marcadal, 2002], the current study also produced nanocrystals embedded in amorphous matrix. But the amorphous phases were not by silicon nitride any more. Si₃N₄ was in crystalline form while the Si and Ti oxides were in amorphous form. Apparently the formation of the oxides has significantly reduced the vitrification temperature of silicon nitride.

Fig. 4-5: High resolution transmission electron microscopy shows the amorphous region in Ti-Si-N-O film.

Fig. 4-6: High resolution transmission electron microscopy shows the presence of Ti-N, Si-N and Ti-Si crystalline phases in Ti-Si-N-O films.

(d) Thickness and resistivity of Ti-Si-N-O films

The average thickness of Ti-Si-N-O film was measured using a surface profilometer. The respective thickness of Ti-Si-N-O film was 215 nm, 262 nm and 300 nm when the silane gas flow rate was 20 sccm, 30 sccm and 40 sccm. The measured resistivity for S-12, S-13 and S-15 were $3.63 \times 10^3 \mu\Omega\cdot\text{cm}$, $4.24 \times 10^4 \mu\Omega\cdot\text{cm}$ and $6.45 \times 10^6 \mu\Omega\cdot\text{cm}$ respectively. Although the films investigated are too thick and resistive to serve as barrier layers in current devices, in this study we focus on the microstructure and the properties of Ti-Si-N-O layers and the resulting implication to barrier properties. According to international technology roadmap for semiconductor 2005 [ITRS, 2005], when the technology node reduces from 90 nm to 65 nm, the required barrier thickness will reduce from 8 nm to 4.8 nm. This ultra thin barrier at the bottom of Cu via can be removed by in-situ re-sputtering process. In other word, via bottom can directly in contact with underneath metal trench without barrier layer. Thus, electrical resistivity of barrier will not be a major issue for future interconnects.

Table 4-2 summarizes the composition, thickness and resistivity of these Ti-Si-N-O films. The results show that the resistivity increased with increasing Si content. A similar result was obtained by Smith *et al* [Smith, 1997]; the film resistivity varied from $400 \mu\Omega\cdot\text{cm}$ for TiN to nearly $1 \times 10^6 \mu\Omega\cdot\text{cm}$ for Ti-Si-N with 25 at. % Si. The variation in film resistivity with Si content may correlate to the crystalline phases in the films. As discussed in section (b), Si_3N_4 (411) to TiN (220) intensity ratio increased from 1.75 to 3.10 as silane gas flow rate changed from 20 sccm to 40 sccm. This means that more Si_3N_4 crystals are present in S-15 compared to S-12. As a result, the film resistivity increases due to the higher volume fraction of this high-resistivity phase.

Table 4-2: Resistivity of Ti-Si-N-O films at different silane gas flow rates.

Sample label	Film Thickness (nm)	Resistivity ($\mu\Omega\cdot\text{cm}$)
S-12	215	3.63E+03
S-13	262	4.24E+04
S-15	300	6.45E+06

(e) Surface morphology and surface roughness of Ti-Si-N-O films

Figure 4-7 shows the surface morphology of Ti-Si-N-O films obtained at different silane gas flow rates. The nodule size was less than 100 nm and surface was fully covered. Change in silane gas flow rate does not have significant effect on the surface roughness, which ranges from 2.2 nm to 3.3 nm by AFM measurement. The surface roughness of these Ti-Si-N-O films as shown in Figure 4-8 is much smoother compared to inductively coupled plasma Ti-Si-N barrier films as discussed in Chapter 3 which has surface roughness between 18 to 23 nm.

Surface coverage and film uniformity are very critical for subsequent copper electroplating process. If the surface coverage and uniformity are poor, electric field will not be evenly distributed and plating voids may form in the recessed areas [Goh, 2002]. In addition, metal can diffuse easily through the uncover region to the dielectric layer. As a result, the device may fail easily. The current work provides an attractive technique for depositing smooth and uniform barrier films.

P-CVD Ti-Si-N-O

Fig. 4-7: FESEM surface morphology of Ti-Si-N-O films at (a) 20 sccm; (b) 30 sccm; (c) 40 sccm silane gas flow rate.

Fig. 4-8: AFM surface morphology of Ti-Si-N-O films at different silane gas flow rates of (a) 20 sccm; (b) 30 sccm; (c) 40 sccm.

4.1.4 Conclusions

A physical-chemical vapor deposition process for Ti-Si-N-O films was successfully developed at temperatures between 35 to 40°C to produce smooth barrier films with surface roughness of 2.2 nm. The amount of Si in the film can be tailored by controlling the silane gas flow rate. The film resistivity is a strong function of Si content in the films. Ti-N, Si-N and Ti-Si nanocrystals are formed and embedded in Ti-O, Si-O and Si-N-O amorphous matrix. As will be shown in the following section, a very good electrical stability of Ti-Si-N-O film against copper ion diffusion is achieved with this type of mixed nanostructure. These characteristics make Ti-Si-N-O films an attractive candidate for future ULSI diffusion barriers.

4.2 Bias-Temperature Stability of Ti-Si-N-O Films

4.2.1 Introduction

In an actual interconnect scheme, barrier is in contact with metal, such as copper. However, copper in comparison to aluminum has a higher tendency to drift into interlevel dielectric as well as into the silicon substrate in the presence of an electrical field even at low temperatures [McBrayer, 1986; Cho, 1993; Chiang, 1994; Loke, 1996], resulting in a degradation of the electrical properties. Therefore, interaction between the metal and the barrier should be minimized for long-term stability and reliability of the chip.

When barrier film is in contact with metal and subjected to typical device operation temperatures, i.e., in the range of 100°C to 200°C, ionic penetration issue becomes a major concern. Interdiffusion or interfacial reaction, if any, should be confined and self-limiting. This implies that the metal-barrier interface stability has to be studied, both in terms of interfacial reaction and metal diffusion under electrical

stress into barrier materials. Technologically, characterization of Cu ion penetration into barrier films has been actively researched recently [Senkevich, 2004; Chen, 2004; Kizil, 2004; Mallikarjunan, 2002; Bartha, 2002; Lanckmans, 2002; Mallikarjunan, 2001; Loke, 1999; Smith, 1996]. For example, Lanckmans *et al* [Lanckmans, 2002] investigated the Cu ion drift diffusion in plasma-deposited amorphous SiC:H. The Cu ion drift rate in the film was retarded with increasing k -value for the a-SiC:H, which was attributed to a reducing hydrogen content and a densification of the film. Besides that, Chen *et al* [Chen, 2004] conducted bias temperature stressed on amorphous SiCN to investigate the barrier ability against copper penetration. This film could sustain the stress of electric field up to 4 MV/cm at 150°C for 1000 seconds. Smith *et al* [Smith, 1996] reported BTS results at 50 V and 200°C on 10 nm thick MOCVD TiSi_xN_y samples. They found that the MTTF of an MOCVD $\text{Ti}_{23}\text{Si}_{14}\text{N}_{45}\text{O}_3\text{C}_3\text{H}_{12}$ sample deposited at 400°C was approximately 10–100 times better than that of PVD TiN. In general, the stability result depends on the materials, bias, testing temperature and duration.

Studies on ternary barrier film with a mixed structure, which is nanostructure embedded in amorphous matrix [Smith, 1997; Marcadal, 2002; Prindl, 2002; Nose, 2003], have been very few and would be attractive. In this section, we evaluate the barrier properties of Ti-Si-N-O films against the metal ions diffusion using bias temperature stressing (BTS) technique. Such study will clarify the driving forces behind metal penetration, and will guide the choice of barrier layers.

4.2.2 Experimental

Cu-gate, metal-insulator-semiconductor (MIS) capacitors, as illustrated in Figure 4-9, was used to study the electrical characteristics of Ti-Si-N-O films used as

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barrier material. 630 nm plasma enhanced chemical vapor deposition (PECVD) SiO₂ was first deposited on a p-type silicon substrate using tetraethyl orthosilicate (Si(OC₂H₅)₄) and oxygen were used as precursors. The deposition temperature was between 350 – 450°C, the pressure was 4-6 torr and the deposition rate was 600-650 nm/min. This was followed by the deposition of Ti-Si-N-O films as described in section 4.1.2.

Fig. 4-9: Experimental capacitor structure to investigate the electrical stability of Ti-Si-N-O (a) with parylene-N in between Cu gate and Ti-Si-N-O film as a control sample, (b) without parylene-N in between Cu gate and Ti-Si-N-O film as a testing sample.

To complete the MIS structures, copper dots at thickness of 200 nm were deposited by electron-beam-evaporation through a shadow mask containing circular holes of diameter ranging from 0.5 mm to 1.5 mm. In the electrical testing, a 1 mm circular dot was selected. The backside of the silicon substrate was puddle-etched in buffered oxide etch (BOE) to remove residual oxide, and lined with a ~300 nm Al layer to obtain ohmic contact with the grounded chuck. Figure 4-9a shows the MIS structures with 50 nm thick parylene-N in between Cu gate and Ti-Si-N-O films. This MIS structure is used as a control sample. Another type of MIS structure is copper electrode on Ti-Si-N-O film without parylene-N layer, as shown in Figure 4-9b. The

stacks were annealed at 250°C in Ar-3% H_2 in a custom built vacuum chamber for 30 minutes before electrical testing.

BTS C–V measurements were made on a HP 4280A 1 MHz capacitance meter/C–V Plotter. A small ac signal of 10 mV rms was superposed on the applied dc bias. The capacitors were vacuum held on an MSI Electronics light shield/hot chuck and were put under nitrogen purge throughout the experiment. BTS experiments were performed at temperatures ranging from 150 – 250°C, bias of 0.5 MV/cm and 1 MV/cm, and biasing time of 5 – 90 minutes. The samples were biased at high temperatures. Then water cooled rapidly down to room temperature (with bias on) at periodic intervals for C–V measurements.

4.2.3 Results and discussion

(I) Cu/Ti-Si-N-O/PECVD SiO_2 /Si Capacitors

(a) *BTS C-V shifts for various barrier films*

Figures 4-10a and b show the C–V plots of the MIS capacitor (Cu/Si-12/PECVD SiO_2 /Si) that were preannealed at 250°C in Ar-3% H_2 for 30 minutes and bias-temperature stressed at 150°C and 0.5 MV/cm and 1 MV/cm respectively for 5, 15, 30, 60, and 90 minutes. There was no flatband voltage shift to the left even after 90 minutes of BTS. In order to further investigate the electrical stability of Si-12, the sample was bias-temperature stressed at higher temperature: 200°C and 0.5 MV/cm. It was found that no flatband voltage shift was apparent, indicating a very stable copper/Ti-Si-N-O interface and no barrier instability as shown in Figure 4-10c. When the capacitor was stressed at 200°C and 1 MV/cm for 5 minutes, a small flatband voltage shift (2.25 V) to the left was observed (Figure 4-10d). There was a total 6.25 V flatband voltage shift to the left after 90 minutes of BTS compared to as-annealed

sample. When the BTS condition was changed to 250°C and 0.5 MV/cm (Figure 4-10e), 250°C and 1 MV/cm (Figure 4-10f), a total of 4.00 V and 25.75 V flatband voltage shifts to the left were observed respectively. Figure 4-11 shows the total flatband voltage shift as a function of different Ti-Si-N-O compositions at different BTS conditions. It clearly indicates that Si-12 shows very good electrical stability and is able to prevent copper ions drift into subsequent dielectric layers even at BTS condition of 200°C and 0.5 MV/cm.

Fig. 4-10: C – V plots of the MIS capacitor (Cu/Si-12/PECVD SiO₂/Si) that thermally annealed at 250°C in Ar-3%H₂ for 30 minutes and bias-temperature stressed at (a) 150°C and 0.5 MV/cm; (b) 150°C and 1 MV/cm; (c) 200°C and 0.5 MV/cm; (d) 200°C and 1 MV/cm; (e) 250°C and 0.5 MV/cm; (f) 250°C and 1 MV/cm.

Fig. 4-11: Total flatband voltage shift as a function of different compositions of Ti-Si-N-O capacitors at different BTS conditions.

No flatband voltage shift were observed when bias temperature stressed at 150°C and 0.5 MV/cm as shown in Figure 4-12a for Cu/Si-13/PECVD SiO₂/Si capacitor (Si/Ti = 0.65). However, flatband voltage shifts 2 V and 1.5 V to the left at BTS conditions of 150°C and 1 MV/cm, 200°C and 0.5 MV/cm respectively. Figure 4-12b shows the C–V plots of capacitor Cu/Si-13/PECVD SiO₂/Si that bias-temperature stressed at 150°C and 1 MV/cm. There was a total 2 V flatband voltage shift to the left after 90 minutes of BTS. Compared to Si-12 (Si/Ti = 0.48) film, Si-13 shows less electrical stability against Cu ions penetration. As shown in Figure 4-11, a larger flatband voltage shifts to the left when the capacitor was bias- temperature stressed at 200°C and 1 MV/cm, 250°C and 0.5 MV/cm, 250°C and 1 MV/cm.

Fig. 4-12: C – V plots of the MIS capacitor (Cu/Si-13/PECVD SiO₂/Si) that thermally annealed at 250°C in Ar-3%H₂ for 30 minutes and bias-temperature stressed at (a) 150°C and 0.5 MV/cm; (b) 150°C and 1 MV/cm; (c) 200°C and 0.5 MV/cm; (d) 200°C and 1 MV/cm; (e) 250°C and 0.5 MV/cm; (f) 250°C and 1 MV/cm.

The third type of barrier material is Si-15 with the highest Si/Ti ratio equal to 0.91. Compared to the previous two barrier materials, it showed the least electrical stability against Cu ions penetration. A small flatband voltage shift (0.75 V) to the left occurred when the sample was bias-temperature stressed at 150°C and 0.5 MV/cm for

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90 minutes as shown in Figure 4-13a. When the BTS conditions were 150°C and 1 MV/cm, 200°C and 0.5 MV/cm, 1.25 V and 3.25 V flatband voltage shifts to the left were obtained respectively as shown in Figures 4-13b and c. Furthermore, as shown in Figures 4-13e and f, significant flatband voltage shifts to the left were observed for more severe BTS conditions of 250°C, 0.5 MV/cm and 250°C, 1 MV/cm.

Fig. 4-13: C – V plots of the MIS capacitor (Cu/Si-15/PECVD SiO₂/Si) that thermally annealed at 250°C in Ar-3%H₂ for 30 minutes and bias-temperature stressed at (a) 150°C and 0.5 MV/cm; (b) 150°C and 1 MV/cm; (c) 200°C and 0.5 MV/cm (d) 200°C and 1 MV/cm; (e) 250°C and 0.5 MV/cm (f) 250°C and 1 MV/cm.

(b) Calculation of total charge injected

Charge injected (ΔQ_m) was calculated from flatband voltage shift (ΔV_{FB}) using the relation [Schroder, 1998]

$$\Delta V_{FB} = -\gamma \frac{\Delta Q_m}{C_i} \quad [1]$$

Where C_i is the accumulation capacitance and γ (as defined below) describes the charge distribution in the dielectric

$$\gamma = \frac{\int_0^t \rho(x) * x dx}{t \int_0^t \rho(x) dx} \quad [2]$$

Here $\rho(x)$ is the charge density per unit volume, x is measured from the metal gate interface, and t is the total thickness of the dielectric. It is assumed that “ γ ” is 1 in the calculation and ions are pile up at the silicon interface.

As shown in Figure 4-14, no charges were detected when the Cu/Si-12/PECVD SiO₂/Si MIS capacitors were bias-temperature stressed at 150°C and 0.5 MV/cm, 150°C and 1 MV/cm, 200°C and 0.5 MV/cm. These results corroborated well with our BTS results as discussed previously as there was no flatband voltage shift at these BTS conditions. The highest amount of charges was detected when the capacitor was bias-temperature stressed at 250°C and 1 MV/cm, and this BTS condition caused the largest flatband voltage shift in all the samples. This shift might be due to the penetration of Cu ions and/or Ti ions into PECVD SiO₂. (In this calculation, it was assumed that singly ionized mobile metal ions drifted into the dielectric both because of the ease of ionization and instantaneous movement under bias, and because the solid solubilities of higher ionized states of most metals were much lower than that of the singly ionized state. [McBrayer, 1986] However, in the present work, we are more interested in

finding out the reasons to explain the small amount of flatband voltage shift (total less than 4 V) at BTS conditions of 150°C and 0.5 MV/cm, 150°C and 1 MV/cm, 200°C and 0.5 MV/cm, in Cu/Si-13/PECVD SiO₂/Si capacitor (Si/Ti = 0.65) and Cu/Si-15/PECVD SiO₂/Si (Si/Ti = 0.91) capacitors.

Fig. 4-14: The total number of charges for Cu/Si-12/PECVD SiO₂/Si MIS capacitors after bias-temperature stressed at different conditions.

(c) Determination of Cu diffusion activation energy

BTS were tested at 150°C, 200°C and 250°C. The results showed that no Cu ions drift into Ti-Si-N-O films at 150°C and 1 MV/cm, 200°C and 0.5 MV/cm. Thus Cu ions density (ions/cm²) data is zero at 150°C and 1 MV/cm test for both Si-12 and Si-13 as shown in Table 4-3.

Table 4-3: Cu ion density for different samples calculated after 5 minutes of BTS at different temperature at 1 MV/cm bias condition

Si-12	Temp (K)	Charge Density after 5 min BTS (ions/cm ²)	(J) Ions flux (ions/cm ² .s)
250°C	523	2.86E+13	9.54E+10
200°C	473	8.15E+12	2.72E+10
150°C	423	0.00E+00	0

Si-13	Temp (K)	Charge Density after 5 min BTS (ions/cm ²)	(J) Ions drift rate (ions/cm ² .S)
250°C	523	3.51E+13	1.17E+11
200°C	473	1.90E+13	6.32E+10
150°C	423	0.00E+00	0
Si-15	Temp (K)	Charge Density after 5 min BTS (ions/cm ²)	(J) Ions drift rate (ions/cm ² .S)
250°C	523	4.17E+13	1.39E+11
200°C	473	2.32E+12	7.72E+09
150°C	423	7.74E+11	2.58E+09

According to Fick’s first law of diffusion [Kirkaldy, 1987]:

$$J = -D \frac{\partial C}{\partial x} \tag{3}$$

$$D = D_0 \exp\left(-\frac{E_a}{RT}\right) \tag{4}$$

Sub (4) into (3),

$$J = -D_0 \exp\left(-\frac{E_a}{RT}\right) \frac{\partial C}{\partial x} \tag{5}$$

Assuming $\frac{\partial C}{\partial x}$ is constant within the Ti-Si-N films (liner approximation).

Where J is Cu ion flux, D₀ is a temperature-independent pre-exponential (m²/s). E_a is the activation energy for diffusion (J/mol), R is the gas constant (8.31 J/mol-K), T is the absolute temperature (K)

Let $A = -D_0 \frac{\partial C}{\partial x}$ which is a constant, equation 5 become,

$$J = A \exp\left(-\frac{E_a}{RT}\right) \tag{6}$$

We get $\ln J = \ln A - E_a \frac{1}{RT}$ [7]

Plot of lnJ versus 1/RT can obtain the activation energy, E_a, which is the slope of the plot.

Fig. 4-15: Cu diffusion activation energy in different Ti-Si-N films. The slope of the plot $\ln J$ versus $1/RT$ is the activation energy for Cu diffusion.

From Figure 4-15, the activation energy for Cu diffusion into Si-11, Si-12 and Si-13 is 748.17 J/mol, 366.85 J/mol and 1040.6 J/mol respectively. The calculated activation energy may not be accurate in this case because the slope of the plot of Si-11 and Si-12 is determined by two points only. Thus, a direct comparison in terms of activation energy between Si-11, Si-12 and Si-13 can not be established.

(d) Determination of the source of the C-V shift

As discussed above, there was no flatband voltage shift for Cu/Si-12/PECVD SiO₂/Si (Si/Ti = 0.48) capacitors at BTS conditions: 150°C and 0.5 MV/cm, 150°C and 1 MV/cm, 200°C and 0.5 MV/cm. But for Cu/Si-13/PECVD SiO₂/Si capacitor (Si/Ti = 0.65) and Cu/Si-15/PECVD SiO₂/Si (Si/Ti = 0.91) capacitors, a total less than 4 V flatband voltage shift to the left were observed at the above BTS conditions. This small amount of flatband voltage shift may be due to Cu ions, Ti ions, and/or interface states. Thus, a control sample as shown in Figure 4-9a was used.

Parylene-N was shown earlier to prevent copper drift [Senkevich, 2004]. A film stack of Cu/50 nm parylene-N/53 nm thermal SiO₂/Si was used to show the effectiveness of parylene-N against copper ion diffusion under bias-temperature stress of 150°C and 1 MV/cm. As shown in Figure 4-16, flatband voltage does not shift from as-annealed to 90 minutes of BTS. This proves that parylene-N can effectively block the Cu ions penetration while bias temperature stresses at 150°C and 1 MV/cm.

Fig. 4-16: C – V plots of the MIS capacitor (Cu/parylene-N/ThermalSiO₂/Si) that thermally annealed at 250°C in Ar-3%H₂ for 30 minutes and bias-temperature stressed at 150°C and 1 MV/cm.

As shown in Figure 4-17, in our control sample, 50 nm thick Parylene-N was used in between Cu electrode and Ti-Si-N-O film and this could help us to exclude one source of positive ions, which is Cu ions, that could cause flatband voltage shifts to the left. Consequently, we are only left with two sources of positive charges, which are Ti ions and interface states. In the control sample, if flatband voltage shifts to the left, the shift is due to the Ti ions diffusing through PECVD SiO₂ and accumulating at the PECVD SiO₂/Si interface. If the flatband voltage shifts to the right, it indicates that there is a reduction of interface states.

Fig. 4-17: Determination of the source of the C-V shift.

Figure 4-18 shows the C–V plots of control samples (Cu/parylene-N/Si-15/PECVD SiO₂/Si) that BTS at 150°C and 1 MV/cm. It clearly shows that flatband voltage shifts 4.25 V to the right, indicating the reduction of interface states. Thus, this tells us that the small amount of flatband voltage shifts to the left in Cu/Ti-Si-N-O/PECVD SiO₂/Si capacitors as discussed previously is due to the presence of interface states that could not be fully healed after 250°C annealing. Further investigation was carried out as a negative bias was applied to the Cu gate electrode; it was found that flatband voltage shifted to the left. This implies that the shift is again due to the interface states and/or hot holes injection from the Si substrate into the oxide layer, which generates defects at the oxide/semiconductor interface and the shift is not related to Ti ions or Cu ions penetration. A small hysteresis is observed, meaning that interface states still exists after BTS. In short, the three different compositions of Ti-

Si-N-O films formed by the r.f. reactive magnetron sputtering process are able to block the metal ions penetration at BTS conditions of 150°C and 0.5 MV/cm, 150°C and 1 MV/cm, 200°C and 0.5 MV/cm.

Fig. 4-18: C – V plots of the MIS capacitor as control sample (Cu/parylene-N/Si-15/PECVD SiO₂/Si) that thermally annealed at 250°C in Ar-3%H₂ for 30 minutes and bias-temperature stressed at 150°C and 1.0 MV/cm.

As discussed above, the electrical stability of Ti-Si-N-O film is reduced with higher Si/Ti ratio, and the reduction of the electrical stability of Ti-Si-N-O films is affected by interface states. As we know, when the silane gas flow rate increases (higher Si/Ti ratio) while other process parameters are fixed (Ti target power, argon gas flow rate and nitrogen gas flow rate), the plasma ion density increases. This will enhance the bombardment of plasma ions to PECVD SiO₂ surface. As a result, a poor quality interface will form between Ti-Si-N-O films and PECVD SiO₂ because of the defects generated by the bombardment, and this explains the small amount of flatband voltage shifts to the left even bias-temperature stressed at 150°C and 0.5 MV/cm in Cu/Si-15/PECVD SiO₂/Si capacitor (Si/Ti = 0.91) capacitors (Figure 4-13a)

To further prove that the right hand shift in flatband voltage in control capacitors (Figure 4-18) is due to the presence of interface states, Cu/parylene-N/Si-15/PECVD SiO₂/Si was annealed at higher temperature: 275°C and 300°C.

Fig. 4-19: C – V plots of the MIS capacitor as control sample (Cu/parylene-N/Ti₁₆Si₁₅N₃₂O₃₇/PECVD SiO₂/Si) that was thermally annealed at 275°C in Ar-3%H₂ for 30 minutes and bias-temperature stressed at 150°C and 1.0 MV/cm.

Fig. 4-20: C – V plots of the MIS capacitor as control sample (Cu/parylene-N/Ti₁₆Si₁₅N₃₂O₃₇/PECVD SiO₂/Si) that was thermally annealed at 300°C in Ar-3%H₂ for 30 minutes and bias-temperature stressed at 150°C and 1.0 MV/cm.

Compared to 250°C annealed C – V curve (Figure 4-18), the total flatband voltage shift is reduced from 4.25 V to 1.5 V as shown in Figure 4-19. This means that

275°C annealing does help to reduce interface states in the control capacitors. Further annealing of the same sample to 300°C found that no flatband voltage shift as shown in Figure 4-20. These results strongly proved that the main contributor of the small amount of flatband voltage shift is due to the interface states. These interface states may come from parylene-N/Ti-Si-N-O interface and/or Ti-Si-N-O/PECVD SiO₂ interface and not from the PECVD SiO₂/Si interface. The removal of these interface states can be achieved by higher temperature annealing.

The following investigation further supports the above statement that *the main contributor of the interface states is from the parylene-N/Ti-Si-N-O interface and/or Ti-Si-N-O/PECVD SiO₂ interface, and not from the PECVD SiO₂/Si interface.*

Table 4-4: The position of initial voltage and C-V shift at different annealing temperatures.

Sample/annealing temperature before BTS testing	BTS condition	Initial voltage corresponds to 95% of the initial capacitance (BTS time: 0 min)	C-V shift
A: 250°C annealed testing sample: Cu/Ti-Si-N-O/PECVD SiO ₂ /Si	150°C and 1.0 MV/cm	– 15.0 V	No C-V shift (Figure 4-13b)
B: 250°C annealed control sample: Cu/Parylene-N/Ti-Si-N-O/PECVD SiO ₂ /Si	150°C and 1.0 MV/cm	– 22.5 V	shifts 4.25 V to the right (Figure 4-18)
C: 275°C annealed control sample: Cu/Parylene-N/Ti-Si-N-O/PECVD SiO ₂ /Si	150°C and 1.0 MV/cm	– 15.5 V	shifts 1.5 V to the right (Figure 4-19)
D: 300°C annealed control sample: Cu/Parylene-N/Ti-Si-N-O/PECVD SiO ₂ /Si	150°C and 1.0 MV/cm	– 12.5 V	No C-V shift (Figure 4-20)

First, we conducted the analysis as shown in Table 4-4 above. In control sample (B), there was more left side shift in the initial voltage position (Initial voltage = -22.5 V) compared to the testing sample (A) (Initial voltage = -15.0 V), meaning that more interface states were present in the control sample. These interface states should be from parylene-N/Ti-Si-N-O interface since this was the new interface that we introduced in the sample stack. Furthermore, when the same control sample was annealed at higher temperature (275°C), initial voltage position was reduced to -15.5 V. Further annealing the sample to 300°C improved the position of initial voltage to -12.5 V (Ideal position of initial voltage is at 0 V).

Furthermore, the process temperature of PECVD SiO_2 is between 350°C to 450°C , and the interface of PECVD SiO_2/Si has gone through these temperatures (250°C , 275°C , 300°C), thus 275°C annealing does not exert any effect on this interface. The reduction of flatband voltage shift (from 4.25 V to 1.5 V to 0 V) as well as the right hand shift in the initial voltage position (from -22.5 V to -15.5 V to -12.5 V) after 300°C annealing implies that the reduction of interface states must be from parylene-N/Ti-Si-N-O interface, and/or Ti-Si-N-O/PECVD SiO_2 interface and not PECVD SiO_2/Si interface.

The reasons for the good barrier performance of the current Ti-Si-N-O system are suggested as follows: (1) Stuffing of oxygen at the boundary of nanocrystals. In the work by Warren *et al* [Warren, 1997-1998], the improved Ti-Si-N barrier properties were believed to be due to the grain boundary stuffing of the crystallized TiN with oxygen. In our Ti-Si-N-O films, Si-N nanocrystals were formed and these crystals could readily accommodate other atoms such as O [Pierson, 1996]. Thus it is believed that O stuffs the boundaries of both Ti-N and Si-N, making the diffusion of Cu ions through the grain boundaries more difficult. (2) The presence of amorphous phase reduces the

density of grain boundaries. Marcadal *et al* [Marcadal, 2002], Eric *et al* [Eric, 2000], Joseph *et al* [Joseph, 2002], Muira *et al* [Muir, 1997] and No *et al* [No, 2000] reported that the improved barrier properties of Ti-Si-N was related to the formation of amorphous phase in the Ti-Si-N film. In these reports, the amorphous matrix consisted of Si-N phase. But the amorphous matrix in our Ti-Si-N-O film was formed by Ti-O, Si-O and Si-N-O phases. These Ti-O, Si-O and Si-N-O bonds play an important role in the barrier performance as discussed next; (3) Thermodynamic data [Barin, 1993] showed that the enthalpies of formation (ΔH_f) of Ti-O and Si-O are -944.746 kJ/mol and -910.866 kJ/mol respectively at 300 K, compared with that of -156.057 kJ/mol for Cu-O. As reported by Mallikarjunan *et al* [Mallikarjunan, 2001], metals ionize when in contact with interfacial oxygen. Ionized copper may then diffuse into the dielectric under applied bias. The tendency for such a diffusion critically depends on the formation of Cu-O bond. When Ti-O and Si-O are already present in the film before Cu deposition, the energy needed to break the Ti-O and Si-O bonds to make O available for Cu-O bond is much higher based on the thermodynamic data. Thus the formation of Cu-O is relatively difficult and the ionization tendency of Cu is reduced with the presence of Ti-O and Si-O compounds.

In short, all these characteristics make Ti-Si-N-O films an attractive candidate for future ULSI diffusion barriers.

(II) Cu/Ti-Si-N-O/Parylene-N/MSQ/Thermal SiO₂/Si Capacitors

In this section, BTS of Cu/Ti-Si-N-O/8 nm parylene-N/300 nm MSQ/6.8 nm thermal SiO₂/Si capacitors were evaluated as shown in Figure 4-21 to investigate the electrical stability of Ti-Si-N-O. Dielectric layer changed to porous ultra-low- k methyl silsesquioxane (MSQ) with 39% porosity and k value of 2.2 and it was deposited by

the spin coating method. Ultra thin parylene-N served the purpose of sealing the porous MSQ. The preparation of Ti-Si-N-O barrier films and deposition of copper gate have been described in section 4.1.2 and 4.2.2 respectively.

Fig. 4-21: Experimental capacitor structure (a) with 8 nm parylene-N/300 nm MSQ/6.8 nm thermal SiO₂ as dielectric layer (b) with PECVD SiO₂ as dielectric layer.

Figure 4-22a shows $C - V$ plots of MIS capacitor (Cu/Si-12/Parylene-N/MSQ/thermal SiO₂/Si) that thermally annealed at 250°C and bias-temperature stressed at 150°C and 0.5 MV/cm. It shows that significant flatband voltage shifts to the left (41 V) was observed after 90 min BTS. This result was unexpected since there was no flatband voltage shifts at the same BTS condition for the Cu/Parylene-N/MSQ/Thermal SiO₂/Si capacitor as shown in Figure 4-23.

Fig. 4-22: $C - V$ plots of the MIS capacitor (Cu/Si-12/parylene-N/MSQ/Thermal SiO₂/Si) that thermally annealed at 250°C in Ar-3% H_2 for 30 minutes and bias-temperature stressed at (a) 150°C and 0.5 MV/cm, (b) 150°C and 1.0 MV/cm.

Fig. 4-23: C – V plots of the MIS capacitor (Cu/Parylene-N/MSQ/Thermal SiO₂/Si) that thermally annealed at **250°C** in Ar-3%H₂ for 30 minutes and bias-temperature stressed at 150°C and 0.5 MV/cm.

When the BTS condition changed to 150°C and 1 MV/cm, significant flatband voltage shifts to the left after 15 minutes of BTS was observed as shown in Figure 4-22b. Thus, it is not necessary to conduct BTS testing at 200°C and 250°C at 0.5 MV/cm and 1 MV/cm as significant flatband voltage shift will occur at the early stage of BTS time. The same results were obtained for different compositions of Ti-Si-N-O (Si-13) capacitors as shown in Figures 4-24a and 4-24b.

Fig. 4-24: C – V plots of the MIS capacitor (Cu/Si-13/parylene-N/MSQ/Thermal SiO₂/Si) that thermally annealed at **250°C** in Ar-3%H₂ for 30 minutes and bias-temperature stressed at (a) 150°C and 0.5 MV/cm; (b) 150°C and 1.0 MV/cm.

The flatband voltage shifts may be due to:

- 1) The diffusion of Ti ions from Ti-Si-N-O film,
- 2) The diffusion of Cu through Ti-Si-N-O films (e.g., bad barrier). But this reason can be excluded since the previous BTS results as discussed in section (I) showed excellent Ti-Si-N-O barrier performance against copper diffusion.
- 3) **Plasma process related issues:** Since parylene-N is very thin (only 8 nm), it will be damaged during the formation of Ti-Si-N-O film on parylene-N/MSQ/Thermal SiO₂/Si substrate. In other word, parylene-N chains may be destroyed by the ionic bombardment during Ti-Si-N deposition, and as a result, this will lead to the penetration of these ions into porous MSQ film and be trapped inside MSQ film. Thus, these ions will move to the thermal SiO₂/Si interface during BTS testing to contribute to the significant flatband voltage shift. If the above hypothesis is true, then we can thermally anneal the sample at higher temperature, such as 350°C (this temperature is compatible with the back-end-of-line process) to remove those trapped ions. These ions can be removed through the diffusion process during annealing.

Fig. 4-25: Schematic diagram shows the sources of ions during plasma process and the causes of the instability of MSQ film.

Thus, the same sample in Figure 4-21a was annealed at 350°C and BTS results were shown in Figure 4-26a and b.

Fig. 4-26: C – V plots of the MIS capacitor (Cu/Si-12/parylene-N/MSQ/Thermal SiO₂/Si) that thermally annealed at 350°C in Ar-3%H₂ for 30 minutes and bias-temperature stressed at (a) 150°C and 0.5 MV/cm; (b) 150°C and 1.0 MV/cm.

In comparing Figures 4-22a with Figure 4-26a, and then Figure 4-22b with Figure 4-26b, significant improvement in BTS results are observed for the same samples that annealed at 350°C. There was only a 2.5 V flatband voltage shift to the left as shown in Figure 4-26a compared to a 41 V flatband voltage shift in Figure 4-22a. For samples that annealed at 250°C, BTS could only be tested up to 15 min as a flat C-V curve was observed, and no C-V characteristic curve could be obtained beyond 15 minutes. On the other hand, for the samples that annealed at 350°C, BTS could be tested up to 90 min as C – V characteristic was obtained as shown in Figure 4-26b.

The improvement in the BTS results for the samples that annealed at 350°C can be explained by the removal of trapped ions (Ar, Ti, Si or N ions) through diffusion process during annealing at 350°C as shown in Figure 4-27, the reduction of interface states, and the repolymerization of parylene-N after annealing at 350°C as shown in Figure 4-27.

Fig. 4-27: Schematic diagram shows the removal of trapped ions and the repolymerization of parylene-N after annealing at 350°C.

4.2.4 Conclusions

Bias temperature stability of different compositions of Ti-Si-N-O films was investigated using metal-oxide-semiconductor (MOS) capacitors. From the results, it can be concluded that all the Ti-Si-N-O films can prevent metal ions penetration at BTS conditions of 150°C and 0.5 MV/cm, 150°C and 1 MV/cm, 200°C and 0.5 MV/cm. Also, the small amount of flatband voltage shifts to the left is due to the presence of interface states, which could not be fully healed at 250°C annealing, and is directly related to the processing issues. Annealing at higher temperature can reduce the interface states. The higher the silane gas flow rate, the less stable the electrical property of Ti-Si-N-O films. Thus, it is suggested that with a low silane gas flow rate, an electrical stable Ti-Si-N-O film can be achieved with less interface states.

Chapter 5

Conclusions and Recommendations

An in-depth analysis of both the physical and electrical properties of Ti-Si-N and Ti-Si-N-O barrier films was conducted in this work. The objectives of this thesis focused on the studies of the processing and overall properties of Ti-Si-N and Ti-Si-N-O barrier films. These studies provide the guidelines in choosing plasma process parameters in the formation of Ti-Si-N and Ti-Si-N-O films and the choice of barrier materials when diffusion performance is concerned.

In this study, Ti-Si-N and Ti-Si-N-O barrier films were successfully formed by low frequency, high density inductively coupled plasma process and low temperature physical-chemical vapor deposition process respectively. The effects of plasma process parameters on the microstructure, phase composition, resistivity, surface morphology, and surface roughness were analyzed in detail. In addition, the barrier performance of Ti-Si-N-O films against copper diffusion was evaluated by thermal and electrical diffusion studies. Finally, electroless copper as a seed layer was successfully deposited on ICP Ti-Si-N films. From these experiments, the conclusions are summarized in the following sections.

5.1 Low Frequency, High Density Inductively Coupled Plasma Ti-Si-N Films

5.1.1 The formation of Ti-Si-N barrier films

Ti-Si-N films are formed through an inductively coupled plasma implantation of N into Ti_xSi_y substrate. The columnar structure of Ti_xSi_y substrate has been completely destroyed in the implanted layers with the formation of nanocrystalline regions. The modification of the columnar structures, which are usually seen in many

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PVD / CVD films, could improve the diffusion barrier performance significantly. The atomic concentration of N ranges from 2 – 67% depends on the implantation depth and nitrogen plasma treatment time. Nitrogen was found to be bonded to titanium and silicon to form titanium nitride and silicon nitride nanocrystals.

It was found that the external bias plays an important role in controlling the sheet resistance of Ti-Si-N film, but not the implantation depth of nitrogen. Furthermore, this work found that increased argon plasma activation time, nitrogen plasma treatment time and argon gas flow rate improve the penetration depth of nitrogen into Ti_xSi_y structure. However, no significant effects on surface roughness and sheet resistance of Ti-Si-N films were observed.

It has been demonstrated that by controlling the process conditions, it is possible to grow Ti-Si-N films with controlled thicknesses and electrical properties. The suggested process conditions should be 100 V external bias, 20 minutes argon plasma activation with 30 sccm argon gas flow rate, and 60 minutes nitrogen plasma treatment.

5.1.2 Thermal stability of Ti-Si-N films

In this study, it was found that high external bias during implantation will degrade the barrier performance. For the sample that was subjected to 300 V external bias, significant Cu diffusion was observed even after 500°C annealing. On the other hand, no significant copper diffusion was observed in the samples subjected to 100 V and 200 V external bias.

With the fixed plasma process parameters (100 V external bias, 20 minutes argon plasma activation with 30 sccm argon gas flow rate, and 30 minutes nitrogen plasma treatment), the effect of annealing temperature on the integrity of Ti-Si-N

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barrier was evaluated. It was found that barrier failure did not occur up to 650°C annealing for 30 minutes, which fulfills the industry requirements for barrier films.

With the diffusion of copper into Ti-Si-N film at higher annealing temperatures (750°C and 850°C), Cu-Ti and Cu-N compounds were formed. No Cu-Si compound was found in the current study for up to 850°C annealing. This has indicated that the addition of Si contributes to the improvement in the diffusion barrier performance. In this polycrystalline mixture of TiN and Si₃N₄ film, diffusion through grain boundaries and other defects become dominant.

Based on the overall requirements, Ti-Si-N layer formed by low frequency, high density inductively coupled plasma process in the current study presents an attractive route to produce effective barrier materials against copper diffusion.

5.1.3 Electroless Cu seed layer On Ti-Si-N barrier films

With Ti-Si-N as a barrier layer, palladium activation time is greatly reduced compared to TiN. The required activation time on Ti-Si-N films was found to be 1 minute or less as compared to 3 minutes on TiN. The reason is that the activation energy for Pd nucleation is lower on the Ti-Si-N surface, which leads to higher Pd nucleation rate. Another contributing factor could be that the plasma implantation damage on Ti-Si-N surface in the form of dangling bonds which serve as free electrons for the reduction of Pd⁺⁺.

In addition, with only 1 minute Pd activation on Ti-Si-N surface, 100% surface coverage of the electroless copper seed layer is obtained, compared to that of 3 minutes Pd activation required on TiN. Besides that, larger copper grain size oriented in (111) plane can be obtained by depositing copper seed layer onto the Ti-Si-N barrier film, which has been subjected to higher argon gas flow rate and longer nitrogen

plasma treatment. As these process conditions may lead to sparsely distributed Pd seeds on Ti-Si-N film, larger copper grains can be produced.

This work, for the first time, provides guidelines for electroless Cu plating on Ti-Si-N surface.

5.2 Low Temperature Physical-Chemical Vapor Deposition of Ti-Si-N-O Barrier Films

5.2.1 *The formation of Ti-Si-N-O barrier films*

This work reports a novel route for the formation of Cu barrier at temperatures as low as 40°C, which is suitable for back-end-of-line processes. The film compositions are $\text{Ti}_{24}\text{Si}_{12}\text{N}_{35}\text{O}_{29}$, $\text{Ti}_{20}\text{Si}_{13}\text{N}_{35}\text{O}_{32}$ and $\text{Ti}_{16}\text{Si}_{15}\text{N}_{32}\text{O}_{37}$.

The current work has found out that the Ti-Si-N-O barrier films consist of mixed crystalline and amorphous structure. The crystal phases are Ti-N, Si-N, and Ti-Si as evidenced by combined XPS, XRD measurements and lattice spacing measurement from HRTEM; while Ti-O, Si-O, and Si-N-O contribute to the amorphous phases in Ti-Si-N-O films. These amorphous phases are found to play an important role in barrier performance.

The resistivity of Ti-Si-N-O films increases with increasing Si content. This correlates well with the high resistivity Si_3N_4 phase in the films. As silane gas flow rate increases, more Si_3N_4 crystals are formed. As a result, the film resistivity increases. This indicates that the properties of Ti-Si-N-O films can be controlled by the process parameters.

5.2.2 *Bias-temperature stability of Ti-Si-N-O films*

Ti-Si-N-O shows very good electrical stability and is able to prevent copper ions from drifting into subsequent dielectric layers at BTS conditions of 150°C and

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0.5 MV/cm, 150°C and 1 MV/cm, 200°C and 0.5 MV/cm, which far exceeds the requirements for industrial applications. These results corroborate well with the charge calculation results. Compared to binary barrier films, Ti-Si-N-O film is an attractive candidate for future back-end-of line devices.

When bias-temperature stressed at 150°C and 0.5 MV/cm in Cu/Ti₁₆Si₁₅N₃₂O₃₇/PECVD SiO₂/Si capacitor (high Si content barrier film), small amount of flatband voltage shifts to the left has been observed and proven that it is not related to Ti ions or Cu ions penetration. There is no copper/Ti-Si-N-O interface instability during the BTS tests. The shift is due to the presence of interface states that could not be fully healed at 250°C annealing and it is directly related to the processing issues. It was found that increases silane gas flow rate will lead to a poor quality interface between Ti-Si-N-O films and PECVD SiO₂, and this is the root cause of the small amount of flatband voltage shifts to the left even bias-temperature stressed at 150°C and 0.5 MV/cm. The solution to reduce these interface states is by annealing the capacitors at a higher temperature such as 300°C.

On the other hand, C – V plots of MIS capacitor (Cu/Ti₂₄Si₁₂N₃₅O₂₉/Parylene-N/MSQ/thermal SiO₂/Si) shows that significant flatband voltage shifts to the left (41 V) after 90 min bias-temperature stressed at 150°C and 0.5 MV/cm. The root cause for this shift in the flatband voltage is due to the damage of very thin parylene-N chains by ions bombardment during plasma process, and as a result, the penetration of ions into porous MSQ film and be trapped inside MSQ film. During BTS testing, these ions will move to thermal SiO₂/Si interface and contribute to the significant flatband voltage shift.

The above problem can be improved by annealing the samples at 350°C. It was found that flatband voltage shift reduces from 41 V to 2.5 V after annealing at high

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temperature. This is due to the removal of trapped ions (Ar, Ti, Si or N ions) through diffusion process during annealing at 350°C, the reduction of interface states, and the repolymerization of parylene-N after annealing at 350°C.

5.3 Comparison between ICP and P-VCD Barrier Properties

	Industry baseline	ICP	P-CVD	Prefer Route
Feasibility to obtain ultra-thin barrier thickness (e.g. 5nm)	PVD process for 65 nm and 45 nm technology node.	Currently obtained 15nm Ti-Si-N film. In the research works, it demonstrated that by controlling the process conditions, it is possible to grow Ti-Si-N films with controlled thicknesses and electrical properties.	Currently obtained 215 nm Ti-Si-N-O film. Such a thick barrier film is due to long deposition time (2 hours). By reducing the deposition time, we are able to obtain ultra-thin barrier films.	P-CVD
Microstructure	Minimizes grain boundaries as diffusion paths.	Nanostructure Ti-Si-N films are mainly composed of two major phases, TiN and Si ₃ N ₄ .	2 – 15 nm Ti-N, Si-N and Ti-Si phases are embedded in Ti-O, Si-O and Si-N-O amorphous phases.	P-CVD. The present of amorphous phase can reduce the diffusion path
Sheet Resistance/Resistivity	Approximately 800 $\mu\Omega\cdot\text{cm}$ for 2 nm thick Ta	Currently obtainable 9 $\mu\Omega\cdot\text{cm}$ for 15 nm thick Ti-Si-N film	Currently obtainable 3.63E+03 $\mu\Omega\cdot\text{cm}$ for 215 nm thick Ti-Si-N-O film	ICP
Surface roughness	Less than 3 nm	Currently obtainable 20 nm	Currently obtainable 2.2 nm	P-CVD provides smoother surface
Thermal diffusion performance	Requirement: 425°C	Can prevent copper diffusion up to 650°C annealing.	NA	-
Electrical diffusion performance	Requirement: 200°C and 0.1 MV/cm	NA	Can prevent copper diffusion at BTS condition: 200°C and 0.5 MV/cm	P-CVD. Combining bias and temperature effects, which simulates the real integrated circuits environment
Conclusion:	Based on the above comparison, P-CVD will be the preferred route to process a better diffusion barrier film.			

5.4 Recommendations For The Future Work

Based on the results as well as problems and limitations encountered in this work, some recommendations have been proposed for further study.

We have proven that implantation of N into Ti_xSi_y substrate can change its columnar structure, leading to improved barrier performance. The lesson learnt could also be employed in modifying the columnar structure of TiN, which is commonly obtained by conventional PVD and CVD processes. Investigation should be carried out to implant Si into the TiN substrate. The study should include correlation among implantation processes, microstructures, film properties, and, ultimately, the barrier performance.

Another interesting work will be the formation of Ti-Si-N film using CVD TiN as a base material followed by silicon (from SiH_4) implantation. This would be a fully plasma enhanced chemical vapor deposition (PECVD) process which can provide conformal step coverage in high aspect ratio vias and trenches. In addition, CVD TiN is an ideal candidate because of its known manufacturing and integration capabilities for W liner applications. The current work could not carry out such a study due to equipment limitation, but we have demonstrated the potential of the ternary system from prospects of materials properties and barrier performance.

A related study would be a quantified adhesion study between electroless Cu and different barrier layers (including the new barriers formed in the current work) and to investigate its failure mechanisms. Although the effects of different process parameters such as chemicals used in the electroless plating bath, plating temperatures, and activation conditions, on the properties of electroless plated Cu seed layer, have been studied by various research groups, there are few reports on the adhesion issues between electroless copper and barrier layers. Many reports have shown that the

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interface condition affect the performance of Cu/low-k interconnects, but quantifying the adhesion strength / toughness has just begun in recent years [Gan *et al*, 2006]. According to the 2004 International Technology Roadmap for Semiconductors, very thin copper seed layer are required for the subsequent electroplating process and sub-micron interconnect technology. Thus it is worthwhile to study the adhesion between electroless Cu and different barrier layers and to investigate its failure mechanisms.

Furthermore, the effect of plating parameters, solution bath chemistry and annealing temperatures after plating, on the properties of electroless copper need to be explored further. This is because in the present research work, limited results of electroless copper deposition on Ti-Si-N films have been reported. Last, but not least, investigation on the direct electroless copper plating on Ti-Si-N films without palladium activation process is also worthy of study in the future. This current study shows that the presence of dangling bonds on Ti-Si-N surface due to plasma process may provide free electrons for the reduction of Cu from Cu^{++} , thus eliminating the activation process.

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List of Publications

The results of in thesis have lead to the publication of the following papers:

1. Y. C. EE, Z. Chen, S. Xu, L. Chan, K. H. See, S. B. Law. (2004). Electroless copper deposition as a seed layer on TiSiN barrier. *Journal of Vacuum Science and Technololgy A*, 22, 1852-1856.
2. Y. C. EE, Z. Chen, L. Chan, Alex K. H. See, S. B. Law, K. C. Tee, K. Y. Zeng, L. Shen. (2004). Effect of processing parameters on electroless Cu seed layer properties. *Thin Solid Films*, 197, 462-463.
3. Y. C. EE, Z. Chen, W. D. Wang, D. Z. Chi, S. Xu, S. B. Law. (2005). Barrier property of TiSiN films formed by low frequency, high density inductively coupled plasma process. *Surface and Coatings Technology*, 198, 291-295.
4. S.P. Chong, Y.C. EE, Z. Chen and S.B. Law. (2005). Electroless copper seed layer deposition on tantalum nitride barrier film. *Surface and Coatings Technology*, 198, 287-290.
5. Y. C. EE, Z. Chen, L. Chan, K. H. See, S. B. Law, S. Xu, Z. L. Tsakadze, P. P. Rutkevych, K.Y. Zeng, L. Shen. (2005). Formation of Ti-Si-N Barrier Film Using Low Frequency, High Density Inductively Coupled Plasma. *Journal of Vacuum Science and Technology B*, 23, 2444-2448.

6. Y. C. EE, Z. Chen, S. B. Law and S. Xu. (2006). Formation and characterization of Ti-Si-N-O barrier films. *Thin Solid Films*, 504, 218-222.
7. Y. C. EE, Z. Chen, T.-M. Lu, Z. L. Dong, and S. B. Law. (2006). Low temperature physical-chemical vapor deposition of Ti-Si-N-O barrier films, *Electrochemical Solid-State Letters*, 9, G100-G103.
8. Y. C. EE, Jasbir S. Juneja, Pei-I Wang, T.-M. Lu, H. Bakhru, L. Chan, S. B. Law, Clare Yong, Z. Chen and S. Xu. (2006). Bias-Temperature Stability of Ti--Si--N--O Films, *Journal of The Electrochemical Society*, 153, G470.
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9. Y. C. EE, Z. Chen, S. B. Law, S. Xu, N. L. Yakovlev, Doreen Lai. (2006). Copper thermal diffusion in Ti-Si-N layers formed by inductively coupled plasma implantation. *Applied Surface Science*, In Press.