ALTERNATIVE NITRIDE DIFFUSION BARRIERS ON SILICON AND GERMANIUM FOR COPPER METALLIZATION

By

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A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

2006
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by

Seemant Rawal
Dedicated to my mother Rasilaben Rawal and my dear wife Purvi Rawal.
ACKNOWLEDGMENTS

I would like to immensely thank my advisor Dr. David P. Norton. His enthusiasm and knowledge on different subjects of science are astounding. Dr. Norton’s exemplary dedication towards his work and students along with his zeal to be the best in the world in his area of research motivated me greatly to pursue and conduct superior quality research. I would like to thank Prof. Rajiv K. Singh for providing me guidance and support during my initial years in USA. I would like to thank Prof. Tim Anderson and Prof. Lisa McElwee-White for their guidance and help with my research. They have helped me to think and analyze my research critically.

I would like to thank my mother, Rasilaben Rawal, for her passion towards education. Her undying zeal towards learning sowed the first seeds in me to respect and acquire knowledge. Many thanks go to my high school chemistry teacher, Mr. Dubey and physics teacher Mr. Parmar for providing support through my 12th standard. Special thanks go to Mahendra Pandya and Geetaben Pandya, for supporting me throughout my undergraduate years. I would like to thank my brother, Rakesh Rawal, and his wife, Padmaja Rawal, for their love and support. Most importantly, I would like to thank my wife, Purvi Rawal, for her unconditional love and support. Her immense understanding and perceptive nature have made my journey cherishing. I would like to thank all my friends and well-wishers for their support and encouragement.

Last but not least, I thank GOD for giving me this life and opportunity to serve HIS world.
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As device dimensions shrink, there is an urgent need to replace conventionally used Al interconnects to achieve increased current density requirements and better performance at future technology node. Copper is a viable candidate due to its lower resistivity and higher resistance to electromigration. However, Cu has its own problems in its integration. It diffuses rapidly through SiO₂, Si and Ge into the active regions of the device, thereby deteriorating device performance. There is therefore a need to find a diffusion barrier for Cu.

Amorphous ternary nitrides are investigated as a candidate diffusion barrier for Cu metallization on single crystal Si and Ge substrates. Ge was chosen as a third element in the binary matrix of WNₓ, HfNₓ and TaN due to its chemical similarity to Si and possible integration in SiGe or Ge based devices. The addition of Ge helps in amorphization of the binary matrix. It hinders grain boundary formation and increases the recrystallization temperature compared to their respective binary nitrides. Cu was deposited in-situ after
nitride deposition. In the case of W-Ge-N on Si, the recrystallization temperature was raised by 400 °C, while for Ta-Ge-N it was raised by 100 °C indicating better diffusion barrier properties than their corresponding binaries.

A bilayer approach for diffusion barrier was also studied. Ge/HfNx bilayer was deposited on Si followed by in-situ deposition of Cu. Copper reacts with Ge and forms Cu$_3$Ge which has low resistivity, is less reactive with oxygen, and is a diffusion barrier for Cu. By combining the material properties of Cu$_3$Ge and HfNx, an excellent diffusion barrier performance was demonstrated under stringent test conditions.
CHAPTER 1
INTRODUCTION

The integrated circuit industry doubles the number of transistors in a chip every 18 months. With more transistors built into a chip, minimum feature size decreases, leading to faster devices. At present, we are moving towards the 45 nm node technology and beyond which is guided by International Technology Roadmap for Semiconductors (2005). For many years, gate length determined the device speed and was the bottleneck for future generation devices. However, with decreasing dimensions, delay in interconnects now plays a major role in influencing device speed. The interconnect delay, also called resistance-capacitance (RC) time constant delay, is mostly caused by an increase in resistance at smaller dimensions. The RC delay is expressed by the following equation:

\[ RC = \frac{\rho \ell^2 \varepsilon_{\text{ILD}}}{t_M \cdot t_{\text{ILD}}} \]

where \( \rho \) is resistivity, \( \ell \) is interconnection length, \( t_M \) is interconnect thickness, \( \varepsilon_{\text{ILD}} \) and \( t_{\text{ILD}} \) are permittivity and thickness of interlevel dielectric (ILD). Also, the current density increases as width of the interconnect decreases. Figure 1-1 shows the increase in RC delay time in interconnects with decreasing feature size which dominates overall delay at sub micron technology nodes.¹

Aluminum has been the interconnect material of choice for many generations with \( \text{SiO}_2 \) (\( \kappa = 3.9 \)) as the dielectric material. This results in a tremendously high RC delay as dimensions decrease. One way to reduce the RC delay is to decrease the dielectric
constant of SiO$_2$. Fluorinated silicon dioxide (FSG) was used with a dielectric constant of 3.7 for the 180 nm technology node.\(^2\) Not until recently was low-k material (\(\kappa = 2.7 – 3.0\)) being integrated in devices. At high current densities, electromigration performance of Al is severely degraded leading to voids and hillock formation. Creation of voids leads to discontinuous circuit causing failure of devices. Figure 1-2 shows void and hillock formation in Al interconnect. Alloying Al with Cu showed an increase in electromigration resistance, but it reached its usability limits as subsequent milestones in IC industry were achieved.

With increased demands on performance, an alternative interconnect material is eventually desired. The logical choice is a transition to Cu interconnects. There are several advantages in using Cu as an interconnect material. Bulk resistivity of Cu is 1.67 \(\mu\Omega\cdot\text{cm}\), which is almost 40% less than Al (\(\rho=2.65 \mu\Omega\cdot\text{cm}\)).\(^3\) Resistance to electromigration property of Cu is highly superior to Al, which leads to better device reliability. Replacing the Al/SiO$_2$ gate stack with Cu/low-\(\kappa\) reduces the RC delay significantly.

However, Cu has its own share of problems. It diffuses rapidly through Si, Ge and SiO$_2$ and forms parasitic silicides (Cu$_3$Si) and hinders the device performance. It forms deep and shallow level traps in Si and Ge, respectively. Cu reacts with dopants and forms Cu-D complexes (D is dopant atom) deteriorating device performance. Cu exhibits poor adhesion on SiO$_2$ and other low-\(\kappa\) dielectrics. In addition to the above difficulties, solutions also need to be found for anisotropic etching, poor corrosion and oxidation properties of Cu. In order to get the desired benefits by switching from Al to Cu interconnect, a viable diffusion barrier is required to prevent Cu diffusion.
The primary purpose of a diffusion barrier is to prevent intermixing of chemical species with each other. This can be achieved via various mechanisms thereby classifying the diffusion barriers based on the method. i.e., passive, sacrificial, stuffed and amorphous diffusion barriers. A passive diffusion barrier is an ideal barrier which does not react with any of the layers it separates. A sacrificial barrier would react with either or both layers that it separates and get consumed. For a sacrificial barrier, the reaction rate between the barrier and the layers is very important. It should be slow enough so that the barrier can perform to acceptable levels for the useful lifetime of the device. For polycrystalline or nanocrystalline thin films, rapid diffusion occurs via grain boundaries, dislocations and surface defects.\(^4\) Diffusion is highly influenced by temperature. The temperature dependence of diffusion coefficient \((D)\) is given by the following equation:

\[
D = D_o \exp \left( \frac{-Q_d}{kT} \right)
\]

where \(D_o\) is temperature-independent pre-exponential factor, \(Q_d\) is the activation energy, \(k\) is the Boltzmann constant and \(T\) is the temperature.

The activation energy for grain boundary diffusion is approximately half the activation energy required for lattice diffusion. As a result, grain boundary diffusion dominates at lower temperatures.\(^4\) For polycrystalline thin films, diffusion through grain boundaries and dislocations is the fastest. This mode of diffusion can be stopped using two approaches. The grain boundaries and/or dislocations can be “stuffed” by impurity atoms which would hinder diffusion through them. Another approach is to lower the amount or eliminate the grain boundaries altogether. This can be achieved by low temperature or room temperature deposition of nanocrystalline or a amorphous diffusion barrier where the short-circuit pathways are lowered or eliminated. This is highly
desirable because of low/no addition to the thermal budget. This may not be the best approach as films deposited at lower temperatures can have undesired modified properties during subsequent high temperature processing steps.

Apart from the primary function of preventing diffusion of Cu, the diffusion barrier should meet other stringent specifications. Some of them are:

- The diffusion barrier should be thermodynamically stable with Cu and underlying substrate under standard operating conditions. It should not react with Cu or the substrate under thermal, mechanical or electrical stresses encountered during other processing steps.

- The density of diffusion barrier should be close to its bulk density in order to avoid any defects, voids or dislocations which can compromise its integrity.

- The diffusion barrier should have reasonable thermal and electrical conductivity to avoid any parasitic capacitance effects and unwanted heating effects.

- The contact resistance of diffusion barrier with Cu and substrate should be minimal.

- Diffusion barrier should behave well under the applied mechanical and electrical stresses during subsequent processing.

- Microstructure of the diffusion barrier should ideally be amorphous at room temperature and remain amorphous after thermal treatment at higher temperatures. In general, diffusion barriers with higher melting temperatures have high recrystallization temperatures.

- The barrier should have good conformality especially over high aspect ratio structures.

- Diffusion barrier should adhere well with Cu and the surrounding material.

- Deposition of diffusion barrier should be compatible with existing processing facilities and infrastructures.
Chapter 2 will present background and a literature review of various diffusion barriers, method of deposition and barrier properties. In Chapter 3, experimental methods used to deposit diffusion barrier films for this study will be explained. Various quantitative characterization techniques used to evaluate the diffusion barrier performance under extreme thermal treatment will also be described. Recrystallization properties and diffusion barrier performance of W-Ge-N deposited on Si/SiO₂ are evaluated in Chapter 4. The behavior and performance of W-Ge-N diffusion barrier deposited on Ge are investigated in Chapter 5. A comparison of barrier properties and performance of HfNₓ and Hf-Ge-N deposited on Ge is described in Chapter 6. Chapter 7 will describe the excellent diffusion barrier properties of a Ge/HfNₓ bi-layer diffusion barrier deposited on Si. Properties of Ta-Ge-N diffusion barrier on Si will be evaluated in Chapter 8 followed by conclusion in Chapter 9.
Figure 1-1. RC delay vs. technology nodes.

Figure 1-2. Void and Hillock formation in Al interconnects.
CHAPTER 2
LITERATURE REVIEW

Due to the unique diffusion property of Cu in Si, Ge, SiO₂ and other low-k dielectrics, there is an imminent need for a diffusion barrier for Cu. There has been a plethora of research on different diffusion barriers. In general, metals or compounds with high melting temperatures are suitable for the purpose because of less chance of having grain boundaries, which are the fastest diffusion pathways. Therefore, refractory based materials seem to be the best choice due to their high melting temperature and decent electrical conductivity. A considerable amount of research has been conducted to find a viable diffusion barrier for Cu based on refractory metals. Most of the research can be classified in three categories.

- Refractory metals as diffusion barriers
- Binary diffusion barriers based on refractory metals
- Ternary diffusion barriers based on refractory metals

This chapter will cover a comprehensive review of the above classifications.

**Refractory Metals as Diffusion Barrier**

As it became evident that switching from Al based interconnects to Cu based interconnects was necessary, initial research focused on refractory metals as candidate diffusion barriers. Primary interest was in Ti, Ta, Cr, and W as Cu diffusion barriers.

**Ti Diffusion Barrier**

Ti based diffusion barriers were extensively used for Al interconnects. A natural choice was to extend its functionality in acting as a Cu diffusion barrier. However, a Ti diffusion barrier fails at 350 °C by Ti-Cu compound formation.⁵ A study conducted by
Ohta et al.\textsuperscript{6} also revealed failure of Ti diffusion barrier at 400 °C indicated by an increase in resistivity after annealing. The resistivity increase was attributed to Cu diffusion through Ti and subsequent reaction with Si to form Cu silicides.

**Ta Diffusion Barrier**

The two major advantages of using Ta as a diffusion barrier in comparison to Ti are its very high melting temperature (3017 °C compared to 1668 °C for Ti) and thermodynamical (interface and solubility) stability with Cu for very high temperatures. The Cu-Ta phase diagram shows that both Cu and Ta are insoluble in each other even at high temperature. Failure of Ta diffusion barrier occurs due to Cu diffusion through grain boundaries formed in Ta after high temperature annealing followed by Cu\textsubscript{3}Si formation at Ta/Si interface.\textsuperscript{7} Ta also reacts with Si and forms silicides thus rendering itself unusable as a Cu diffusion barrier.

**Cr Diffusion Barrier**

Cr was studied as a diffusion barrier for Cu because of its good corrosion resistance properties and excellent adhesion promoter.\textsuperscript{8} However, Cu/Cr/Si multilayer structure showed a huge increase in resistivity after annealing at temperatures higher than 400 °C. This was attributed to Cu-Cr binary phase formation. The formation of such a phase compromises the integrity of the Cu/Cr/Si multilayer structure resulting in Cu silicide formation indicating diffusion barrier failure.\textsuperscript{6}

**W Diffusion Barrier**

W is a better diffusion barrier compared to Ti and Cr. It is chemically and thermodynamically stable with Cu.\textsuperscript{9} Initial study showed that Cu/W/Si structures behaved well even after annealing at 600 °C. However, it failed after annealing at 700 °C.\textsuperscript{6} Cu intermixes with W even at low temperatures of 260 °C, thus rendering it non-viable as a
solution to Cu diffusion. Preferentially oriented W(110) failed after annealing at 690 °C for 1 hr due to consumption of W by a uniform silicidation reaction. Selective chemical vapor deposited W layer on p⁺-n junction diodes led to failure after annealing at temperatures above 650 °C.

**Binary Diffusion Barrier**

In order to overcome the drawbacks of lower recrystallization temperatures and formation of grain boundaries in refractory metals used as diffusion barriers, their respective binaries were explored. This class of diffusion barriers can generally be classified in three categories.

- Refractory intermetallics
- Refractory carbides
- Refractory nitrides

These individual classifications will be explored further in the following sections.

**Refractory Intermetallics**

Several of the refractory intermetallics were studied as Cu diffusion barriers. TiW was used extensively in Al-based interconnects and so was also tried as a diffusion barrier for Cu interconnects. The study showed that TiW (30 at. % Ti) not exposed to air before deposition of Cu failed at 775 °C when RTA annealed in N₂ gas for 30 seconds. The authors also summarized results of a variety of Cu/diffusion barrier/Si systems. Table-1 in reference 13 shows a list of diffusion barrier investigated between Si and Cu. Amorphous Ni₆₀Nb₄₀ diffusion barrier failed at 600 °C after annealing for 60 min. A different composition of Ni₅₇Nb₄₂ failed at a lower temperature of 500 °C after 60 min. The authors also investigated the feasibility of Ni₆₀Mo₄₀ as a candidate diffusion barrier for copper. It failed at 500 °C after annealing for 60 min. Amorphous Ir-Ta alloy was investigated for Cu diffusion barrier application. Sandwich structure of Si/a-Ir₅₅Ta₄₅/Cu/
a-Ir$_{45}$Ta$_{55}$ failed after annealing at temperatures higher than 700 °C. Failure occurred at 750 °C by interdiffusion of Cu and Si as detected by Rutherford backscattering spectrometry. It was also observed that the recrystallization temperature of a-Ir$_{45}$Ta$_{55}$ was lowered from 900 °C to 750 °C due to the presence of Cu. Alloyed Ta-Co$^{16}$ was shown to act as a Cu diffusion barrier deposited by e-beam evaporation. However, an intermetallic phase of Co$_2$Ta and metal-silicide phase of Co$_2$Si formed after annealing at 500 °C. Recently, a study conducted by J.S. Fang et al.$^{17}$ explored the possibility of using sputtered Ta-TM (TM = Fe, Co) as diffusion barriers for Cu. Ta$_{0.5}$Fe$_{0.5}$ diffusion barriers failed at 650 °C while Ta$_{0.5}$Co$_{0.5}$ failed at 700 °C after annealing, indicating better performance of Ta$_{0.5}$Co$_{0.5}$.

**Refractory Carbides**

Interest in refractory carbides to serve the purpose of copper diffusion barriers was due to two reasons. First, they have a high melting temperature, and second, they have low resistivity indicating higher thermal and chemical stability. Among the refractory carbides studied, primary interest has been in Ti, Ta and W based carbides. A detailed study of TiC$_x$ as copper diffusion barriers was carried out by S.J. Wang et al.$^{18}$ However, the Cu/TiC$_x$/Si structure was unstable after annealing at temperatures higher than 600 °C for 30 min. A more sensitive electrical characterization done by measuring leakage current across Cu/TiC$_x$/p$^+$ n-Si diode structure revealed an early failure just after annealing at 500 °C for 30 min. As many as 60% of the diodes measured for leakage current after annealing at 530 °C had the leakage current in the range of 10$^{-5}$ A/cm$^2$, which is three orders of magnitude higher than the leakage current measured at room temperature. Approximately 80% of the diodes had a leakage current in the range of 10$^{-3}$
A/cm² after annealing at 550 °C, indicating a failure temperature somewhere around 500 °C.

TaC has a melting temperature of 3985 °C¹⁹ suggesting good thermal stability, and room temperature resistivity of 27 µΩ-cm,²⁰ thus making it a potential candidate as a Cu diffusion barrier. In this study, Junji Imahori et al.²⁰ compared films with different carbon concentrations, namely Ta₅₃C₄₇, Ta₄₀C₆₀, and Ta₂₀C₈₀. Of these, Ta₅₃C₄₇ films performed better than others. However, it too failed after annealing at temperatures higher than 600 °C for 30 minutes. Films with 60 and 80% C concentrations failed primarily due to diffusion of Cu through the amorphous C phase and lesser diffusion of Cu occurred through grain boundaries of TaC. However, the prime reason for failure of Ta₅₃C₄₇ was due to the Cu diffusion through the grain boundaries with Cu activation energy of 0.9 eV. A study of the interfacial reactions in the Cu/TaC/Si before and after annealing was conducted to determine the failure mechanism of the barrier layer.²² The failure temperature was a function of thickness as 7, 35 and 70 nm TaC films failed at 600 °C, 650 °C and 750 °C respectively. The thicker TaC film integrity was compromised at a lower temperature of 600 °C due to the formation of amorphous Ta(O,C)ₓ layer at the Cu/TaC interface.

WCₓ was studied as a candidate diffusion barrier for Cu due to its high melting temperature of around 2785 °C²³ and low electrical resistivity.²⁴ A hexagonal closed pack W₂C phase was achieved by chemical vapor deposition at a growth temperature of 600°C. This growth temperature is fairly high keeping in mind future technology requirements where incorporation of low-κ materials will put an even more stringent temperature constraint.²⁵ Low temperature CVD process to deposit W₂C was demonstrated by Y. M.
Sun et.al. \textsuperscript{26} TEM studies revealed 5-6 nm W\textsubscript{2}C crystallites in an amorphous matrix with a W/C ratio of 2:1 until 450 °C. The Cu/W\textsubscript{2}C/SiO\textsubscript{2}/Si stack remained intact after 400 °C annealing for 8-9 hours. Unfortunately, higher temperature annealing was not done in the study which would have revealed capacity of the diffusion barrier to withstand higher thermal stress. Room temperature sputter deposited WC\textsubscript{x} was tested as a candidate diffusion barrier for Cu on Si. \textsuperscript{24} Fifty nanometer WC\textsubscript{x} failed according to analytical results after annealing at temperatures higher than 650 °C for 30 min. Electrical measurements, however, lowered the failure temperature to 550 °C. At 700 °C, the metallurgical stability of the WC\textsubscript{x}/Si interface is compromised. W reacts with Si to form W\textsubscript{5}Si\textsubscript{3} at the WC\textsubscript{x}/Si interface. Cu diffuses through the barrier layer and possibly through defects in the barrier layer into the Si substrate to form Cu\textsubscript{3}Si phase. In as-deposited condition, 60% of the measured diodes fail with a leakage current of 10\textsuperscript{-9} A/cm\textsuperscript{2}. Also, 60% of the diodes fail after annealing at a temperature of 550 °C with a leakage current of 10\textsuperscript{-7} A/cm\textsuperscript{2}.

**Refractory Nitrides**

The activation energy for Cu to diffuse through grain boundaries is low making this the fastest diffusion pathway and killer of devices. A method to stop Cu diffusion is to block these super highways by “stuffing” them. Oxygen was used as a stuffing agent in TiN diffusion barriers used for Al metallization. Al reacts with O\textsubscript{2} and forms an aluminum oxide phase that hinders Cu from further diffusion. However, the same concept could not be applied to Cu. \textsuperscript{3} Nitrogen is a good stuffing agent that can solve the purpose. Excess nitrogen in the film moves out to the grain boundaries and stuffs them. Cu diffusing through the grain boundaries experiences a repulsive force from the nitrogen thus stopping it from diffusing through the barrier film. \textsuperscript{27} Refractory nitrides are
interesting candidates for Cu diffusion barrier application due to their lower resistivity, high melting temperatures, lower heat of formation indicating better stability and the ability to block Cu diffusion by stuffing the grain boundaries by nitrogen. Some of the binary refractory nitrides investigated for Cu diffusion barrier applications are Ti, Ta, W and Hf based which will be discussed further in detail.

TiN was extensively used as a diffusion barrier for Al based metallization. Considerable effort was made to utilize the existing knowledge and processing methods for Cu based metallization as well. However, TiN deposited by both PVD and CVD methods resulted in a columnar grain structure in which grain boundaries run through the entire thickness of the barrier film. These columnar grain boundaries provide easy pathways for Cu diffusion and subsequent reaction with Si to form silicides. The properties of TiN films greatly depend on the deposition conditions which affect the microstructure, density and other relevant barrier properties of the film. The resistivity values range from 20 – 2000 µΩ-cm and density ranges from 3.2 – 5.0 g/cm³. A comparative study of different deposition methods and conditions to deposit TiN films was done by Park et al. Porous films have lower densities making them susceptible for impurities like oxygen which alter the diffusion barrier properties. The TiN films failed in the temperature range of 500 – 750 ºC depending on the film properties, 500 ºC being for CVD deposited films having lowest density and 750 ºC being for sputter deposited films having highest density. Atomic layer deposition techniques were also tried for TiN barrier deposition with focus on the influence of microstructure, resistivity and impurity content on film barrier properties. However, the barrier film failed after annealing at 500 ºC for 1 hr. The major drawbacks of CVD based techniques are unwanted C and O
impurities, particulate generation, high deposition temperatures, and uncontrolled thickness variations across the surface.

WNₓ is also an attractive candidate for Cu diffusion barrier applications due to its low resistivity and the ability to be deposited as an amorphous phase. Due to the absence of grain boundaries, Cu diffusion is hindered or slowed. However, the phase of WNₓ mainly governs the barrier properties. A tungsten rich WNₓ (x ≤ 0.5) phase tends to dissociate at temperatures as low as 450 °C into W and W₂N leading to barrier failure by diffusion of Cu through the grain boundaries due to lower recrystallization temperatures. A nitrogen rich WNₓ phase (x = ≥ 1) tends to be amorphous and remain amorphous for higher temperatures, but the gain is traded off with higher resistivity. Uekubo et al demonstrated the feasibility of W₂N as a diffusion barrier, as compared to W and WN, and showed that 8 nm W₂N was able to stop Cu diffusion in Si until 600 °C for 30 min. Failure of the diffusion barrier was due to recrystallization and grain boundary formation. An array of deposition methods have been tried to deposit WNₓ like sputtering, inorganic CVD, plasma-enhanced CVD, metal-organic CVD, and ALD.

TaN is being currently used for Cu diffusion barrier applications due to its high melting temperature and thermal stability. Among the various phases of Ta-N, stoichiometric TaN has a melting temperature of 3087 °C and heat of formation (ΔH_f = -120 kJ/mol) making it more stable than Ta₂N which has a melting temperature of 2050 °C and heat of formation of ΔH_f = -98 kJ/mol. Chemical vapor deposition of tantalum nitride results in an insulating tetragonal Ta₃N₅ phase which is not suitable for diffusion barrier applications. A bi-layer structure of Ta/TaN is currently being used
to overcome the obstacle of adhesion problem of TaN. TaN does not adhere well to Cu but it does adhere with SiO₂. In case of Ta, it adheres well to TaN but not with SiO₂ and is not an effective diffusion barrier by itself. Also, TaN helps nucleate Ta in the α-Ta phase, which has a BCC structure and a resistivity of ~15-30 µΩ·cm, as compared to when Ta is directly deposited on SiO₂ where it nucleates in the β-Ta phase, with a resistivity of ~150-220 µΩ·cm. However, with device dimensions shrinking, conformality of high aspect ratio is very critical. PVD has been used until now for deposition of liner and Cu seed layer, with ionized PVD (I-PVD) being the latest in the technology that has been able to extend the functionality to lower dimensions. However, with future technology constraints, the liner thickness should be less than 10 nm. Since the overall liner-Cu seed layer thickness requirement decreases, either some major modifications have to be done to the I-PVD process or a switch to a better conformal process like atomic layer deposition (ALD) has to be adopted.

Ternary Diffusion Barriers

The activation energy required for Cu diffusion through the grain boundaries is low. Binary diffusion barriers have been investigated in which one of the elements, like nitrogen, “stuffs” the grain boundaries and disallows Cu diffusion by blocking. However, at higher temperatures the binary compound recrystallizes, forming parasitic grain boundaries that should be avoided. Another way to solve the problem of creating a diffusion barrier for Cu is to form an amorphous matrix that acts as a diffusion barrier and remains amorphous (not recrystallized) when annealed at higher temperatures. This can be achieved by adding a third element into the binary matrix. This addition frustrates the binary lattice structure and delays or avoids the recrystallization process when it is annealed at higher temperatures. Considerable research has been done on amorphous
ternary nitride diffusion barriers for Cu metallization. Most of the research work has been
done by incorporating Si, B or C as the third element in the binary matrix of refractory
nitrides. Some of the work will be discussed below.

TiSi$_x$N$_y$ were initially studied as Ti based liners and used as diffusion barriers for
Al metallization. Amorphous TiSi$_x$N$_y$ is attractive due to the absence of grain boundaries.
The properties of diffusion barriers depend on the method of deposition and its chemical
composition. Chemical vapor deposited TiSi$_x$N$_y$ films (25 nm thick) were studied as
candidate diffusion barriers for Cu.$^{51}$ The barrier failed after annealing at temperatures
higher than 700 °C for 30 min. Unfortunately, the barrier resistivity is too high (800 μΩ-
cm) for applications. MOCVD deposited TiSiN films were also investigated as diffusion
barriers for Cu.$^{52}$ The deposition steps involved a H$_2$/N$_2$ plasma treatment to increase the
density of the film. Comparison of films that were plasma treated and not plasma treated
was done. Films were characterized by secondary ion mass spectroscopy (SIMS) and
Secco etch method for diffusion barrier failure. Secco etch revealed that failure occurred
in films that were not plasma treated after annealing at 550 °C for 1 hr. For plasma treated
films, failure occurred after annealing at 600 °C for 1 hr. SIMS detected Cu diffusion in
the sample that was not plasma treated at 450 °C, whereas Secco etch revealed etch pits
in the same sample after annealing at 550 °C.

TaSi$_x$N$_y$ (x=1.4, y=2.5) films with different thickness (t= 5-40 nm) were sputter
deposited on Si by Lin et al.$^{53}$ to evaluate their diffusion barrier characteristics. Electrical
measurements on a p$^+$n diode structure revealed failure of 5 nm TaSi$_x$N$_y$ after annealing
at 500 °C for 30 min. The TaSi$_x$N$_y$ structure remained amorphous even after annealing at
800 °C, which is a good indicator that addition of Si to the TaN matrix was effective in
keeping the lattice structure amorphous. Failure of the diffusion barrier was due to Cu diffusion through localized defects into Si. The nitrogen content plays an important role in determining the diffusion barrier characteristics. With the increase in the nitrogen content, the diffusion barrier properties are enhanced as the nitrogen helps in preventing formation of TaSi$_2$ phase after annealing at higher temperatures in Ta-Si-N films.$^{54}$

There has been some research on WSi$_x$N$_y$ diffusion barriers for Cu metallization. LPCVD deposited WSi$_x$N$_y$ shows promise as a diffusion barrier compared to Ta and Ti counterparts.$^{55,56}$ Efforts are also made to take advantage of good conformal coverage obtained using the CVD deposition process while achieving superior diffusion barrier properties similar to those achieved by PVD methods.$^{56}$ Researchers have worked on using boron or carbon as a third element in the binary matrix.$^{57}$ W-B-N seems to be a better diffusion barrier compared to W-Si-N due to its lower resistivity while having the same performance as W-Si-N.$^{57}$
Sputtering

Sputtering is a physical vapor deposition technique where incident ions remove atoms (sputter) from the target surface by momentum transfer process. Sputtering was discovered in the 19th century by Grove and Pulker and reported by Wright in 1877. The number of atoms removed from the target surface by a single incident ion is called the sputtering yield. The sputtering yield depends on the mass of the atoms (target) and ions, bombardment energy of the incident ions, angle of incidence and binding energy of the atoms in the target material. Table 3-1 shows the sputter yields of different ions when bombarded on the target materials as indicated. Different classifications are used to define a particular sputtering technique depending on the type of sputtering configuration and also on the type of a reactive species inside the deposition chamber. As a result, there are different sputtering techniques like DC sputtering, RF sputtering, triode sputtering, magnetron sputtering and “unbalanced” magnetron sputtering. Depending on the absence or presence of a reactive species, it can be called non-reactive or reactive sputtering, respectively. The energy transfer taking place due to collision between two hard spheres can be given as:

\[
\frac{E_i}{E_i} = \frac{4M_sM_i\cos^2\theta}{(M_i + M_s)^2}
\]
where $E_t$, $E_i$ are the energy of the target and incident particle respectively, $M_t$, $M_i$ are the mass of the target and incident particle and $\theta$ is the angle of incidence with respect to the surface normal of the target.

Currently, almost any target material can be deposited by sputtering due to the latest advancement in technology. Co-sputtering can be carried out to deposit a compound on the substrate by sputtering two targets simultaneously or by sputtering a single target in a reactive atmosphere or by using a compound target in an inert atmosphere. Some of the advantages of the sputtering deposition process are given below.

- Ability to coat large areas with uniform thickness
- Low-temperature deposition process
- Flexibility of target materials choice including insulators and semiconductors
- Target composition is replicated in the composition of deposited film.
- Good adhesive property obtained in the deposited films
- Sputtering can be up, down or sideways
- Reactive sputtering possible
- Reproducibility
- Environmentally friendly process technology
- Can be easily scale up for commercial production

The two major kind of sputtering configurations conventionally used are DC and RF magnetron sputtering. They are described in detail below.

**DC Magnetron Sputtering**

In a DC sputtering process, the target is the cathode and either the substrate or the chamber walls are the anode. A very high negative DC voltage (several kV) is applied to the cathode. Ar gas is supplied in the chamber to create plasma. Ionized Ar$^+$ ions are accelerated to the cathode, bombarding the surface and sputtering atoms from the cathode surface. They also generate secondary electrons that ionize the gas atoms creating increased amounts of Ar$^+$ ions. This increases the probability of collisions at the cathode surface. A circular magnet (magnetron) below the target traps the electrons emitted from
the cathode surface to remain near the cathode. These electrons hop in a cycloid fashion on the target surface due to \((E \times B)\) forces acting on it. As the electrons are trapped near the surface region, the probability of creating more \(\text{Ar}^+\) ions increases which increases the sputtering yield. Another advantage of using the magnetron source is that low gas pressures can be used inside the chamber to maintain a stable plasma. Since the gas pressure is low, internal gas collisions decrease leading to higher yields of sputtering target material. As there is less chance of internal gas collisions, the sputtered materials impact the anode surface with a high kinetic energy. Figure 3-1 shows a schematic DC sputtering chamber set-up. The disadvantage of DC sputtering is that the cathode material needs to be conductive. Insulating materials cause a charge build-up near the surface quenching the plasma.

**RF Magnetron Sputtering**

The major difference between DC and RF magnetron sputtering is the source. In radio frequency (RF) sputtering, an RF source is used, typically 13.56 MHz. A matching network is used to optimize power transfer from the RF source to the discharge and a blocking capacitor is used in the circuit to create a DC bias. With the use of an RF source, sputtering of insulating targets has been made possible. Figure 3-2 shows a schematic set-up of a RF sputtering. The sputtering process is similar to DC sputtering. Low gas pressures can be used for RF sputtering. One consideration during RF sputtering is to use target materials with high thermal conductivity. Low thermally conductive materials develop a high enough thermal gradient due to the sputtering process to cause brittle fracture of the target.
Characterization

Characterization is an important part of research. It helps in identifying physical, electrical, magnetic, optical and chemical properties of the samples that helps in understanding the fundamental behavior of the material being studied. Some of the characterization techniques used in this study are discussed below.

X-ray Diffraction

X-ray diffraction (XRD) is one of the most versatile non-destructive technique used to date to identify the crystalline phases and crystallinity of the sample. Advances in X-ray diffraction and understanding the basic physics between the interaction of X-ray’s and the sample have given access to a plethora of information. Currently, information regarding strain, in-plane epitaxy, defect structure, film thickness etc. can easily be obtained from the constructive and destructive interference of X-rays with the sample.

Figure 3-3 shows a basic X-ray diffraction set up. Cu Kα radiation is generated and impinged on the sample. This radiation undergoes constructive or destructive interference after reflecting from the sample depending on the path difference between the incident and reflected X-rays. Constructive interference will cause a peak at a particular 2θ angle according to Bragg’s rule as given below:

\[ n \lambda = 2d \sin \Theta \]

where \( \lambda \) is the wavelength of X-ray (Cu Kα radiation 1.54 Å), \( d \) is the distance between two consecutive (hkl) planes and \( \Theta \) is the angle between the incident X-ray and the sample surface. In a cubic system the d-spacing is given as:

\[ d_{hkl} = \frac{a_o}{\sqrt{h^2 + k^2 + l^2}} \]

where \( a_o \) is the lattice constant.
For a single crystal, there are only specific orientations that satisfy the Bragg’s law. Diffraction peaks from these planes appear in the diffraction pattern. However, for a polycrystalline film having differently oriented grains, diffraction peaks appear when those grains meet the diffraction conditions.

The full width at half maximum of an X-ray diffraction peak gives information about the grain size. The relationship is called the Scherrer equation:

\[ t = \frac{0.9 \lambda}{BCos\Theta} \]

where \( t \) is the grain size, \( \lambda \) is the wavelength of X-ray, \( B \) is the full width at half maximum and \( \Theta \) is the Bragg angle.

**Auger Electron Spectroscopy**

Auger electron spectroscopy is an excellent technique for surface and sub-surface analysis. It is a highly sensitive technique as it probes only from few angstroms to few nanometers in depth from the surface. Usually, an electron beam is used to probe and excite electrons in the atoms of the sample. As the core shell electron leaves the atom, it is in an excited state. A higher shell electron fills the core shell vacancy and the energy emitted by this transition is transferred in exciting another electron to emit from the atom which is called the Auger electron. Depending on the kinetic energy of the electron measured, the binding energy of the emitted Auger electron is calculated by the following equation:

\[ K.E = (E_K - E_L) - E_L \]

where \( K.E \) is the kinetic energy of the Auger electron, and \( E_K \), \( E_L \) and \( E_L \) are the energies of the K and L shells, respectively.
A total of three electrons are needed in order to fulfill an Auger transition. As a result, elements like H and He are undetectable with AES. Suppose an electron from the K-shell of an element is removed by photons or electrons. The electron from the L shell fills up this vacancy with enough energy left to emit an electron from the L shell. This is called a KLL transition. Similarly, now higher shells would fill up the L shell and would result in a LMM type of transition. The Auger equipment can be combined with an ion gun, which would sputter the sample and expose a new surface to be examined. A group of all those data points would give the depth profile characteristics of the sample studied. This is therefore a very good method to study interfaces and diffusion profiles of elements inside the sample. The following information can be obtained from an Auger profile.

- Type of elements
- Amount percentage of the elements
- Chemical state of elements
- Valence band density of states

**X-ray Photoelectron Spectroscopy**

As the name suggests, a high energy photon source (X-ray) is bombarded on the surface of the sample. It ejects a core shell electron in the atom transferring it to an excited state. The atom returns back to ground state as the higher shell electron fills up the core shell vacancy, emitting the excess energy in the form of photon or by emitting an Auger electron. The kinetic energy of the emitted core shell electron is detected which gives a plethora of information about the sample. The expression of kinetic energy measured is as below:

\[ K.E = h\nu - B.E \]
X-ray photoelectron spectroscopy is a very sensitive technique for surface analysis as it probes only few angstroms from the surface. This is because only few electrons near the surface are able to escape the sample while most of the electron excited by the x-ray lose their energy by collisions with atoms and are not able to exit the surface. The flux of electrons able to exit the surface of the sample without being scattered \( (I_d) \) is given by the following expression:

\[
I_d = I_o \exp\left(\frac{-d}{\lambda_c \sin \Theta}\right)
\]

where \( I_o \) is the original flux of electrons generated at depth \( d \), \( \lambda_c \) is the inelastic mean free path of electrons, \( \Theta \) is the angle of electron emission.

As the binding energy of an electron is a characteristic of an atom, elemental information can be obtained by XPS. Also, a general trend is that if the charge on an atom increases, so does the binding energy of the electron. As a result, the valence state of the atom can be known. Amount percentage of the element present can be determined by peak intensity. The valence electrons participate in the bonding process and thus compound information can also be known from XPS data analysis. A depth profile is possible. However, it is very time consuming.

**Scanning Electron Microscopy and Energy Dispersive Spectroscopy**

Scanning electron microscopy is used for surface and cross-section imaging, topographical information and compositional information of a binary alloy system. An electron beam strikes the sample surface and various kinds of elastic or inelastic interactions occur resulting in emission of electrons. The electrons emitted out of the sample are of generally two types

- Secondary electrons
- **Back-scattered electrons**

When the incident primary beam of electrons impinge on the sample surface, they can undergo inelastic scattering by colliding with electrons of the sample, transferring some of its energy to them which exit the surface of the sample depending on the amount of energy transferred. If sufficient energy is transferred, then electrons from the sample exit the surface and are collected by the detector. Electrons with energy of less than 50 eV are classified as secondary electrons. The primary beam can also undergo elastic scattering with the nucleus of the atom where transfer of energy is null or very small. These electrons have high energy and can exit the surface easily. The amount of back-scattered electrons depends on the atomic number of the atom. A higher atomic number (Z) yields a higher amount of back-scattered electrons which results in increased brightness of the image. However, for a constant Z, the back scattering yield remains unchanged if the primary beam energy is above 5 keV. The secondary electron yield does not depend much on the Z. The backscattering and secondary electron images can be used to complement each other in seeking information.

Since the primary beam has high energy, it can remove core electrons from the atom thus exciting it. The atom goes back into the ground state by filling the core vacancy by an electron from a higher orbital. The excess energy can either be emitted in the form of a photon or an Auger electron. The emitted photon can be detected and used for further study depending on its energy. This method is called as energy dispersive spectroscopy (EDS). Since the emitted photon is characteristic of the atom from which it emits, elemental information of the sample can be known. An elemental map of the surface can be created with use of today’s instruments. Quantification of the amount of a
particular element can be carried out depending on the peak intensity and using ZAF correctional factors, where \( Z \) is atomic number, \( A \) is absorption and \( Z \) is secondary x-ray fluorescence.

**Atomic Force Microscopy**

The topography and roughness of thin films can be determined using atomic force microscope. The probe in an AFM is a sharp tip created at the end of a cantilever beam having a spring constant of 0.1-1.0 N/m. As the tip is brought near the surface of the sample, van der Waals forces become active between the tip and sample surface atoms resulting in the deflection of the tip. This deflection is monitored and measured by a laser striking the back of the cantilever beam which plots the surface of the sample as the tip is moved across the sample. A general schematic of the AFM set up is show in Figure 3-4. The tip can be rastered over the sample surface and a 3-D plot can be obtained with nanometer spatial resolution. Lower spatial resolution can be obtained if the scanned area is reduced and slow scans are used. AFM is operated in two modes namely contact mode, where the tip is in contact with the sample surface, and tapping mode, where the tip is vibrated over the sample surface. The tapping mode is particularly useful for analyzing soft samples like polymers.

**Transmission Electron Microscopy**

The wave nature of electron was first theorized by Louis de Broglie in 1925. The term “electron microscope” was first used by Knoll and Ruska in 1932 when they build the first electron microscope and obtained images. TEM is an excellent tool to obtain high resolution lattice images and diffraction patterns of electron transparent samples. The high spatial resolution is due to the fact that high energy electrons are used to probe
the sample which have extremely small wavelength (on the order of Å). The wavelength of the electron depends on the energy as per the expression:

\[ \lambda \approx \frac{1.22}{\sqrt{E}} \]

where \( \lambda \) is wavelength of electrons in nm, \( E \) is energy of electrons in eV.

A typical TEM operates at 200 to 400 keV. A highly coherent beam of monochromatic electrons is focused on the sample using a series of electromagnetic lenses. Some of the possible interactions between sample and the electrons are shown in Figure 3-5. For transmission electron microscopy, information is collected below the sample from the deflected and un-deflected electrons on a fluorescent screen to form images or diffraction pattern depending on where it’s focused below the sample. Unlike scanning electron microscope, the entire sample is in focus all the time as along as its electron transparent. Some of the drawbacks of TEM are as follows

- Limited sampling volume
- Complex data interpretation
- Beam damage
- Sample preparation

Electron diffraction is a very important quantitative characterizing technique to analyze a sample. Information from a particular area of a sample can be obtained by using selected area aperture (SAD) which focuses only on the area of interests. Other information, like defects (line and point defects), burger’s vectors, 3-D loops, crystal orientation, orientation relationship between film and substrate or multilayer films and sample crystallinity can be obtained.
**Focused Ion Beam**

The samples required for TEM in this study were prepared by focused ion beam (FIB) technique. Focused ion beam uses an electron beam for imaging and a gallium ion source for imaging as well as milling. The reason for using Ga+ ions for milling is because the mass of Ga is approx. 127000 times that of electron and so provides a huge momentum transfer. The Ga source is heated to a liquid on a tip and Ga+ ions are extracted and focused on the sample by applying a bias. The ion source is also used for milling purposes to prepare an electron transparent sample. Platinum is used to avoid milling the area of interest. Once the sample is electron transparent it is set free and transferred using glass rods to a grid for TEM analysis. Some of the advantages of using FIB as compared to conventional TEM sample preparations are

- Selected feature can be prepared for analysis
- Excellent control over the cross-section to be prepared
- Insulating samples can also be used
- No mechanical damage in the area of interest

**Van der Pauw Measurement and Four Point Probe**

Van der Pauw technique is used to measure the resistivity of the sample in the semiconductor industry due to its ease and simplicity. The technique doesn’t depend on the shape of sample. Four ohmic contacts are prepared on the four corners or periphery of a sample. An acceptable version of sample geometry for this measurement is shown in Figure 3-6. As shown in the Figure3-7, a DC current is applied between contacts 1 and 2 \((I_{12})\) and voltage is measured along contacts 3 and 4 \((V_{43})\). This resistance \(R_A\) is measured as follows:

\[
R_A = \frac{V_{43}}{I_{12}}
\]
This is followed by another measurement by applying DC current between contacts 1 and 4 ($I_{14}$) and voltage is measured between contacts 2 and 3 ($V_{23}$). This gives resistance $R_B$ as given by the following equation:

$$R_B = \frac{I_{14}}{V_{23}}$$

The sheet resistance $R_S$ is related to $R_A$ and $R_B$ through the following equation:

$$\exp\left(\frac{-\pi R_A}{R_S}\right) + \exp\left(\frac{-\pi R_B}{R_S}\right) = 1$$

The bulk resistivity can be calculated as per the expression:

$$\rho = R_S d$$

where $d$ is thickness of the film

The sheet resistance of copper before and after annealing was measured by four point probe. A schematic set-up of four point probe is as shown in Figure 3-8. The DC current ($I$) is supplied through the extreme probes and corresponding voltage ($V$) is measure by the inside probes. The sheet resistivity $\rho$ of a thin film of thickness ($d$) is calculated by using the following equation:

$$\rho = \frac{\pi d}{\ln 2} \left(\frac{V}{I}\right)$$

And the sheet resistance ($R_S$) is given by

$$R_S = k \left(\frac{V}{I}\right)$$

where $k$ is the geometric factor and its value is 4.53 for semi-infinite thin film.
Table 3-1. Sputtering yields of different ions.

<table>
<thead>
<tr>
<th></th>
<th>Be (9)</th>
<th>Al (27)</th>
<th>Si (28)</th>
<th>Cu (64)</th>
<th>Ag (106)</th>
<th>W (184)</th>
<th>Au (197)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>He⁺ (4 amu)</strong></td>
<td>0.24</td>
<td>0.16</td>
<td>0.13</td>
<td>0.24</td>
<td>0.2</td>
<td>0.01</td>
<td>0.07</td>
</tr>
<tr>
<td><strong>Ne⁺ (20 amu)</strong></td>
<td>0.42</td>
<td>0.73</td>
<td>0.48</td>
<td>1.8</td>
<td>1.7</td>
<td>0.28</td>
<td>1.08</td>
</tr>
<tr>
<td><strong>Ar⁺ (40 amu)</strong></td>
<td>0.51</td>
<td>1.05</td>
<td>0.5</td>
<td>2.35</td>
<td>2.4-3.1</td>
<td>0.57</td>
<td>2.4</td>
</tr>
<tr>
<td><strong>Kr⁺ (84 amu)</strong></td>
<td>0.48</td>
<td>0.96</td>
<td>0.5</td>
<td>2.35</td>
<td>3.1</td>
<td>0.9</td>
<td>3.06</td>
</tr>
<tr>
<td><strong>Xe⁺ (131 amu)</strong></td>
<td>0.35</td>
<td>0.82</td>
<td>0.42</td>
<td>2.05</td>
<td>3.3</td>
<td>1.0</td>
<td>3.01</td>
</tr>
</tbody>
</table>
Figure 3-1. Schematic diagram of DC sputtering system with parallel plate discharge.

Figure 3-2. Schematic diagram of RF sputtering system with a capacitive, parallel plate discharge.
Figure 3-3. Schematic diagram of X-ray diffraction set-up.

Figure 3-4. Schematic set-up principle of an atomic force microscope.
Figure 3-5. Interaction output between a high-energy electron beam and thin specimen.

Figure 3-6. Sample geometries for Van der Pauw measurements.
Figure 3-7. Schematic diagram of Van der Pauw configuration for measurement of $R_A$ and $R_B$ resistances, respectively.

\[ R_A = \frac{V_{43}}{I_{12}} \]

\[ R_B = \frac{V_{14}}{I_{23}} \]
Figure 3-8. Schematic diagram of four point probe measurement.
CHAPTER 4
PROPERTIES OF W-Ge-N AS A DIFFUSION BARRIER MATERIAL FOR COPPER

Introduction

For present and future integrated electronic technologies, the use of barrier materials to enable materials integration is becoming increasingly important. In current Si technology, the push for higher circuit density and low RC time delays has made copper the material of choice for interconnects due to its higher resistance to electromigration and lower resistivity as compared to Al. Unfortunately, Cu is known to show poor adhesion to most dielectric materials and rapidly diffuses into SiO$_2$ and Si. This obviously degrades the electrical properties of devices$^{58}$, creating the need for intermediate layers that provide a barrier to Cu diffusion.

When considering the role of microstructure in diffusion processes, amorphous materials are generally better suited than polycrystalline phases, as grain boundaries provide high diffusivity pathways for Cu diffusion through the barrier material. Among the material systems currently being developed, binary nitrides, such as TaN$^{59,60}$ and WN$_x$$^{61,62}$ are receiving significant attention. For Ta-based barriers, the Ta-Cu phase diagram indicates that Ta and Cu are effectively immiscible even at their melting temperature. Unfortunately, recrystallization of TaN films occurs at approximately 600 $^\circ$C, which is relatively low for diffusion barrier applications. WN$_x$ is also an interesting candidate as it is relatively easy to synthesize as an amorphous film. In this case, the nitrogen content in WN$_x$ films has a significant influence on its diffusion barrier properties. For WN$_x$ films with low nitrogen content, the recrystallization temperature
can be on the order of 450 °C. Higher nitrogen content yields higher recrystallization temperature. WNₓ films grown by physical vapor deposition have been reported to exhibit a recrystallization temperature as high as 600 °C. Yet, the primary mode of failure remains diffusion through grain boundaries that form during heat treatments.

One approach to achieve higher recrystallization temperature is to consider ternary compositions. The additional element added to the refractory metal-nitride composition frustrates the recrystallization behavior, rendering a stable amorphous mixture at high temperatures and thus minimizing grain boundary diffusion. While failure of ternary diffusion barriers still occurs through grain boundaries formed due to decomposition and recrystallization of the film, this process generally takes place at higher processing temperature. For this reason, there is significant interest in ternary nitride alloys, such as Ta-Si-N, W-Si-N, W-B-N, and Ta-W-N due to their high recrystallization temperature as compared to the binaries. In this study, we report on the diffusion barrier properties of W-Ge-N thin films for Cu metallization. The W-Ge-N alloy is chemically similar to W-Si-N, should be more resistant to recrystallization than WNₓ, and may prove attractive for integration with SiGe or Ge devices.

**Experimental Details**

The W-Ge-N films were deposited at the rate of 8.64 nm/min on thermally grown SiO₂ (630 Å)/n-type (100) Si substrates by reactive sputter deposition. For comparison, WNₓ films were also deposited under similar conditions. The substrates were sequentially cleaned with trichloroethylene, acetone, and methanol for 5 min each in an ultrasonic bath. The substrates were then loaded into the multi-target R.F. sputter deposition system via a load-lock. The base pressure of the sputtering chamber was 7 x 10⁻⁶ Torr. Typical forward sputtering power for the W and Ge targets was 200 W and 100 W, respectively.
Nitrogen was incorporated into the films by leaking a mixture of Ar and N₂ at the ratio of 1 : 0.9 into the chamber at a fixed chamber pressure of 11.5 mTorr. The thickness of the films was measured using a stylus profilometer. In the experiments reported here, film thickness was maintained in the range 300 to 360 nm. All targets were pre-sputtered before deposition to remove any contaminant present on the target surface.

To assess the compatibility and diffusion properties of W-Ge-N with respect to Cu metallization, the nitride layer deposition was followed by in situ deposition of a Cu film 90 nm thick. During Cu deposition, Ar gas was used as the sputter deposition gas at a fixed chamber pressure of 15 mTorr. After deposition, the individual samples were annealed in a separate vacuum chamber with a base pressure of 4 x 10⁻⁵ Torr at 400, 600 and 800 °C for 1 hr to study and compare the diffusion barrier properties of the films. The crystallinity of films and formation of any intermetallic compounds by annealing were characterized by X-ray diffraction (XRD) measurements. Resistivity was measured by the Van der Pauw method, while Auger electron spectroscopy was used to characterize the Cu diffusion profile in the nitride films. Energy dispersive spectrometry (EDS) was used to determine the composition of the films.

**Results and Discussion**

Initial studies focused on the crystallinity of the W-Ge-N films, both as-deposited and after high temperature annealing. Figure 4-1 shows XRD spectra of WNₓ and W-Ge-N films, both as-deposited and annealed at 400, 600, and 800 °C. The data show that films of both compositions are amorphous in the as-deposited condition. For the WNₓ films [Fig.4-1(a)], recrystallization is clearly evident in the XRD pattern for annealing temperature of 400 °C and higher. The onset of grain structure will provide undesired diffusion paths via the grain boundaries. In contrast, the W-Ge-N film shows no evidence
of recrystallization upon annealing at 400 or 600 °C. The XRD data [Fig.4-1(b)] for W-Ge-N films annealed at 400 and 600 °C show no peaks related to the nitride material. Only at 800 °C do polycrystalline peaks appear. The addition of Ge to the W-N solid presumably frustrates crystallization, thus rendering the films amorphous for more severe annealing conditions relative to WNₓ. It should also be noted that the W-Ge-N film was far less susceptible to oxidation via ambient atmosphere exposure as compared to WNₓ. This may prove advantageous in terms of device processing.

To assess the behavior of these films as diffusion barriers to Cu, the chemical profile of the annealed structures was determined by Auger electron spectroscopy. Figure 4-2 shows the depth profiles for the WNₓ film (a) as-deposited and upon annealing at (b) 600 °C, and (c) 800 °C. For the as-deposited diffusion barrier layer in Figure 4-2(a), there is a well-defined interface between Cu and WNₓ and the SiO₂ buffer layer is evident. In contrast, after annealing at 600 °C, the Cu signal is seen throughout the barrier layer and into the SiO₂/Si. This is in agreement with the XRD data, which show the formation of grain structure upon annealing at a temperature of 600 °C. Annealing at 800 °C [Fig. 4-2(c)] yields a Cu diffusion profile similar to that for the 600 °C anneal. There is also some apparent intermixing of W and SiO₂ seen at the WNₓ/SiO₂ interface in the Auger depth profiles of the annealed samples, which is perhaps related to a change in surface roughness. The intensity of the nitrogen profile decreases slightly as we increase the annealing temperature to 800 °C. This may reflect the decomposition of WNₓ and liberation of N₂ from the films under those conditions. This is not unexpected as Affolter et al. ⁶⁹ have shown that nitrogen is liberated from W-N alloy thin films when annealed at temperatures above 700 °C.
The chemical composition of Cu/W-Ge-N/SiO$_2$/Si structures was also examined with Auger electron spectrometry. Figure 4-3 shows the chemical depth profiles in (a) as-deposited W-Ge-N and after annealing at (b) 600 °C and (c) 800 °C. In Figure 3(a), distinct interfaces at the Cu/W-Ge-N and W-Ge-N/SiO$_2$ boundaries show that there is no Cu diffusion during growth. At an annealing temperature of 600 °C, the interfaces and layers remain distinct, consistent with no or minimal diffusion of Cu through the barrier layer. These results suggest that W-Ge-N films possess superior diffusion barrier properties as compared to WN$_x$. At an annealing temperature of 800 °C, Cu is observed in the diffusion barrier as seen for the WN$_x$ film. Again, Cu diffusion correlates with the appearance of grain structure in the film (i.e., (111) reflection of $\beta$-W$_2$N in the XRD pattern). This is also consistent with N loss suggested by the AES sputter profile, and thus its ability to stuff the diffusion pathways.

The resistivity of the W-Ge-N films was measured using the Van der Pauw method. In general, the resistance of the as-deposited W-Ge-N films is higher than WN$_x$. As shown in Figure 4-4(a), the resistivity of WN$_x$ and W-Ge-N decreases as the annealing temperature increases. While the resistivity of WN$_x$ decreases upon annealing at 400 °C, the resistivity for W-Ge-N remains relatively unchanged after annealing at 400 °C. There is a progressive decrease in resistivity for both materials with further increase in annealing temperature. The change in resistivity correlates with onset of grain structure, suggesting electron transport across grain boundaries. The decrease may also be due to the loss of nitrogen from the films. The resistivity of WN$_x$ is two orders of magnitude lower than W-Ge-N at 800 °C reflecting the robustness of W-Ge-N film, for which increased decomposition temperature slows nitrogen evolution. Figure 4-4(b)
shows the resistivity of W-Ge-N films vs. sputtering power to the Ge target. Clearly, the resistivity scales with Ge content in the film.

**Conclusion**

In conclusion, the diffusion barrier properties of W-Ge-N thin films have been investigated. X-ray diffraction shows recrystallization of WN\textsubscript{x} films at an annealing temperature of 400 °C and higher, while W-Ge-N films show recrystallization peaks only at an annealing temperature of 800 °C, suggesting that the addition of Ge frustrates the recrystallization behavior of WN\textsubscript{x}. The AES data show complete Cu diffusion across the WN\textsubscript{x} layer for an annealing temperature of 600 °C, while for W-Ge-N films the Cu/W-Ge-N and W-Ge-N/SiO\textsubscript{2} interfaces remain distinct at that temperature, indicating that W-Ge-N has better diffusion barrier properties. The resistivity of both films decreases with increasing anneal temperature, with the resistivity of WN\textsubscript{x} two orders of magnitude lower than W-Ge-N after annealing at 800 °C. This behavior is consistent with enhanced stability of W-Ge-N with respect to film decomposition and subsequent nitrogen evolution.
Figure 4-1. X-ray diffraction patterns of as-deposited and annealed films at different temperature of (a) WNₓ films (b) W-Ge-N films.
Figure 4-2. AES depth profiles of Cu/WNₓ/SiO₂/Si (a) as-deposited (b) annealed at 600 °C/1 hr (c) annealed at 800 °C/1 hr.
Figure 4-3. AES depth profiles of Cu/W-Ge-N/SiO2/Si (a) as-deposited (b) annealed at 600 °C/1 hr (c) annealed at 800 °C/1 hr.
Figure 4-4. Resistivity vs. annealing temperature (a) for W-Ge-N and WN_x films. Also shown (b) is the resistivity as a function of sputter target power for the Ge and W targets.
CHAPTER 5
INVESTIGATION OF W-Ge-N DEPOSITED ON Ge AS A DIFFUSION BARRIER
FOR Cu METALLIZATION

Introduction

The progression to ever-decreasing semiconductor device dimensions brings with it new challenges for material integration. As SiGe-based microelectronic technology moves toward a 45 nm technology node, there is an imminent need to replace Al interconnects. Cu is an attractive candidate because of its low resistivity and high resistance to electromigration as compared to Al. Replacing Al/SiO₂ interconnect technology with Cu/low-k dielectrics can yield a large reduction in RC time constant delay, providing for a significant motivation to carry out the replacement search for Al. Unfortunately, Cu has known problems with adhesion to low-k materials. It also has a high diffusion rate in silicon and germanium creating deep level traps in Si and a shallow level in Ge located at 0.04 eV near the valence band.

Diffusion barriers are needed to achieve integration of Cu with Si-Ge and Ge. In diffusion barrier materials the diffusion pathways are interstices, vacancies and grain boundaries. Diffusion through grain boundaries is fastest and more prominent. By “stuffing” the grain boundaries with selected dopants, diffusion can often be hindered. In general, amorphous materials are highly preferred due to the absence of grain boundaries. Common diffusion barrier materials studied for Cu metallization are refractory metal-nitrides, which include TaN, TiN, HfN and WNₓ, However, these have limited utility as viable diffusion barriers because of their relatively low recrystallization
temperatures. Recrystallization of amorphous diffusion barriers can often be inhibited by the addition of a third element to the matrix. Previous results show higher recrystallization temperature for W-Ge-N as compared to WNₓ as the introduction of Ge effectively frustrates the matrix.⁸⁰

SiGe devices have higher mobility as compared to Si devices and the flexibility of band-gap engineering, thus being applicable in high speed electronics. The properties of the metal/SiₓGe₁₋ₓ contact layer is important for semiconductor device applications. Considerable research has been done on the chemical reactivity of metals, such as Co, Ti,⁷²,⁸² Pt,³⁄,⁸³ Pd,⁸⁴ and Cu⁸⁵ on SiGe. In most cases, it results in the formation of metal-Si, metal-Ge, or metal (SiₓGe₁₋ₓ) alloys in the temperature range of 400-600 °C. In particular, direct deposition of Cu on Si₁₋ₓGeₓ results in the formation of unstable Cu₃(Si₁₋ₓGeₓ) in the temperature range of 250-400 °C.⁸⁵ One solution could be to grow a metal-rich Cu₃Si or Cu₃Ge phase directly on Si₁₋ₓGeₓ. Unfortunately the Cu₃Si phase reacts with oxygen when exposed to air. The Cu₃Ge phase is more stable and less reactive with oxygen.⁸⁶ In general, the need to identify viable barriers of Cu integration with Ge-based structures persists. In this work, we report on the diffusion barrier properties of W-Ge-N thin films deposited on Ge for Cu metallization. The properties are compared to WNₓ deposited on Ge under similar conditions to evaluate its suitability and properties. Due to the ternary nature of this diffusion barrier, W-Ge-N is expected to have better recrystallization properties as compared to WNₓ.

**Experimental Details**

W-Ge-N films were deposited on p-type Ge (001) by reactive sputtering. The Ge substrates were cleaned by a standard procedure reported elsewhere⁷⁷ to remove any
organic residue or impurity on the surface. The substrates were loaded in the reactive sputter chamber with a base pressure of $3 \times 10^{-6}$ Torr via a load-lock. Nitrogen was incorporated in the film by flowing a mixture of N$_2$ and Ar at a ratio of 1:3 at a fixed pressure of 10 mTorr. Prior to deposition, all targets were cleaned by pre-sputtering by flowing Ar+N$_2$ in the chamber. Forward sputtering power for the W and Ge targets were 200 W and 100 W respectively. The deposition rate for W-Ge-N film on Ge was 10.2 nm/min under the above mentioned conditions. Thickness was measured by a stylus profilometer and was kept in the range of 50 to 300 nm.

Cu metallization was carried out in-situ after depositing W-Ge-N thin films to determine suitability as a diffusion barrier. Sputter deposition of Cu was carried out by flowing Ar gas at a fixed chamber pressure of 5 mTorr. After depositing the film stack, individual samples were separately annealed in the range of 400 °C – 700 °C in a tube furnace. Ar gas was flowed through the tube furnace at 65 sccm for at least 10 hours before starting the annealing to remove any residual air mixture. Typical annealing experiment was carried out for 1 hr to study the diffusion barrier properties of the film. X-ray diffraction was used to identify any intermetallic phases and access the crystallinity of the films after annealing. Cu diffusion profile through the film was determined by Auger electron spectroscopy (AES) and Energy dispersive spectrometry (EDS). Interface properties were determined by cross-section transmission electron microscopy (X-TEM).

**Results and Discussion**

Crystallinity and high temperature phase formation of the Cu/W-Ge-N/Ge film structure before and after annealing was determined by XRD. The XRD spectra for Cu/WN$_x$/Ge and Cu/W-Ge-N/Cu film structure is shown in Figure 5-1, both as-deposited
and annealed in the temperature range of 400 – 700 °C. The WNₓ diffusion barrier shows little crystallization in as-deposited condition as evident by (111) peak, whereas W-Ge-N film is amorphous. The (111) peak intensity increases at 500 °C indicating further crystallization as evident from Figure 5-1(a). This leads to increase in the formation of undesired grain boundaries that provide fast diffusion paths. Cu diffuses through the grain boundaries and reacts with the underlying Ge substrate resulting in the formation of a Cu₃Ge phase that is clearly evident from Figure 5-1(a). In comparison, there is no recrystallization of W-Ge-N films at 500 and 600 °C. However, at 600 °C, Cu reacts with Ge in the W-Ge-N layer, and subsequently with Ge substrate to form the Cu₃Ge phase which is evident from Figure 5-1(b). This results in depletion of Ge from the W-Ge-N film. Upon further high temperature annealing, recrystallization of the Ge-depleted W-Ge-N takes place leading to barrier failure. This result indicates that adding Ge to W-N alloy effectively hampers the recrystallization process even at high annealing temperatures as compared to WNₓ.

The Cu diffusion profile through the diffusion barrier in as-deposited and annealed structures was determined by Auger electron spectroscopy. The film thickness for WNₓ and W-Ge-N was 50 nm for the AES chemical profile study. Figure 5-2 shows the chemical profile of Cu for Cu/WNx/Ge structure (a) as-deposited and after annealing at (b) 400 °C and (c) 500 °C. The Auger profile shows negligible Cu diffusion in WNₓ at 400 °C. However, upon annealing to 500 °C, Cu is seen to rapidly diffuse through the barrier film and to the substrate. This is in agreement with XRD data at 500 °C where it shows increased crystallization of WNₓ, thus increasing the grain boundaries, i.e., diffusion pathways, resulting in the formation of Cu₃Ge phase. The nitrogen signal
intensity steadily decreases at subsequent high temperature annealing compared to the as-
deposited sample indicating decomposition of WN$_x$ by liberating N$_2$ at higher
temperatures.

The chemical profile of Cu/W-Ge-N/Ge structures was also measured by Auger
electron spectroscopy as shown in Figure 5-3(a) as-deposited and after annealing at (b)
400 °C and (c) 500 °C. As is evident, there is little or no Cu diffusion through the barrier
upon annealing at temperatures less than 500 °C. The Cu/W-Ge-N and W-Ge-N/Ge
interfaces are distinct in as-deposited and 400 °C annealed samples. At 500 °C, Cu starts
consuming the Ge in the film. This is also supported by XRD data [Fig. 5-1(b)], where a
small intensity (-111) Cu$_3$Ge peak appears for annealing temperature of 500 °C. Upon
annealing at higher temperature, Cu completely consumes the Ge in the film, thereby
depleting the W-Ge-N matrix. This results in the recrystallization of WN$_x$ as is evident
from Figure 5-1(b) at 700 °C resulting in rapid Cu diffusion. The result above suggests
that W-Ge-N hinders recrystallization by frustrating recrystallization of the matrix and is
a better diffusion barrier as compared to WN$_x$. The high oxygen content noticed in the
chemical profiles is due to background oxygen during sputtering. The negative enthalpies
of formation of W-O and Ge-O bond are 672 kJ/mol and 659.4 kJ/mol respectively
indicating the stability of the compound after formation. Longer pre-sputtering time of
target could help in reducing the oxygen content in the deposited film.

Figure 5-4 and Figure 5-5 shows the Cu diffusion profile in WN$_x$ and W-Ge-N
film annealed at 500 °C, respectively, which was measured by Energy dispersive
spectroscopy (EDS) attached to a cross-section transmission electron microscope
(XTEM) system. As seen in Figure 5-4, Cu signal is seen throughout the WN$_x$ film and
into the Ge substrate. However, very little (half counts as compared to WNₓ) Cu signal is seen coming from the W-Ge-N (Fig. 5-5) diffusion barrier. This result corroborates the above mentioned XRD and AES data suggesting excellent diffusion barrier properties for W-Ge-N as compared to WNₓ. The interface properties were determined by XTEM. Figure 5-6 shows XTEM images of (a) Cu/WNₓ/Ge structure and (b) Cu/W-Ge-N/Ge structure both annealed at 500 °C. The WNₓ/Ge and W-Ge-N/Ge interfaces are abrupt, indicating no intermixing or reactions between them even after annealing. However, the Cu/WNₓ and Cu/W-Ge-N interface is rough, suggesting some intermixing and Cu diffusion in WNₓ films. XTEM images shows well-defined (111) grain structure for Cu films deposited on W-Ge-N [Fig. 6(b)] as compared to WNₓ films [Fig. 6(a)]. This may be important as (111) oriented Cu films has high resistance to electromigration.

**Conclusion**

In conclusion, the diffusion barrier properties of W-Ge-N thin films deposited on p-Ge (001) substrates were investigated. W-Ge-N films have a higher recrystallization temperature (700 °C) as compared to WNₓ films as shown by X-ray diffraction. The failure of W-Ge-N diffusion barrier films at high temperatures occurs by Cu diffusing through the grain boundaries formed by recrystallization of Ge depleted W-Ge-N. This Ge depletion is caused by the consumption of Ge in the barrier film by Cu at high temperatures, thereby forming the Cu₃Ge phase. Removal of Ge from the film makes the W-Ge-N barrier more likely to recrystallize. In contrast, failure of WNₓ diffusion barrier at high temperature takes place by diffusion of Cu through WNₓ grain boundaries. Nitrogen evolution from the film at high temperature causes decomposition of the diffusion barrier, thus enhancing crystallization of WNₓ film. The AES data clearly
shows complete Cu diffusion throughout the WN$_x$ layer at 500 °C annealing temperature, whereas there is little or negligible Cu diffusion through W-Ge-N films. This suggests that W-Ge-N is a better diffusion barrier. This is substantiated by the Cu profile measured by EDS. The Cu films deposited on W-Ge-N have better orientation as compared to WN$_x$ after annealing at high temperatures, thereby increasing its resistance to electromigration.
Figure 5-1. X-ray diffraction patterns of as-deposited and annealed films at different temperature of (a) WNₓ films (b) W-Ge-N films.
Figure 5-2. AES depth profiles of Cu/WNx/Ge (a) as-deposited (b) annealed at 400 °C/1 hr (c) annealed at 500 °C/1 hr.
Figure 5-3. AES depth profiles of Cu/W-Ge-N/Ge (a) as-deposited (b) annealed at 400 °C/1 hr (c) annealed at 500 °C/1 hr.
Figure 5-4. EDS depth profile of Cu/WN$_x$/Ge annealed at 500 °C/1 hr.
Figure 5-5. EDS depth profile of Cu/W-Ge-N/Ge annealed at 500 °C/1 hr.
Figure 5-6. X-TEM images of (a) Cu/WNₓ/Ge annealed at 500 °C/1 hr (b) Cu/W-Ge-N/Ge annealed at 500 °C/1 hr.
CHAPTER 6
COMPARATIVE STUDY OF HfNₓ AND Hf-Ge-N DIFFUSION BARRIERS ON Ge

Introduction

For many years, aluminum has been the primary interconnect metal for Si-based integrated circuits. However, with device dimensions shrinking to sub-45 nm and demands for high current density increasing, the conductivity and electromigration properties of Al become limitations to performance. In response, Cu is beginning to replace conventional Al interconnects given its better electromigration resistance and lower electrical resistance. The use of low resistivity Cu compared to Al significantly reduces the circuit time constant delay to make the circuit faster. As the need for high speed electronics grows, there is also a renewed interest in Ge and SiGe based devices because of inherent advantages of Ge over Si, i.e., smaller E_g, higher mobility of charge carriers and lower dopant activation energy. Si_{1-x}Ge_x-based devices are also of interest because of the innate flexibility to tailor the bandgap through the alloy composition. These factors provide sufficient impetus to investigate barrier layer materials needed in incorporating Cu interconnects in Si_{1-x}Ge_x and Ge-based devices.

For interconnect applications, copper cannot be deposited directly on Si-Ge since it diffuses rapidly in Si and Ge creating deep level traps. For the case of Si, it forms copper silicides at saturation. It also passivates dopants by forming Cu-D (D is dopant atom) covalent pairs thus altering the intended doping levels. Copper is also known to diffuse rapidly in Ge with an average diffusion coefficient of 3 x 10^{-5} cm²s⁻¹ in the 700 to
900 °C temperature range. Copper introduces three acceptor levels in Ge, two at $E_v+0.04$ and $E_v+0.32$ eV and another at $E_c-0.26$ eV respectively. Direct deposition of Cu on $Si_{1-x}Ge_x$ results in the formation of $Cu_3(Si_{1-x}Ge_x)$ and passivation of the dopants. In addition to the above issues, Cu also exhibits poor adhesion to dielectrics commonly used in Si device structures.

Considerable work has focused on identifying viable Cu diffusion barrier materials on Si. Since amorphous materials lack grain boundaries that are fast diffusion pathways, they are ideally suited for application as a diffusion barrier. Recent material systems that have been studied as possible Cu diffusion barriers for Si include refractory metal nitrides, such as TaN, TiN, WN$_x$. These binary nitrides, however, tend to recrystallize at moderate temperature, thus becoming susceptible to rapid Cu diffusion. There is significant interest in identifying diffusion barrier materials that remain amorphous at high processing temperature and effectively block Cu diffusion. Increasing the temperature necessary for crystallization can often be achieved by the addition of a third element to a binary matrix material. Some of the ternary materials systems that have been studied include Ta-Si-N, W-Si-N, W-Ge-N. In this paper, we report on the recrystallization of HfN$_x$ and Hf-Ge-N thin films deposited on Ge and their diffusion barrier properties for Cu metallization.

**Experimental Details**

HfN$_x$ and Hf-Ge-N thin films with varying thickness (15, 50 and 300 nm) were deposited on p-Ge (001) single crystal substrates by reactive sputtering at room temperature. Prior to deposition, the substrates were cleaned with trichloroethylene, acetone and methanol in an ultra-sonic bath for 5 min each to remove any organic residue from the surface. The substrates were introduced in a reactive sputter deposition chamber
with a base pressure of $3 \times 10^{-7}$ Torr via a load-lock. Nitrogen was incorporated in the film by flowing Ar and N$_2$ in the chamber at a ratio of 3:1. The total chamber pressure during deposition was 10 mTorr. Prior to deposition, the targets were cleaned in-situ by pre-sputtering with Ar+N$_2$ at a fixed chamber pressure of 15 mTorr. The forward sputtering power for Hf and Ge was 200 and 100 W, respectively. The typical deposition rate for HfN$_x$ and Hf-Ge-N films was 1.8 and 6.23 nm/min, respectively. Identical thickness was achieved for both films by varying the deposition time. Film thickness was measured by a stylus profilometer.

Nitride film deposition was followed by in-situ deposition of Cu films. The forward power used for Cu deposition was 200 W. The Cu thickness was maintained constant at 300 nm for all films. The deposition was carried out by flowing Ar inside the chamber at a fixed chamber pressure of 5 mTorr. Individual film stacks were then separately annealed in a tube furnace in the temperature range of 400 to 700 °C for 1 hr. Before starting the annealing process, the tube was purged by flowing Ar gas at 65 sccm for at least 10 hrs. The film crystallinity before and after annealing was determined by X-ray diffraction (XRD) while the film surface morphology and roughness after annealing were determined by field emission-scanning electron microscopy (FE-SEM). The chemical depth profile of Cu diffusion through the diffusion barrier was determined by energy dispersive spectroscopy (EDS). The chemical state analysis of Cu and intermetallic compound formation with Ge was investigated by X-ray photoelectron spectroscopy (XPS). Interface reactions and properties were determined by cross-section transmission electron microscopy (X-TEM).
Results and Discussion

The HfNx films were amorphous in the as-deposited condition and showed no signs of recrystallization for any film thickness even after high temperature annealing. A lack of crystallization upon annealing is desirable as formation of grain boundaries leads to rapid Cu diffusion. The HfNx diffusion barrier properties are expected to be attractive based on its high melting temperature (3330 °C). Materials that have a high melting temperature also generally show a have high recrystallization temperature since both process involve bond breaking. HfN films have been shown to be stable to thermal decomposition up to 1000 °C. Fig. 1 shows the X-ray diffraction patterns for Cu/HfNx/Ge as-deposited and after high temperature annealing in the range of 400 to 700 °C in an Ar atmosphere. For 300 and 50 nm thick HfNx diffusion barrier films that were annealed at a temperature of 600 °C or greater, the Cu films exhibit a shift in the Cu (111) peak towards smaller 2θ values. This may indicate a reaction with the HfNx film. It is noted, however, that for the 300 nm thick HfNx barrier, no Cu3Ge phase was formed even after annealing at 700 °C. For the 50 nm thick HfNx film (Fig 1b), as aforementioned, there is a definitive shift of Cu (111) peak at 700 °C annealing temperature which may be due to reaction of Cu with the underlying HfNx layer. Also evident for the 50 nm thick HfNx sample is the formation of non-stoichiometric Cu3-xGe phase after annealing at 700 °C. This indicates Cu diffusion through the HfNx diffusion barrier and reaction with the underlying Ge substrate. Cu3-xGe phase could also have been formed by possible Ge out-diffusion through the diffusion barrier and subsequent reaction with Cu. For the ultra-thin HfNx diffusion barrier film (15 nm), the barrier fails at lower temperature as evident from Fig. 1c that shows Cu3Ge phase formation after annealing at 500 °C and above. The 400 °C anneal pattern, however, does not reveal evidence of barrier failure.
The properties of Cu/Hf-Ge-N/Ge multilayers were then examined and compared to the Cu/HfNₓ/Ge samples. Fig. 2 shows X-ray diffraction patterns for Cu/Hf-Ge-N/Ge as-deposited and after high temperature annealing in the range of 400 to 700 °C in Ar atmosphere. Based on the behavior of the thickest film, the Hf-Ge-N films remained amorphous after annealing at a temperature as high as 700°C for all film thicknesses. For the 300 nm thick Hf-Ge-N film (Fig. 2a), there is little or no shift in the Cu (111) peak even after annealing at 700 °C. For the 50 nm thick Hf-Ge-N film thickness (Fig 2b), Cu₃Ge phase formation is evident after annealing at 600 °C indicating that Cu has diffused through the barrier film to react with the underlying Ge substrate. It is also noted for the 600 °C annealed sample that the Cu (200) and (111) peaks are no longer present, suggesting significant loss of Cu to the underlying material. At 700 °C annealing temperature, sufficient Cu diffuses through the barrier layer to form stoichiometric Cu₃Ge phase, again indicating barrier failure.

These data suggests that, while Hf-Ge-N and HfNₓ have similar recrystallization behavior, the diffusion barrier properties of HfNₓ are superior. In particular, the absence of the Cu (200) peak for the film on 50 nm thick Hf-Ge-N annealed at 600 °C suggests significant diffusion as compared to HfNₓ.

One possible factor in determining the properties of the two materials relates to the relative percentages of the elements present in the diffusion barrier. As mentioned before, HfNₓ and Hf-Ge-N films were deposited at the rate of 1.8 and 6.23 nm/min, respectively. As the forwarding power to Hf was kept constant during deposition of both films, the total Hf content in the HfNₓ sample is about 3.5 times greater than that for the corresponding Hf-Ge-N film of the same thickness. This results in the deposition of a Ge-
rich Hf-Ge-N film. Cu is known to react readily with Ge. For example, at room
temperature, a 20 nm Cu$_3$Ge reaction layer will form at a Cu/Ge interface in 24 hrs in a
binary reaction couple$^{103}$ and the reaction rate should increase with increased anneal
temperature. The atomic percentages of each element present in Hf-Ge-N film as
measured by Auger electron spectroscopy were 3 at. % nitrogen, 41.5 at. % oxygen, 28.8
at. % germanium and 26.7 at. % hafnium, respectively, in as-deposited condition.

The surface morphology of the barrier materials was revealed by field emission-
scanning electron microscopy. Fig. 3 shows a comparison of FE-SEM micrographs for
(a) Cu/HfN$_x$/Ge and (b) Cu/Hf-Ge-N/Ge annealed at 500 °C; samples that retained barrier
integrity as evidenced by the XRD patterns shown in Fig. 1b and 2b. The thickness of
each HfN$_x$ and Hf-Ge-N layers was 50 nm. The grain structure observed in the
micrographs is that of the Cu. Note that there is no evidence of delamination. Fig. 4
shows the FE-SEM micrographs for 50 nm thick (a) Cu/HfN$_x$/Ge and (b) Cu/Hf-Ge-N/Ge
films annealed at 600 °C. After annealing at 600 °C, the surface morphology is
significantly different for the copper films on HfN$_x$ as compared to that on Hf-Ge-N
films. For Cu on the HfN$_x$, the Cu films are continuous with a roughness similar to that
seen for the 500 °C anneal. For the Cu on Hf-Ge-N, however, significant Cu segregation
is observed. This is consistent with the suppression of the (002) Cu peak for this
structure and annealing temperature. Reaction with the Hf-Ge-N and possible Cu
diffusion through the Hf-Ge-N film leads to depletion of Cu from the surface and
segregation of Cu islands. This apparent Cu loss on the surface is in agreement with the
XRD data showing the appearance of Cu$_3$Ge peaks for Cu films on Hf-Ge-N barriers that
are annealed at 600°C. No such peaks are detected for the comparison HfNₓ film suggesting improved diffusion barrier quality of the latter film.

The interface properties and reactions were examined by cross-section transmission electron microscopy. Fig 5 shows the X-TEM images of the 50 nm thick (a) Cu/HfNₓ/Ge and (b) Cu/Hf-Ge-N/Ge films after annealing at 600 °C for 1 hr. Cu diffusion is clearly seen in the Hf-Ge-N film with the formation of Cu₃Ge phase formed below the diffusion barrier film. The image of the HfNₓ film, however, shows a negligible amount of Cu diffusion as indicated by a continuous Cu film on the surface and no indication of formation of the Cu₃Ge phase. The discontinuous layer at the HfNₓ/Ge interface is due to delamination of HfNₓ. This could be due to TEM sample preparation prepared by focused ion beam (FIB). The chemical diffusion profile of Cu was determined by energy dispersive spectroscopy attached to the cross-section TEM. Figs. 6 and Fig. 7 show the chemical diffusion profile of Cu after annealing at 600 °C for 1 hr for the HfNₓ and Hf-Ge-N films respectively. A Cu signal is present in the Hf-Ge-N barrier layer and Cu₃Ge has clearly formed by transport through the barrier film to the Ge substrate. In contrast, HfNₓ shows little Cu signal is seen from the Ge substrate indicating that the HfNₓ barrier layer prevented Cu diffusion to the Ge substrate. The EDS peak positions of Cu and Hf overlap each other. As a result, a bump in the Cu intensity profile is observed in the HfNₓ layer. Also, a strong Hf EDS intensity is seen from the entire region of the Cu layer due to the EDS detector’s inability to differentiate between Cu and Hf.

The chemical state of Cu and intermetallic phase formation after annealing was determined by X-ray photoelectron spectroscopy (XPS). Fig. 8 compares the Cu 2p₃/2
peak shifts in Cu/Hf-Ge-N/Ge film for different sputtering times in the (a) as deposited material (b) after annealing the film at 600 °C for 1 hr and Ge 2p\textsubscript{3/2} peak shifts in (c) Cu/Hf-Ge-N/Ge for different sputtering times after annealing at 600 °C. The Cu surface of the as-deposited film is clearly oxidized forming a CuO layer. This is evident from the characteristics satellite peaks formed for Cu\textsuperscript{+2}. After sputtering, however, the peak shifts and matches with pure Cu (932.8 eV). As seen in Fig. 8b, after annealing the 50nm Cu/Hf-Ge-N film at 600 °C, the Cu 2p\textsubscript{3/2} peak in the as-received condition forms at 934.8 eV indicating its reaction with Ge and formation of Cu\textsubscript{3-x}Ge. This is also consistent with the XRD and X-TEM data which show the formation of Cu\textsubscript{3-x}Ge. The peak intensity increases with sputtering time as more Cu participation in the Cu-Ge bond is revealed. Apparently, there is slight shift in the Cu 2p\textsubscript{3/2} peak to 933.3 eV after 60 minutes sputtering indicating that Cu might react with oxygen and form a Cu-O compound. The Ge 2p\textsubscript{3/2} peak appears at 1221.9 eV after annealing at 600 °C. The Ge 2p\textsubscript{3/2} peak intensity increases with sputtering time indicating increased Ge participation in the Cu-Ge bond formation. There is a shift in the Ge 2p\textsubscript{3/2} peak position to 1221 eV after sputtering for 60 minutes. This might be due to reaction with oxygen and formation of Ge-O bond.

**Conclusion**

In conclusion, a comparative study of the diffusion barrier properties of Hf-Ge-N and HfN\textsubscript{x} deposited on (001) Ge single crystal wafers was conducted. The FE-SEM images show almost identical surface morphology of Cu films after annealing at 500 °C. Annealing at 600 °C, however, results in considerable extent of diffusion across the Hf-Ge-N films leaving a discontinuous Cu film on the surface. Furthermore, sufficient Cu transport occurs to form Cu\textsubscript{3}Ge which is evident from XRD data. In contrast, little or no diffusion takes place for HfN\textsubscript{x} films of the same 50 nm thickness and annealing condition
leaving Cu films continuous and smoother. This is also substantiated by cross-sectional TEM images which clearly show the formation of a Cu₃Ge below the Hf-Ge-N diffusion barrier, but no such phase is formed in the comparison HfNx film after annealing at 600 °C. The chemical valence state was determined by XPS and the results point to Cu-Ge bond formation after high temperature annealing. The chemical diffusion profile measured by EDS shows Cu signal emanating from the Hf-Ge-N diffusion barrier and the underlying Cu₃Ge phase formed after annealing at 600 °C. There is little or no Cu signal, however, observed in the HfNx diffusion barrier and underlying Ge substrate, indicating that the HfNx diffusion barrier was successful in preventing Cu diffusion to the substrate. It is thus concluded that HfNx is an attractive diffusion barrier for Cu on Ge, while Hf-Ge-N demonstrates limited utility.
Figure 6-1. X-ray diffraction patterns of Cu/HfNx/Ge films in as-deposited and annealed conditions for varying thickness of (a) 300 nm, (b) 50 nm, and (c) 15 nm.
Figure 6-2. X-ray diffraction patterns of Cu/Hf-Ge-N/Ge films in as-deposited and annealed conditions for varying thickness of (a) 300 nm, (b) 50 nm, and (c) 15 nm.
Figure 6-3. FE-SEM images of 50 nm films annealed at 500 °C for 1 hr: (a) Cu/HfNₓ/Ge and (b) Cu/Hf-Ge-N/Ge.

Figure 6-4. FE-SEM images of 50 nm films annealed at 600 °C for 1 hr: (a) Cu/HfNₓ/Ge and (b) Cu/Hf-Ge-N/Ge.
Figure 6-5. X-TEM images of 50 nm films annealed at 600 °C for 1 hr: (a) Cu/HfNₓ/Ge and (b) Cu/Hf-Ge-N/Ge.
Figure 6-6. EDS depth profile of 50 nm thick Cu/HfNₓ/Ge annealed at 600 °C for 1 hr.
Figure 6-7. EDS depth profile of 50 nm thick Cu/Hf-Ge-N/Ge annealed at 600 °C for 1 hr.
Figure 6-8. XPS chemical state data of Cu 2p peak at various sputtering times for 50 nm thick film of Cu/Hf-Ge-N/Ge (a) as deposited and (b) annealed at 600°C for 1 hr.
CHAPTER 7
EFFECT OF Ge OVERLAYER ON THE DIFFUSION BARRIER PROPERTIES OF HfN_x

Introduction

Cu is gradually replacing Al as an interconnect material in integrated circuits due to its lower resistivity and higher electromigration resistance. The limitations on materials properties will become more stringent with shrinking device dimensions as we move towards the 45 nm device node technology. For example, the current density and the associated heat generation increase rapidly as more devices are packaged on a single chip. The properties and behavior of interconnects become the limiting factor in determining the circuit speed under these extreme circumstances. Although Cu is preferred in metallization schemes for resistivity reasons, it rapidly diffuses in Si creating deep level traps and reacts with dopant atoms, deteriorating device performance. There is thus a need to find a diffusion barrier material for Cu metallization. Ideally, a single crystal diffusion barrier with no defects is highly desirable due to lack of grain boundaries. Growth of single crystal barriers, however, is not practical due to the process restrictions (e.g. thermal budget) and material properties (e.g. lattice parameter and thermal expansion coefficient mismatches between Cu and the underlying substrate (Si or low κ material). An amorphous system is then preferred due to lack of grain boundaries, which provide facile pathways for diffusion of Cu. Avoiding recrystallization and the formation of grain boundaries is thus necessary for the diffusion barrier to function. Refractory metal nitrides are being studied intensely as diffusion barriers for Cu because
of their high melting temperatures. Some of the refractory metal nitrides being considered are \( WN_x \), \( TaN \), and \( TiN \). Diffusion barriers of these materials fail at relatively low temperature (500 to 600 °C) due to recrystallization. Ternary diffusion barriers such as W-Si-N, Ti-Si-N, W-B-N, and W-Ge-N have better diffusion barrier properties owing to higher recrystallization temperatures compared to their respective binary systems.

Recently \( HfN_x \) has received significant interest as a diffusion barrier material due to its high melting temperature (3330 °C), which translates to higher recrystallization temperatures. Failure of diffusion barriers typically takes place due to recrystallization of the barrier film giving rise to parasitic grain boundaries. The integrity of the diffusion barrier can be enhanced in several ways, for example, by adding a third element into the binary matrix, choosing a refractory nitride system having very high melting temperature, or by combination of materials that collectively hinder Cu diffusion. In this paper it is demonstrated that the third approach is a viable one to formulating a diffusion barrier for Cu metallization. Specifically, a novel bilayer diffusion barrier of Ge (25 nm)/HfNx (7 nm thick) on Si is tested as a barrier for Cu. The candidate diffusion barrier is compared with a simple HfNx layer deposited under identical conditions. The results indicate that the integrity of the diffusion barrier was maintained even under strenuous test conditions.

**Experimental Details**

Ge/HfNx diffusion barrier films were deposited on p-Si (001) single crystal wafers by a reactive sputtering process. The native oxide on Si was first etched by dipping the substrate in 7:1 buffered oxide etchant and rinsing with D.I. water. After drying the substrates with ultra high purity N₂ gas, the substrates were loaded into the deposition
chamber via a load-lock. The chamber base pressure was maintained at 3 x 10⁻⁷ Torr. The sputtering targets were pre-cleaned before deposition by flowing Ar gas inside the chamber at a fixed chamber pressure of 15 mTorr. The forward sputtering power used for Hf and Ge targets was 200 and 100 W, respectively. HfNₓ diffusion barrier films were deposited by flowing Ar + N₂ gas inside the chamber at a fixed pressure of 10 mTorr. Once the desired thickness of HfNₓ was achieved, the N₂ flow was stopped and a Ge over layer was deposited via Ar ion sputtering. The thicknesses of the HfNₓ and Ge films were maintained at 7 nm and 25 nm, respectively, by varying deposition time.

Cu thin films were deposited in-situ on the Ge layer at a fixed pressure of 5 mTorr without breaking vacuum. Forward sputtering power used for Cu was 200 W. The thickness for the Cu film was 300 nm for all samples. The substrate was rotated at 20 rpm throughout each deposition process to ensure film uniformity. Subsequent to Cu metallization, individual diffusion barrier samples were annealed separately in a tube furnace in the temperature range 400 to 700 °C for 1 hr to test the integrity of the diffusion barriers. Ultra high purity Ar gas was used to purge the tube furnace at a flow rate of 65 sccm for at least 10 hr. Individual samples were also annealed at 500 °C for 1 to 3 hr. The film crystallinity and intermetallic phase formation were determined using a Phillips APD 3720 X-ray diffractometer (XRD) while the Cu depth profile was determined using a JEOL Superprobe 733 energy-dispersive spectrometer (EDS). The integrity of the interface was assessed by examining cross-sections on a JEOL 2010F high-resolution transmission electron microscope (HRTEM). Samples were prepared using Dual beam strata DB235 focused ion beam (FIB) and the surface roughness of Cu was determined using atomic force microscopy (AFM) on a SPM/AFM Dimension 3100.
Results and Discussion

Thick HfNx films (thickness 300 nm) without a Ge layer were first grown with an apparent amorphous structure in the as-deposited condition since no diffraction peak was observed that was assignable to HfNx and the underlying Si (400) reflection at 69.155° was evident (not shown). The HfNx (thickness 300 nm) remained amorphous even after annealing at high temperature (400 – 700 °C) (not shown). Figure 1 shows the X-ray diffraction patterns of thinner HfNx (7 nm) diffusion barrier films with (Fig. 1a) and without Ge (Fig. 1b). The sample with only a 7 nm thick HfNx film, however, failed after annealing at 400 °C for 1 hr as evident from the formation of Cu3Si (Figure 1b). By providing an over layer of Ge, the efficacy of HfNx was significantly enhanced (Figure 1a). The integrity of the Ge/HfNx stack remains intact up to 600 °C annealing temperature indicating a significant increase in its performance as a diffusion barrier. Only after annealing at 700 °C are copper silicide peaks evident, indicating improved performance of the bilayer diffusion barrier until 600 °C. For Ge/HfNx films annealed at 500 °C in the range of 1 to 3 hrs (Figure 1c), the diffusion barrier stack does not show any indication of Cu transport across it. The integrity of the Ge/HfNx stack at these severe test conditions is very encouraging.

This excellent performance can be attributed to a combined effect of both Ge and HfNx. Ge was deposited as an over layer because of its rapid reactivity with Cu to form Cu3Ge, which also has a high electrical conductivity.23,103,123 Moreover, the Cu3Ge is less reactive with oxygen86 than Cu3Si and itself is a good diffusion barrier for Cu.95 Using Ge as a stand alone diffusion barrier for Cu, however, fails at 500 °C as evident by formation of copper silicide peaks (Fig. 1d). When Ge is used as an over layer, it reacts with Cu to form Cu3Ge, which hinders Cu diffusion. After passing through the Cu3Ge layer, Cu
encounters the amorphous HfN\textsubscript{x} layer, which further limits its diffusion. This is an excellent example of a synergistic effect of two different materials in achieving a common goal. The Cu intensity peak ratio between Cu (111) and (200) increases as the temperature is increased. It also increases when annealed at constant temperature but with increasing anneal time. This apparent recrystallization of Cu to yield a preferred orientation of Cu along the [111] direction is advantageous as Cu has superior resistance to electromigration in the [111] direction.

Figure 2 shows the atomic depth profiles in Cu/Ge/HfN\textsubscript{x}/Si film stacks before and after annealing at 500 °C. As clearly seen in Figure 2a for the as-deposited stack, there is a noticeable overlap of the Cu intensity profile with the Ge over layer. This supports the hypothesis that Cu reacts with Ge even at room temperature. The EDS peak positions of Cu and Hf overlap each other. As a result, a bump in the Cu intensity profile is observed in the HfN\textsubscript{x} layer. Also, a strong Hf EDS intensity is seen from the entire region of the Cu layer due to the EDS detector’s inability to differentiate between Cu and Hf. The Cu intensity profile declines sharply as it moves inside the Si substrate indicating no Cu diffusion into the Si at room temperature. For samples annealed at 500 °C for 1 hr (Fig. 2b) and 3 hr (Fig. 2c), the Cu intensity profile again decreases sharply as the scan moves into the Si substrate. This is consistent with the XRD data, which also show no sign of Cu diffusion and formation of copper silicides. The oxygen content as measured by auger electron spectroscopy in HfN\textsubscript{x} films was approx. 20 at. %. This can be rectified by using lower base pressure and longer target pre-sputtering times.

The surface roughness was quantitatively measured by atomic force microscopy. Figure 3 shows AFM plots of the same Cu/Ge/HfN\textsubscript{x}/Si stacks profiled in Figure 2. As
evident in these images, there is no significant change in the rms roughness values between the as-deposited samples (5.182 nm) and samples annealed at 500 °C for 1 hr (9.373 nm) and 3 hr (6.476 nm). The data suggest that the Cu layer is fairly smooth with the small amount of roughness likely produced by the reaction of the Cu with Ge. Subsequent annealing does not promote further reaction or surface atom migration.

The film interface integrity and abruptness were determined by high-resolution TEM for the same 3 samples analyzed by EDS depth profiling and AFM. As shown in Figure 4 the HfN\textsubscript{x}/Si film interface appears to be very abrupt for all three samples, which suggests no intermixing between the layers. This is consistent with the XRD data, which show no evidence of copper silicide formation for annealing at 600 °C for 1 hr and at 500 °C for 3 hr.

**Conclusion**

In summary, the effectiveness of a novel Ge(25 nm)/HfN\textsubscript{x}(7 nm) bilayer to serve as a diffusion barrier for Cu was investigated. XRD data suggests that the barrier stack does not fail even after annealing at 600 °C for 1 hr and shows no signs of copper silicide formation even after annealing at 500 °C for 3 hr, indicating excellent diffusion barrier quality of the Ge/HfN\textsubscript{x} bilayer structure. The as-deposited Cu/Ge/HfN\textsubscript{x}/Si (001) stack as well as ones annealed at 500 °C for 1 and 3 hr were further examined by EDS, AFM, and HRTEM. Elemental EDS profiles show a sharp decline in the Cu intensity profile at the HfN\textsubscript{x}/Si interface, indicating no Cu diffusion into the Si substrate. The results of these measurements also suggest that Cu reacts at room temperature with the Ge to form Cu\textsubscript{3}Ge. The Cu film surface was smooth in the as-deposited condition with no significant changes after annealing at 500 °C for 3 hr. This is beneficial as smoother films exhibit lower contact resistance. Lattice images of the HfN\textsubscript{x}/Si interface reveal atomic
abruptness, indicating excellent stability of the diffusion barrier and showing no signs of intermixing. Annealing of a single HfN\(_x\) layer barrier, however, showed Cu silicide formation at 400 °C. Overall, the 32 nm Ge/HfN\(_x\) bilayer stack has excellent diffusion barrier properties for Cu metallization due to synergistic behavior of two different material systems.
Figure 7-1. X-ray diffraction patterns of as-deposited films and annealed ones at the temperature shown in the figure: a) Cu/Ge(25nm)/HfNx(7nm)/Si (001) for 1 hr; b) Cu/HfNx(7nm)/Si (001) for 1 hr; c) Cu/Ge(25nm)/HfNx(7nm)/Si annealed at 500 °C for increasing time durations and d) Cu/Ge(25nm)/Si (001) for 1 hr.
Figure 7-1. (cotd.).
Figure 7-2. EDS depth profile of Cu/Ge(25nm)/HfNₓ(7nm)/Si for a) as-deposited; b) annealed at 500 °C for 1 hr; and c) annealed at 500 °C for 3 hr.
Figure 7-3. AFM images of Cu/Ge(25nm)/HfN₅(7nm)/Si for a) as-deposited: b) annealed at 500 °C for 1 hr; and c) annealed at 500 °C for 3 hr.
Figure 7-4. HRTEM images of Cu/Ge(25nm)/HfNₓ(7nm)/Si for a) as-deposited: b) annealed at 500 °C for 1 hr; and c) annealed at 500 °C for 3 hr.
CHAPTER 8
PROPERTIES OF Ta-Ge-N AS A DIFFUSION BARRIER FOR Cu ON Si

Introduction

As the minimum feature size in integrated circuits continues to decrease, there is a need to replace Al in interconnects due to the limited conductivity and poor electromigration performance of Al under high current densities. Cu is a viable alternative for replacing Al due to its 1.7 times lower resistivity compared to Al and better electromigration properties under high current densities. In addition, the RC time delay achieved by an Al/SiO₂ stack needs to be lowered significantly to increase the device speed. The RC time constant can be significantly lowered by combining Cu with a low-k material thus enhancing the performance of the device.

Although the aforementioned properties of Cu are advantageous for device manufacture, Cu diffuses very effectively through Si, SiO₂ and Ge, degrading the electrical properties of the device. It is an acceptor in Ge introducing traps at E_v + 0.04 eV, E_v + 0.32 eV and E_c – 0.26 eV. Cu is a donor in Si and creates traps from 0.2 to 0.5 eV above the valence band. It also reacts with Si to form parasitic copper silicides at the interface. In addition, Cu reacts with dopants in Si to form complexes that affect the device characteristics. Thus, use of Cu as an interconnect for future technology nodes will require a viable diffusion barrier. There has been a significant interest in refractory nitrides such as WNₓ, TiN, HfNₓ, and TaN₆¹,¹¹⁰,¹¹⁴-¹¹⁶,¹²¹,¹²⁶-¹²⁸ as diffusion barrier candidates for Cu metallization. These diffusion barriers, however, typically fail at moderate temperature (400-600 °C) limiting their use. The primary mode of failure for
these diffusion barriers is by Cu diffusion through grain boundaries formed by recrystallization of the barrier material upon annealing. By increasing the recrystallization temperature, grain boundary formation can be delayed, thereby increasing the robustness of the diffusion barrier. Addition of a third element to the binary matrix induces amorphization at room temperature and also delays the recrystallization process, making ternary solutions interesting as diffusion barrier candidates. Some of the ternary nitride diffusion barriers being studied include W-Si-N, Ta-Si-N, and W-Ge-N.99,81,129

In this paper, we report on the barrier layer properties when Ge is added to TaN. Ge is of interest because it displays chemical behavior similar to that of its congener Si and might be compatible with future Ge and SiGe based devices. Diffusion barrier properties of Ta-Ge-N were compared with TaN deposited under identical conditions. The results indicate that a Ta-Ge-N diffusion barrier fails at a higher temperature than TaN, suggesting superior diffusion barrier properties.

**Experimental Details**

Ta-Ge-N diffusion barriers were deposited on p-Si (001) wafers by reactive sputtering process at room temperature. Prior to deposition, the wafer was etched in 7:1 buffered oxide etch to remove its native oxide and then rinsed with deionized water. The substrate was loaded in the sputtering chamber that is maintained at $3 \times 10^{-7}$ Torr base pressure. Sputtering targets were pre-sputtered before deposition at an Ar pressure of 15 mTorr to remove any contamination on the surface. The forward power used for Ta and Ge was 200 W and 100 W, respectively. The diffusion barrier films were then deposited by flowing Ar and N$_2$ at a chamber pressure of 10 mTorr. For comparison, TaN diffusion
barriers were deposited under identical circumstances. The diffusion barrier film thickness was maintained at 50 nm in all cases.

Cu was then deposited on the nitride in-situ at room temperature without breaking vacuum. Pre-sputtering of the Cu target was carried out to remove any contaminants prior to deposition. The forward sputtering power for Cu was 200 W. Cu was deposited on the diffusion barrier by flowing UHP Ar gas at a chamber pressure of 5 mTorr. The thickness of Cu was maintained at 300 nm in all cases. Substrates were rotated at 20 rpm during all depositions to maintain film uniformity. Individual samples were then annealed separately in a tube furnace in the temperature range 400 to 700 °C for 1 hr. Before annealing, the furnace tube was purged by flowing Ar gas at 65 sccm for at least 10 hrs. The diffusion barrier analysis was conducted using a Phillips APD 3720 X-ray diffractometer (XRD) to detect any intermetallic phase formation between Cu and Si, which would indicate bulk Cu diffusion in the substrate leading to barrier failure. The chemical depth profile of Cu through the diffusion barrier was determined by AES Perkin-Elmer PHI 660 Scanning Auger Multiprobe (AES). Film surface morphology was evaluated by using a JEOL JSM 6335F field-emission scanning electron microscope (FE-SEM). Sheet resistance of Cu was measured by four-point probe.

Results and Discussion

Figures 1 shows the X-ray diffraction patterns for Cu/TaN/Si and Cu/Ta-Ge-N/Si both as-deposited and after annealing in the temperature range 400 to 700 °C for 1 hr. As evident from Figure 1, both TaN and Ta-Ge-N films are amorphous in as-deposited condition with only Cu (111) and (200) peaks present. Upon annealing at 400 °C in Ar atmosphere for 1 hr, sufficient Cu diffuses through TaN into the Si substrate to form copper silicide (Fig. 1a), indicating diffusion barrier failure. Cu film crystallinity
increases after 400 °C annealing, as evidenced by the sharpening of the Cu (111) and (200) peaks. Further annealing at higher temperature induces bulk Cu diffusion into the Si substrate as evidenced by a decrease in the intensity of the Cu peaks after 500 °C annealing. After 600 °C, the Cu peak finally disappears with a corresponding increase in copper silicide peak intensity indicating complete Cu diffusion through the TaN diffusion barrier. In comparison, for the Ta-Ge-N diffusion barrier there is no formation of copper silicide peaks after annealing at 400 °C indicating superior diffusion barrier properties (Fig. 1b). Cu film crystallinity increases as evident by an increase in sharpness of Cu (111) and (200) peaks. Only after annealing the Ta-Ge-N diffusion barrier films at 500 °C, does the observation of copper silicide peaks indicate barrier failure. Subsequent annealing at higher temperature results in behavior similar to that of TaN. The addition of Ge to the binary TaN matrix, however, raises the diffusion barrier failure temperature by at least 100 °C, resulting in better diffusion barrier properties of Ta-Ge-N films.

The film morphology was examined by field-emission scanning electron microscopy. The film surface morphology was featureless and identical in as-deposited condition (not shown). After annealing at 400 °C, however, delamination of Cu films on TaN is evident as seen in Figure 2a. The delamination was sufficiently severe that Cu peeling occurred from the TaN diffusion barrier even by soft nitrogen blowing. In the case of Ta-Ge-N (Fig. 2b), there was no delamination of Cu consistent with better adhesion properties. Thus, addition of Ge to TaN could eliminate the need for the Ta layer that is normally used to prevent delamination of Cu from TaN, thus saving a process step.
The chemical depth profile of Cu through the diffusion barrier was determined by Auger electron spectroscopy. Figure 3 shows the Auger depth profile for Cu/TaN/Si as-deposited and after annealing at 400 °C for 1 hr. The as-deposited depth profile shows distinct interfaces at Cu-TaN and TaN-Si layers indicating no Cu diffusion. After annealing at 400 °C, however, Cu signal is seen throughout the diffusion barrier and into the substrate suggesting significant Cu diffusion and thus TaN barrier failure. This supports the XRD data in which copper silicide peak formation is evident after 400 °C annealing (Fig. 1a). Figure 4 shows the Auger depth profile for the Cu/Ta-Ge-N/Si structure as-deposited and after annealing at 400 °C for 1 hr. In contrast to TaN, the Cu/Ta-Ge-N and Ta-Ge-N/Si interfaces are quite distinct both in as-deposited condition and after annealing at 400 °C for 1 hr. The Cu profile is identical for Figures 4a and 4b indicating no Cu diffusion through the diffusion barrier. The lack of evidence for copper diffusion in the depth profile is consistent with the XRD data that show no copper silicide peak formation even after annealing at 400 °C.

Cu sheet resistance was measured by four-point probe. Figure 5 shows the sheet resistance of Cu for TaN and Ta-Ge-N in as-deposited and after high temperature annealing conditions. The sheet resistance of Cu decreases after annealing until 300 °C or higher for both TaN and Ta-Ge-N. This could be due to grain growth and increased crystallization of Cu after annealing. Increase in grain size causes decrease in grain boundaries, which contributes to lower electron scattering. Upon annealing at 500 °C (Figure 5), the sheet resistance of Cu increases drastically. This increase is consistent with Cu diffusion and formation of copper silicides as evident by X-ray diffraction patterns.
Conclusion

In summary, the properties of Ta-Ge-N thin films as diffusion barriers for Cu have been investigated. X-ray diffraction patterns showed that the addition of Ge to the binary TaN matrix causes the diffusion barrier failure temperature to increase by at least 100 °C as compared to TaN. Delamination does not occur for Cu deposited on Ta-Ge-N while significant delamination is observed for Cu deposited on TaN as evidenced by FE-SEM. The AES depth profile showed significant Cu diffusion through TaN diffusion barriers and into the Si substrate after annealing at 400 °C, while no Cu diffusion occurs at similar temperature through the Ta-Ge-N diffusion barrier suggesting superior diffusion barrier properties of Ta-Ge-N thin films. The sheet resistance of Cu initially decreased with increase in annealing temperature for both TaN and Ta-Ge-N suggesting Cu grain growth. With further temperature increase, Cu diffusion eventually occurs through both diffusion barriers leading to formation of highly resistive copper silicides with a corresponding increase in the Cu sheet resistance.
Figure 8-1. X-ray diffraction patterns of as-deposited and annealed at the temperature shown in figure of a) Cu/TaN/Si (001) for 1 hr: b) Cu/Ta-Ge-N/Si (001) for 1 hr.
Figure 8-2. Field-emission SEM images after annealing at 400 °C for 1 hr for a) Cu/TaN/Si (001) and b) Cu/Ta-Ge-N/Si (001).
Figure 8-3. AES depth profile of Cu/TaN/Si (001) for a) as-deposited and b) annealed at 400 °C for 1 hr.
Figure 8-4. AES depth profile of Cu/Ta-Ge-N/Si (001) for a) as-deposited and b) annealed at 400 °C for 1 hr.
Figure 8-5. Sheet resistance of Cu vs. annealing temperature for TaN and Ta-Ge-N.
CHAPTER 9
CONCLUSIONS

There is an imminent need for a viable diffusion barrier for copper metallization for future technology nodes. In general, ternary refractory nitride diffusion barriers are superior to their respective binary nitrides for diffusion barrier applications. The major reason for increased functionality of ternary diffusion barriers is because of their increased recrystallization temperatures. By adding a third element in the binary matrix, the crystal lattice is disrupted causing an increase in recrystallization temperatures. The initial part of the research was focused on investigating the recrystallization behavior of W-Ge-N diffusion barriers deposited on Si/SiO₂ substrates and comparison of relevant diffusion barrier properties with WNₓ films. By adding Ge to the binary matrix of WNₓ, the crystal structure was disrupted causing the recrystallization temperature of WNₓ to increase from room temperature to 600 °C after annealing for 1 hr. as seen from the X-ray diffraction results. The chemical depth profile of Cu as determined by auger electron spectroscopy supported the superior behavior of W-Ge-N films for barrier applications as compared to WNₓ. The decrease in resistivity of both W-Ge-N and WNₓ films can be attributed to grain growth with increase in annealing temperature and possible nitrogen evolution at higher temperatures. The failure of ternary diffusion barrier occurs by diffusion of copper through grain boundaries formed at higher temperatures.

A similar study was conducted using p-Ge (001) substrates for possible integration in Ge or SiGe based devices. The results again suggested that the recrystallization behavior of W-Ge-N films was increased to higher temperatures by
addition of Ge to WNₓ matrix. The depth profile as measured using energy dispersive spectroscopy on cross-section TEM samples and auger electron spectroscopy suggests increased copper diffusion in WNₓ films as compared to W-Ge-N films after annealing at 500 °C for 1 hr indicating better diffusion barrier properties of W-Ge-N films. The high oxygen content in the films could be due the background oxygen in the chamber.

A comparative study of HfNₓ and Hf-Ge-N deposited on single crystal Ge substrates with varying thickness was carried out to evaluate their barrier properties and performance. HfNₓ was chosen for this study due to its high melting temperature. In general, high melting temperature relates to higher recrystallization temperatures. The study indicated similar recrystallization behavior for both films although the diffusion barrier performance of HfNₓ was superior to Hf-Ge-N films. The reason can be attributed to Ge content in Hf-Ge-N films. As the Hf-Ge-N films were Ge-rich, copper diffuses and reacts with Ge very fast through the barrier and subsequently with the substrate causing barrier failure. The energy dispersive spectroscopy depth profile conducted on cross-section TEM samples suggested significant copper diffusion in Hf-Ge-N films as compared to HfNₓ. The oxygen content in the films was high. Bonding information of Cu-Ge as investigated by X-ray photoelectron spectroscopy revealed Cu₃ₓGe formation as supported by X-ray diffraction patterns.

The above studies were carried out by co-sputtering Ge target with either W or Hf targets. A study was conducted by forming a continuous overlayer of Ge on HfNₓ deposited on p-Si (001) substrates. Copper reacts readily with Ge to form Cu₃Ge, which has good copper diffusion barrier properties and also has low resistivity. The Ge/HfNₓ bilayer showed superior performance for copper diffusion barrier applications as
compared to stand alone HfNx film when annealed at higher temperatures in Ar atmosphere for 1 hr. The Ge/HfNx film stack showed no signs of failure even after annealing at 500 °C for 3 hrs indicating its superior properties. The surface morphology and roughness of copper films showed no change after annealing. The Cu (111) to (200) XRD peak ratio increased with increasing annealing time at 500 °C. This is beneficial as Cu has excellent electromigration resistance in the [111] direction. The interface study as determined using high resolution transmission electron microscope revealed abrupt Si-diffusion barrier interface even after annealing at 500 °C for 3 hrs.

A concluding study was conducted by adding Ge to TaN binary matrix to evaluate the diffusion barrier performance. The recrystallization temperature was increased by 100 °C as suggested by X-ray diffraction patterns. The surface morphology showed delamination of copper deposited on TaN but not when it is deposited on Ta-Ge-N films. The chemical depth profile suggested significant copper diffusion through TaN as compared to Ta-Ge-N at similar temperatures suggesting the robustness of Ta-Ge-N films. The sheet resistance of copper deposited on both films decreases with increased annealing temperatures suggesting grain growth at higher temperature. The sheet resistance increases rapidly when annealed at higher temperatures suggesting intermetallic Cu-Si phase formation.

Based on the above work, the following conclusions can be drawn.

1. Addition of a third element in a binary refractory nitride matrix effectively frustrates the matrix and promotes amorphization at higher temperatures. This is evident from the X-ray diffraction patterns of W-Ge-N films deposited on Si/SiO2 and Ge substrates. The results show that the recrystallization temperature of WNₓ films deposited on Si/SiO2 was increased from room temperature to 600 °C. The WNₓ films deposited on Ge were crystalline at room temperature. However, addition of Ge to the matrix caused amorphization and increased the recrystallization temperature to 600 °C.
2. Addition of Ge in the binary refractory nitride system improved the diffusion barrier performance in some materials such as W-Ge-N and Ta-Ge-N films. This is evident from the X-ray diffraction pattern in the said cases which shows failure of ternary diffusion barrier at higher temperatures than their respective binary nitrides. The chemical depth profile suggests significant copper diffusion through binary nitrides indicating barrier failure. However, little or no copper diffusion occurs through ternary nitrides. In the case of HfNₓ films, addition of Ge did not improve the barrier performance as suggested by the X-ray diffraction patterns, energy dispersive spectroscopic analysis and cross-section transmission electron spectroscopic analysis. This was because of formation of Ge-rich Hf-Ge-N films which caused rapid reaction and diffusion of copper through the film and subsequent failure.

3. The bilayer stack of Ge/HfNₓ is an attractive candidate for copper diffusion barrier applications. By formation of a Ge overlayer, a continuous film of Cu₃Ge can be formed by its reaction with Cu on HfNₓ. The bilayer stack shows no signs of failure suggesting superior performance even after undergoing strenuous barrier test conditions as evident from the X-ray diffraction, energy dispersive spectroscopy and cross-section TEM results. The selective orientation of Cu in the [111] direction shows promise due to its superior electromigration resistance properties in that direction.
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BIOGRAPHICAL SKETCH

Seemant Rawal was born in Vadnagar, Gujarat, India, on 4th May 1975. He did his high school till 10th standard in Mumbai, India. Later, he moved to Mehsana, Gujarat, and completed his 11th and 12th standard education. He got admitted to the Metallurgical Engineering Department, M.S. University, Baroda, from where he completed his undergraduate bachelor’s degree (B.E) in metallurgical engineering in 1997 with distinction.

After his B.E., he worked as application engineer in Electrotherm (I) Ltd. and later in Indabrator Ltd., two medium sized companies manufacturing M.F. induction melting furnace and shot blasting machines, respectively.

He was admitted to Materials Science and Engineering Department, University of Florida, in August 2001 and joined Dr. Rajiv Singh’s group. He worked on UV effect on nitrogen incorporation in high-k gate dielectrics and non-melt laser annealing of Cu(InGa)Se₂ solar cells. He joined Dr. David Norton’s group in September 2003 and worked on transition metal doped perovskite. Later he changed his research topic and worked on ternary nitride diffusion barrier for Cu interconnects. The diffusion barrier project was supported by the National Science Foundation.

Mr. Rawal and his advisor devised a novel diffusion barrier for Cu interconnects on Si using a bi-layer approach. The diffusion barrier was deposited by reactive sputtering in the nanofabrication laboratory at the University of Florida.