NANO-CRYSTALLIZATION INHIBITION IN 5 nm Ru FILM DIFFUSION BARRIERS
FOR ADVANCED Cu-INTERCONNECT

Bed P. Sharma, M.Sc., MS

Dissertation prepared for the degree of

DOCTOR OF PHILOSHOPY

UNIVERSITY OF NORTH TEXAS

December 2013

APPROVED:

Mohamed El. Bouanani, Major Professor
Richard F. Reidy, Committee Member
Jincheng Du, Committee Member
Samir Aouadi, Committee Member
Bibhudutta Rout, Committee Member
Narendra B. Dahotre, Chair of the Department of Materials Science and Engineering
Costas Tstatsoulis, Dean of the College of Engineering
Mark Wardell, Dean of the Toulouse Graduate School
Sharma, Bed P. Nano-crystallization Inhibition in 5 nm Ru Film Diffusion Barriers for Advanced Cu-Interconnect. Doctor of Philosophy (Materials Science and Engineering), December 2013, 127 pp., 1 table, 46 figures, chapter references.

As the semiconductor industries are moving beyond 22 nm node technology, the currently used stacked Ta/TaN diffusion barrier including a copper seed will be unable to fulfill the requirements for the future technologies. Due to its low resistivity and ability to perform galvanic copper fill without a seed layer, ruthenium (Ru) has emerged as a potential copper diffusion barrier. However, its crystallization and columnar nanostructure have been the main cause of barrier failures even at low processing temperatures (300 °C -350 °C). In this study, we have proposed and evaluated three different strategies to improve the performance of the ultrathin Ru film as a diffusion barrier for copper.

The first study focused on shallow surface plasma irradiation/amorphization and nitridation of 5 nm Ru films. Systematic studies of amorphization and nitrogen incorporation versus sample bias were performed. XPS, XRD and RBS were used to determine the physico-chemical, crystallization and barrier efficiency of the plasma modified Ru barrier. The nitrogen plasma surface irradiation of Ru films at substrate bias voltage of -350 V showed an improved barrier performance up to 400 °C annealing temperatures. The barrier barely started failing at 450 °C due mainly to nitrogen instability.

The second study involved only amorphization of the Ru thin film without any nitrogen incorporation. A low energy ion beam irradiation/amorphization on Ru thin film was carried out by using 60 KeV carbon ions with different irradiation doses. The irradiation energy was chosen high enough so that the irradiation ions pass through the whole Ru thin film and stop in the SiO2/Si support substrate. The C-ion fluence of $5 \times 10^{16}$ atoms/cm$^2$ at 60 KeV made the Ru film
near amorphous without changing its composition. XRD and RBS were used to determine the relationship between crystallization and barrier efficiency of the carbon irradiated Ru barrier. The amorphized Ru film showed an improved barrier performance up to 400 °C annealing temperatures similar to the plasma nitrided Ru films. The barrier barely began to fail at 450 °C due mainly to crystallization.

The third study focused on a study of Al doping of nitrided Ru thin films and their crystallinity with the aim of obtaining a completely amorphous Ru based barrier and stable nitridation. The addition of 4% Al and 14% of nitrogen in Ru produced a near amorphous film. Nitrogen in the film remained stable until the annealing temperature of 450 °C for 10 min in N₂ atmosphere. Crystallization growth of the film was inhibited until 450 °C. At 500 °C, the crystallization of the Ru films barely started, but the degree of its crystallization is minimal. The Ru-Al-N film was demonstrated to be an effective diffusion barrier for copper until the annealing temperature of 450 °C and began to fail at 500 °C. The Al doping was shown to stabilize the nitrogen in the Ru thin film barrier inhibiting its crystallization and leading to improved diffusion barrier performance and a gain in processing temperatures of 150 °C -200 °C over the as prepared pure Ru thin film barriers.
ACKNOWLEDGEMENTS

I would like to express my sincere gratitude and respect from the bottom of my heart to my supervisor Dr. Mohamed El Bouanani for his continuous guidance and supports in this journey of PhD dissertation. His attitude of “showing by doing” brought me in the stage of this success, and I could be a beneficiary of his ideas, skills, and experiences. His suggestions, encouragements, and comments not only helped me to deal with the challenges come across this dissertation but also would be the source of light to brighten the path of my future career. He did not fix himself as an advisor for the research work, but friendly shared his personal experiences and feelings which helped me to learn the procedure of the life.

I would like to express my sincere thanks to my committee members Dr. Richard F. Reidy, Dr. Jincheng Du, Dr. Samir Aouadi, and Dr. Bibhudutta Rout. I would highly appreciate their comments and suggestions for making this dissertation good.

I thank to my colleague Hui Che for his help in the lab. I would like to express my thanks to Dr. Prakash Raj Poudel, and Dr. Venkata Kummari for their help in ion beam irradiations. I would like to thank to Noberto Hernandez Como for getting me the access to work with him in clean lab facility at UTD. I would like to express my thanks to Dr. Vaishali Ukirde for her kind suggestions and comments. I thank to Sanjay Karna and Kiran Shrestha for their suggestions. I would not forget to thank all my friends at MTSE for their help and supports.

At last, but not the least, I would like to express my gratitude to my wife Bimala Paudel for her continuous supports and encouragements, and being patient and helpful in this academic journey. Finally, I would like to express my gratitude to my brothers and sisters-in-law, and dedicate this dissertation work to my father late Rabi Prasad Sharma and mother Kalawati Sharma.
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1.1 Background

Starting in 1965, after the invention of the silicon integrated circuit in 1960, Moore’s law about the doubling of transistor density on an integrated circuit and the reducing of the manufacturing cost by half has been valid and remains so today. In the beginning, Moore announced the doubling of the density of components per chip in one year and later on with an increased density of components, doubling occurred in the period of 18 to 24 months.\(^1\,^2\) The cost of production and speed of operation of devices is at the heart of Moore’s law. Processing a single wafer containing hundreds of chips with billions of devices causes the dividing of cost among them, which eventually reduces the manufacturing cost.\(^3\) In this regard, Moore’s law has driven the semiconductor industry assertively towards the downscaling of the feature sizes of devices. The final chip structure, which is operational, has two parts, called front-end-of-line (FEOL) where transistors remain and back-end-of-line (BEOL) where the metal interconnects create circuits connections from the inside transistors level to the outside. The shrinking in the size of a chip is achieved with the dimensional scaling of both FEOL and BEOL. Due to the rapid downscaling in the feature size of integrated circuits, metal interconnect lines in BEOL are to be narrower and more closely spaced. These closely spaced metal interconnects result in the high magnitude of resistance times capacitance (RC) time constant. The RC time delay is the major speed limiter when the device node reduces to sub-quarter-micron.\(^4\) The minimizing of RC delay forced the transition from aluminum copper (Al-Cu), tungsten (W), and silicon dioxide (SiO\(_2\))-based interconnects to Cu and low dielectric constant metallization schemes\(^5\). For an interconnect line of thickness about 80 nm with a pure copper, the resistivity ranges from 1.7 to
around 2.0 $\mu\Omega$-cm depending on the processing techniques, underlying substrate, film texture and morphology. For the similar thickness of pure Al interconnect, the resistivity ranges from 3.0 to 3.5 $\mu\Omega$-cm. Again, a transition to low k material from SiO$_2$ is expected to reduce the dielectric constant from 4.5 to around 2. When the values of resistivity and dielectric constant are combined, a transition from Al/SiO$_2$ to Cu/low k interconnect provides the reduction in RC time delay by around 4 times. This shows the transition to copper and low k dielectric material increases the speed of operation of a device by fourfold. Copper is the right choice compared to silver and gold, as silver has a corrosion problem and gold suffers from a contamination problem and high cost. Copper has drawn much attention not because of its higher conductivity, but also its superior resistance to electro-migration and stress migration over aluminum and its alloys. Higher electro-migration resistance allows the circuit to operate at higher current densities, which is essential for the trend of integrated circuits shrinking. Also, minimizing both electro-migration and stress migration is very important because they decrease the reliability of ICs, and in the worst case, they lead to failure of the entire circuit.

1.2 Diffusion Barrier for Copper Interconnect

Though copper is now the pinnacle of interconnection material in the development of ultra large scale integration (ULSI), the dark side in the copper interconnects is the fast and easy diffusion of copper atoms through a Si-based low dielectric constant (k) materials, which causes the degradation in the performance of the circuit. Thus the transition to Cu/low k technology has generated great challenges for the identification and development of suitable material and process technologies to form reliable copper-based interconnect.
This includes the critical need of existence of a diffusion barrier between copper and the silicon-based dielectric to prevent copper diffusion. The diffusion barrier is a very thin layer of metals or their nitrides placed between two other materials so as to protect the diffusion of atoms from one to another. This kind of layer not only acts as the barrier but also overcomes the poor adhesion to low k materials that are under consideration for use in giga-scale interconnects technology. To be an effective diffusion barrier, the barrier material should not only have good adhesion between the layers by means of bonding that comes from chemical reaction of limited range at both boundaries, but also be inert with respect to those adjacent materials. Fig. 1.1 shows the schematic diagram of the diffusion barrier of copper interconnects. Again, the material properties
that account for the degree of barrier failure are chemical or metallurgical reactivity of barrier materials with copper or substrate material, density of the barrier material, and microstructure of barrier material. A practical barrier material should be inert and should not react with copper and substrate due to any thermal, mechanical, and electrical stress conditions during the processing step and normal operation conditions. The material should be dense enough and free from voids, defects, or loosely packed grain boundaries. Also, the microstructure should be as such as to eliminate the diffusion path due to the grain boundary.\(^7\)

1.3 Diffusion Mechanism

When chemically different materials are placed in close proximity, atomic migration occurs to establish an equilibrium by lowering the overall free energy of the system.\(^9\) The presence of concentration difference, existence of negative free energy of reaction, application of electric field, presence of thermal energy, and generation of strain gradient, whether individually or a combination of some or all, are responsible for the atomic migration.\(^8\)

If we consider the multilayer structure of a multicomponent solid, the general expression of atomic flux can be expressed as\(^9\)

\[
J_i = C_i \frac{D_i}{KT} F_i
\]

(1)

where,

\(C_i\) = the concentration of ith element

\(D_i\) = diffusivity of ith element at temperature \(T\)

\(F_i\) = driving force due to gradient of chemical potential

\(K\) = Boltzmann’s constant
The driving force $F_i$ is expressed as the gradient of negative chemical potential $\mu_i$

$$F_i = -\nabla\mu_i \quad (2)$$

The chemical potential $\mu_i$ is expressed as

$$\mu_i = K T \ln C_i + \mu_i(C_i) + \sigma_i \nu_i + q_i \Phi_i + \cdots \quad (3)$$

Expression (3) indicates that the chemical potential originates due to the concentration $C_i$, internal chemical free energy $\mu_i(C_i)$, and other external components such as stress $\sigma_i$, and electric potential $\Phi_i$. Here $\nu_i$ and $q_i$ are the atomic volumes and charges.

Combining equation (2) and (3)

$$F_i = -\frac{K T}{C_i} \nabla C_i - \nabla \{\mu_i(C_i)\} - \sigma_i \nabla (\nu_i) + q_i E_i \quad (4)$$

where $\nabla (\nu_i) = \epsilon_i$ represents the deformation strain and $E_i$ represents the electric field.

Equation (4) shows that four components are responsible for the origination of the driving force. These are concentration gradient, internal chemical energy gradient, applied stress, and the electric field.

Combining equations (1) and (4) give the expression for atomic flux:

$$J_i = C_i \frac{D_i}{K T} \left( -\frac{K T}{C_i} \nabla C_i - \nabla \{\mu_i(C_i)\} - \sigma_i \epsilon_i + q_i E_i \right) \quad (5)$$

From equation (5), it is clear that for the existence of atomic flux, both the diffusivity $D_i$ and the driving force should be non-vanishing. Thus the roles of diffusivity and driving force are equally
important for maintaining the atomic flux. The reduction in atomic flux is due to either the reduction of diffusivity or the reduction of driving force.

For the damage to occur there should be local depletion and accumulation of the matter, and atomic flux is not completely responsible for this. The condition for damage formation is given by the continuity equation which is

\[
\frac{dc}{dt} = -\nabla \cdot \mathbf{J} + \frac{C - C_0}{\tau}
\]  

(6)

This equation (6) shows that the rate of depletion or accumulation depends on the negative of flux divergence and the rate of dissipation of the excess concentration from the equilibrium position, where \(\tau\) is the time constant for the process. The gradient of the macroscopic parameters such as stress and temperature are responsible for generating the flux divergence in a bulk solid. For the case of multilayers structure, two other kinds of inhomogeneity are also responsible. One is due to interface and the other is due to microstructural defects. In a multilayers structure, the structural inhomogeneity is more important than the macroscopic parameters for the diffusion paths for mass transport.

The temperature dependence diffusion coefficient is given by the Arrhenius coefficient, which is written as

\[
D = D_0 \exp\left(-\frac{Q}{kT}\right)
\]  

(7)

Where \(D_0\) is a constant, \(Q\) is the activation energy for diffusion, \(K\) is Boltzmann’s constant, and \(T\) is temperature in Kelvin. The diffusion parameters \(D_0\) and \(Q\) implicitly contain information on the thermodynamic and kinetic properties of the defects responsible for diffusion. Consider the case of copper thin film on top of a barrier layer of thickness \(b\). Let us consider the case of barrier failure when copper atoms cross the barrier. This happens when the diffusion length \(l\) of
copper reaches the same value of thickness \( b \) of the barrier layer. This condition can be written as\(^{12}\)

\[
l = 2\sqrt{Dt} = b
\]  

\( \text{Or } D = \frac{b^2}{4t} \)  

where \( t \) is the time for annealing.

Solving equation (7) and (9), the expression for the failure temperature \( T_f \) is obtained as

\[
T_f = \frac{E_a}{[K \ln(4D_o t/b^2)]}
\]  

(10)

When the thickness \( b \) of the barrier layer and annealing temperature \( t \) change to \( b' \) and \( t' \) respectively, then the normalized failure temperature can be written as

\[
T_f^n = \frac{E_a}{[K \ln(4D_o t'/b'^2)]}
\]  

(11)

The expression (11) is valid only when \( E_a \) and \( D_o \) are not changing with the thickness and annealing temperature. If the annealing temperature of the barrier layer material is below its melting point, then \( E_a \) and \( D_o \) are unchanged with the annealing temperature.\(^{12}\) Notably, the barriers having different microstructures have different values of \( E_a \) and \( D_o \).

In the case of copper and diffusion barrier systems, there are different mechanisms by which the barrier failure occurs that include\(^{13}\) copper atoms diffusion through the bulk defects present in barrier material, diffusion of copper atoms through grain boundaries, and loss of diffusion barrier integrity because of a chemical and metallurgical reaction with copper.

Dislocations and grain boundaries themselves contain vacancies and interstitials. Consequently, atom-vacancy exchange and the direct migration of interstitial atoms are the most important
process contributing to diffusion. But the motion of point defects in the crystal lattice and along dislocation and grain boundary is different, and due to that, activation energy for the different diffusion process is also different. According to Gjostein,14 there exists a direct linear relationship between the activation energy for a particular diffusion process and melting temperature of a metallic solid (barrier material). The activation energy for the bulk diffusion is given as $Q \text{ (cal/mol)} = 34 \ T_m \ (K)$ and for grain boundary diffusion it is given as $Q' \text{(cal/mol)} = 17.8 \ T_m \ (K)$. These conditions provide a reasonable guideline in the selection of appropriate material for diffusion barrier applications. In particular, it seems the materials with elevated melting points could act as good barriers. Further, grain boundary diffusion seems to have lower activation energy than that of bulk diffusion. This is why the polycrystalline materials with high angled grain boundaries are not preferred for diffusion barriers. From this, we can easily understand the critical role that microstructure plays in the performance of the diffusion barrier of the barrier material.

The structure dependence of atomic flux for diffusion is important when we consider the thin film structures of barrier layers. Because that in a multilayer thin film structure, reducing the mass transport is usually a difficult task due to the presence of driving forces and diffusing paths, modification of the microstructure of the barrier layer is very important. Mono-crystalline thin film barriers are best in preventing the diffusion, but these are impossible in terms of practical applications because of time, effort, and costs. Therefore, amorphization of barrier layers to overcome the grain boundary is one of the applicable solutions for the diffusion barrier for the copper interconnects.
1.4 Materials Selection and Microstructure for Diffusion Barriers

In addition to the ability of a material to perform as a viable diffusion barrier, the selection of a barrier material appropriate for copper interconnect technology must satisfy a list of target specifications. These specifications include:

(a) high thermal and structure stabilities against surrounding insulator and conductor materials
(b) excellent adhesion characteristics to adjacent metallization layers
(c) suitable texture to drive the nucleation and growth of subsequent Cu conductor layers with desirable morphology
(d) enhanced resistance to thermal and mechanical stresses
(e) acceptable thermal and electrical conductivities
(f) low overall contact resistance for the resulting metallization stack
(g) excellent compatibility with integrated circuitry fabrication flows, including the ability to be deposited within the thermal budget limitations of microelectronics processing

For many years, people have tried to improve the function of the diffusion barrier. Understanding the diffusion barriers requires the knowledge of diffusion mechanisms, barrier reactions, co-relations between the microstructure of barrier and atomic diffusion, and barrier failure mechanisms. Microstructure plays an important role for atomic diffusion. The vacancy, dislocations, grain boundary, preferred orientation, and crystallinity are the microstructure variables. The structural stability of the barrier material at preferred orientation is highest, and it prevents the copper diffusion more. Film microstructure is categorized as single crystal, polycrystalline, nanocrystalline, and amorphous. Polycrystalline materials as the diffusion barriers are found to show poor performance. The reason behind this poor performance is the presence of grain boundaries, which are the easiest and most effective paths for atomic diffusion.
Thus these materials are the least desirable for the diffusion barrier application. Single crystal as a diffusion barrier could be the ideal one, but it is almost unlikely to deposit the material in single crystalline form because of material and processing type constraints, which include lattice mismatch with the underlying substrate and thermal budget limitations. The most desirable diffusion barriers are the stable amorphous materials. The film microstructure for liner or barrier materials such as single crystal, polycrystalline, nanocrystalline, and amorphous are schematically shown below in Fig. 1.2.

Fig. 1.2 (a): Single crystal

Fig. 1.2 (b): Polycrystalline
The various material systems such as refractory metals (Ti, Ta, W, Pd, Nb etc.), refractory metallic alloys (Ti$_x$W$_{1-x}$, Ni$_x$Mo$_{1-x}$, Ir$_x$Ta$_{1-x}$ etc.), polycrystalline or amorphous refractory metal-silicon alloys or compounds (W$_x$Si$_{1-x}$, TaSi$_2$, CoSi$_2$, Mo$_x$Si$_{1-x}$ etc.), polycrystalline or amorphous refractory metal-nitrogen, metal-carbon, metal boron (TiN$_x$, HfN, W$_2$N, TaN$_x$, TiC, TiB$_2$ etc.), polycrystalline or amorphous silicon-nitrogen, silicon-carbon (SiN$_x$, SiC, Si$_3$N$_4$, SiC$_x$N$_y$ etc.), and amorphous ternary barriers (Ti$_x$Si$_y$N$_{1-x-y}$, W$_x$Si$_y$N$_{1-x-y}$, Ta$_x$Si$_y$N$_{1-x-y}$ etc.) have been studied for this application. But the day to day shrinking of feature sizes in giga-scale integrated circuit technology to increase the density of devices per chip as predicted by Moore’s law and the fast signal transmission by minimizing the resistance times capacitance (RC) delay has caused to fade out the applicability of various reported diffusion
barriers. Research is going on to explore the alternative materials to use as a single-layered diffusion barrier. Ruthenium is one of the most promising materials. In this dissertation, we will address the issues related to Ru for use as a diffusion barrier, and our approach of materials engineering and modification on ultrathin Ru film in order to make a better performing diffusion barrier.

Chapter 2 of this dissertation includes the literature review about the Ru-based diffusion barrier, its issues, and the works related to the improvement of the performance of the barrier. Chapter 3 includes a summary of the motivation behind the materials engineering and modifications performed on Ru film in order to improve the barrier capability of ruthenium in the present work. Chapter 4 includes the experimental techniques used for sample preparation, modification, and characterization. Chapters 5, 6, and 7 include the different techniques of material modifications on Ru film and the results related to the modifications. Chapter 8 is the conclusion of the dissertation.

1.5 Reference


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Integrated circuitry (IC) having sufficiently high speed and more diverse functionality is the market driven needs in the twenty-first century. This demand will be met by a new IC design with innovative material and process solutions. Transition to the copper/low K-based interconnect has significantly reduced the RC time delay, but this kind of transition has invited challenges in the identification and development of robust material and process technologies for the excellent diffusion barrier tuning to the trend of device structures shrinking. Finding the appropriate diffusion barrier to prevent copper diffusion has been a research topic for many years. Though various materials have been studied for this purpose, tungsten (W), tantalum (Ta), and titanium (Ti) based binary and ternary compounds are the most studied materials.

From a technical and economical point of view, TiN could be a good option for the diffusion barrier to copper-based interconnects. However, TiN deposited via CVD (chemical vapor deposition) process was found to fail through grain boundary diffusion, which is due to its columnar type morphology,\(^1\) where grain boundaries run along the whole thickness of film and provide the easy pathway for copper diffusion. Studies were performed to prevent the problem of fast diffusion of copper through the grain boundary by creating the amorphous microstructure of TiN thin films by means of a metal-organic chemical vapor deposition (MOCVD) technique, but MOCVD deposited thin films below 450 °C showed the presence of high levels of carbon, oxygen, and hydrogen contamination, which led to a low density, high resistivity, and porous TiN microstructure making it a poor barrier to Cu diffusion.\(^2\) Different attempts were performed to find the remedy of this failure and optimize the barrier performance. Plasma enhanced
MOCVD with the multiple deposition and plasma treatment cycles was found to enhance the stability and performance of the TiN barrier, which could survive the temperature up to 650 °C. But the thickness of the film was 50 nm, which is too thick for the sub-quarter-micron device application. In spite of various attempts, the Ti/TiN based barrier could not provide good performance for thickness below 20 nm.

In comparison to Ti, Ta is thermodynamically more stable with respect to copper. The study of the phase diagram between Ta and Cu shows that they are neither miscible nor do they react to produce a compound until they reach their melting points. The other reason why Ta can be an effective diffusion barrier is that Tantalum silicide, a layered internal structure formed at Ta/Si interface, is found to be more stable than copper silicide (Cu3Si) up to 650°C. As a barrier with high melting point requires high activation energy for copper diffusion, Ta being of higher melting point (3017°C) element than Ti (1668°C), copper needs significantly high activation energy (2.48 eV) to diffuse through Ta. While reducing the thickness of the Ta barrier, the barrier failure was caused by the formation of Cu3Si at the Ta/Si interface.

Tantalum nitride has been used for many years in semiconductor industries for a diffusion barrier. Tantalum nitride exists in different forms such as Ta2N, TaN, Ta5N6, Ta4N5, and Ta3N5, and all of them have high melting points and elevated heat of formation. The stoichiometric Tantalum nitride (TaN) shows excellent structural strength due to its high melting point (3090°C) and heat of formation (~ -60Kcal/mol). The bond in tantalum nitride (Ta-N) being stronger than the Ta-Si bonds, higher activation energy is needed for the silicide formation, and due to which TaNx/Si interface is more stable than its Ta/Si counterpart, which indicates that Tantalum nitride can be an effective barrier in comparison to Ta. TaNx forms a close-packed arrangement of Ta atoms with nitrogen (N) atoms occupying interstitial sites, so all
tantalum nitrides are highly stable thermodynamically with respect to copper. In the advanced copper metallization technologies, MOCVD-grown tantalum nitride film and inorganic low temperature CVD-grown Ta and TaN films have been found to be very useful as researchers found resistivity decreasing from 10,000 to 920 μΩ·cm when substrate temperature was increased from 500°C to 650°C. This value of resistivity is still too high for ultra large scale integration technology.

Tungsten nitrides, which are also in such different forms as tantalum nitrides, have been attractive liner material because of their excellent mechanical and physical properties with highly refractory nature. Another advantage of WNx is that it can easily be deposited in an amorphous form that makes it a good barrier due to the absence of grain boundaries in it. When the nitrogen in nonstoichiometric WNx is less than 0.5 (x<0.5), the amorphous nitride starts to crystallize at 450 °C, which causes the premature failure of the barrier because of grain boundary diffusion. Again, when x≥1, then nitride becomes nitrogen rich compound, and it possesses a higher crystallization temperature of nearly 600 °C, but this also significantly increases the resistivity greater than 1000 μΩ·cm.

Ta/TaN has become the predominant industry solution, but other nitrides and silicon nitrides have also shown promise. A great deal of effort is underway to develop ALD barriers, which are expected to become the predominant future solution for copper diffusion. ALD TaN and WNC (carbide) are also in development, but concerns about their interface properties with Cu are always there. One potential solution is the Ta flash layer on top of the TaN followed by PVD Cu to provide the required interface to electrochemical deposition (ECD) of Cu. Though TaN is a stable diffusion barrier for the copper interconnect, there are many technical challenges in continuing with this diffusion barrier for the advance metallization in ultra large scale
integration. TaN is a high resistive barrier, and direct copper electroplating on it is difficult. Copper electroplating is the most excellent choice for the cheapest and fastest procedure, which provides the low resistive interconnect for large volume production. The technology node is shrinking very rapidly, which demands the ultra-thin diffusion barrier of thickness below 5 nm to provide the sufficient volume for copper electroplating in the patterned feature. If the barrier layer is thicker itself, there is less room for copper wiring, which not only invites the difficulty of copper filling but also the increased resistivity of interconnects due to size effect. Scaling down the double stack Ta/TaN barrier down to 5 nm is a technical challenge. This demands the exploration of a new material that can form the single stack barrier with the possibility of seedless Cu electroplating. A viable solution for depositing a copper direct plateable diffusion barrier is the atomic layer deposition (ALD). This allows the self-limiting film growth mode through surface saturated reactions and atomic-scale control of film thickness with excellent step coverage.

Ruthenium (Ru) has been an attractive material for the study of the diffusion barrier for advanced copper interconnects. It has a lower electrical resistivity (\(\rho=7.6 \ \mu\Omega \text{ cm}\)) than that of \(\alpha\)-Ta (\(\rho=15-30 \mu\Omega \text{ cm}\)), and it has been suggested as a diffusion barrier for seedless copper metallization. Ru has good adhesion to copper. As the interface between two metals has lattice match in size and structure, the adhesion energy is lower. Ru has smaller lattice mismatch with Cu than the lattice mismatch between Ta and Cu, which leads to lower interface energy and enhanced adhesion of Ru on Cu. In addition, many studies have shown the successful growth of Ru thin films with excellent step coverage by ALD using a variety of Ru metallorganic precursors. However, Ru thin film itself could not show a better performance for the diffusion barrier for copper interconnects. The failure of the barrier has been reported after as
a low temperature as 300 °C for 5 nm film. The Ru barrier of 15 nm thickness could block the copper diffusion only up to 450 °C.\textsuperscript{24} This kind of failure of the Ru barrier at even a low temperature is due to its columnar structure with the grain boundaries perpendicular to the Si substrate.

Various works related to Ru diffusion barriers have been published. A bilayer structure consisting of Ru/TaN\textsuperscript{25} was found to be a more stable diffusion barrier than the Ru barrier itself. A 20 nm thicker Ru/TaN barrier was found to be stable till 800 °C, whereas Ru barrier of similar thickness was found to fail at 600 °C due to the formation of ruthenium silicide. A ruthenium film of 15 nm thickness on a NiSi/Si substrate was studied for the barrier performance in Cu contact metallization\textsuperscript{26}. The structure Cu/Ru/NiSi/Si was found to be stable until 650 °C. The failure of the structure was found to be due to the decomposition of NiSi at the elevated temperature, where copper reacts with Si to form copper silicide. Perng \textit{et al.}\textsuperscript{27} report the properties of Ru(5nm)/WCoCN(5nm) stacked layers as a seedless Cu barrier. Its barrier properties were compared with the 10 nm single Ru barrier. The stacked barrier was found to effectively block the copper diffusion up to 600 °C, which is an improvement of thermal stability by over 100 °C than that of the Ru (10 nm) barrier. Electrical evaluation of Ru-W(-N), Ru-Ta(-N), and Ru-Mn films of around 100 nm thickness as a Cu diffusion barrier has been performed by H. Wojcki \textit{et al.}\textsuperscript{28} A wide range of stoichiometries has been analyzed regarding the crystallization, barrier properties, resistivity, Cu adhesion, and direct copper plating behavior. An addition of 10% tungsten (W) or tantalum (Ta) into Ru already improved the barrier performance against copper diffusion comparable to TaN. The film composition of Ru\textsubscript{50}W\textsubscript{50}, Ru\textsubscript{50}Ta\textsubscript{50}, and Ru\textsubscript{95}Mn\textsubscript{5} were found as outstanding barriers. However, only the film composition Ru\textsubscript{90}Ta\textsubscript{10} and Ru\textsubscript{95}Mn\textsubscript{5} offered excellent copper adhesion and the possibility of direct Cu plating. Yang \textit{et al.}\textsuperscript{29}
reported the performance of a Ru(5 nm)/WHfN(5 nm) barrier against copper diffusion and compared with the Ru (10 nm) and Ru(5 nm)/WN(5 nm) barrier of similar thickness. Ru (10 nm) and Ru(5nm)/WN(5 nm) barrier failed after annealing at 500 °C and 750 °C, respectively. These barriers failed due to grain boundary diffusion. However, the barrier structure Ru(5 nm)/WHfN(5 nm) could prevent the copper diffusion until 800 °C. The improved performance with the addition of Hf is attributed to the amorphization and enhanced crystallization temperature of the film. A sputter deposited bilayer structure consisting of Ru(7nm)/WSiₓNᵧ(8 nm) \(^{30}\) was investigated as a direct-plateable diffusion barrier for Cu interconnects, and this structure was compared with Ru single layer of thickness 15 nm. The bilayer structure prevented the copper diffusion for the annealing temperature of up to 550-750 °C, whereas Ru barrier failed at 400 °C. The improvement in the performance of the double stack diffusion barrier has been attributed to the amorphous phase with the stable bond formation of N with Si and W in the WSiₓNᵧ structure. The diffusion barrier performance of nanostructured and amorphous Ru-Ge diffusion barriers for copper metallization has been reported by Guohua He et al. \(^{31}\) A barrier structure consisting of Cu(Ru)(25 nm)/Ru-Ge (15 nm) effectively suppressed Cu diffusion into Si until 873 K. The Ru-Ge composition was 22.7% and 77.3% respectively and the layer was amorphous. The annealing in N₂/H₂ (10% H₂) atmosphere resulted in the self-forming graded Ru(RuOₓ)/RuGeₓCuᵧ diffusion barrier from Cu/Cu(Ru)/Ru-Ge/Si system even at as low a temperature as 473 K. This phenomenon of forming a self-graded barrier with oxidation of Ru and diffusion of Cu to Ru-Ge region during annealing caused the higher stability of the structure. A comparative study of effectiveness of copper diffusion among the sputtered deposited Ru-Ti, Ru-N, and Ru-Ti-N thin films has been reported by Ji Li et al. \(^{32}\) The thermal stability, phase formation, surface morphology, and atomic depth profile of the Cu/Ru-Ti(10 nm)/Si, Cu/Ru-N(10 nm)/Si, and
Cu/Ru-Ti-N(10 nm)/Si structure were investigated after different annealing temperatures. The morphology of copper on top of Ru-Ti film was found to better than that of Cu on Ru-N film. Cu/Ru$_2$Ti/Si film showed the formation of Ru$_2$Si$_3$ at the annealing temperature of 500 °C. However, Cu film on the Ru-Ti-N layer remained stable after annealing at 550 °C. Thus Ru-Ti-N layer was found to be of the best thermal stability compared to Ru-N and Ru-Ti films. M. Damayanti et al.\textsuperscript{33} have studied the effect of dissolving nitrogen in ruthenium thin film for the purpose of a diffusion barrier. They prepared 10 nm Ru film deposited in the N atmosphere. The film was found to be amorphous in the presence of nitrogen. The formation of stable nitride of Ru is not reported yet. Annealing caused the decomposition of RuNx and released the dissolved nitrogen even at a lower temperature of 275 °C. Though the silicide formation was delayed until 900 °C, the 10 nm barrier failed at 500 °C. Perng et al.\textsuperscript{34} reported phosphorous doped Ru film for advanced Cu diffusion barrier. They deposited 30 nm Ru film on phosphosilicate glass (PSG) on Si substrate. The concentration of phosphorous in PSG is around 6-8%. Thermal annealing of Ru film in N$_2$ atmosphere at 500 °C was carried out to diffuse the phosphorous into Ru film from PSG. The diffused phosphorous into Ru blocked the grain boundary and helped to reduce the copper diffusion paths. This process improved the performance of the Ru barrier for copper metallization. Li et al.\textsuperscript{35} reported improvement of AlCrTaTiZr alloy diffusion barrier for copper metallization with the addition of 20% Ru. Performance of the 50 nm AlCrTaTiZr was found to be similar with the performance of a 5 nm AlCrTaTiZrRu diffusion barrier. The barrier worked for 30 min until 700 °C.

From the review of the reported in the literature, two types of approaches addressed the poor diffusion barrier performance of Ru and getting a suitable seedless copper metallization. The first approach is the combination of Ru with the robust and superior materials functioning as
a diffusion barrier to make a double stack, where Ru acts as the seed layer for copper plating. Different sputter deposited double stack layers such as Ru/TaN, Ru/Ta,\textsuperscript{36} Ru/WNx,\textsuperscript{37} and ALD deposited Ru/TaCN\textsuperscript{38} have been suggested, which show the improved performance against Cu diffusion to a similar thickness of Ru single layer. However, double-stack layer diffusion barrier requires additional processing and fabrication steps that can increase the time and processing cost. Moreover, less volume of a trench is available for Cu electro fill. The second approach is to modify the microstructure of Ru by means of co-sputtered deposition of Ru or plasma enhanced ALD deposition with the addition of materials to make multicomponent films. A successful growth of direct Cu platable films such as Ru-TaN,\textsuperscript{39} Ru-TaN,\textsuperscript{40} Ru-WCN,\textsuperscript{41} and RuSiN\textsuperscript{42} has been reported. However, a plasma enhanced ALD-based process resulted in the limited conformality due to a high probability of surface recombination of active radicals in higher aspect structures.\textsuperscript{43,44} Also, many co-sputter deposited thin films report the performance of thicker film, which cannot fulfill the future generation Cu metallization.

Many studies of diffusion barrier in Ru in combination with other materials were carried out for solving the grain boundary problem with Ru. Microstructure plays an important role in the performance of a diffusion barrier, and Ru thin film has the prominent columnar grain boundaries. Modifications on Ru thin film to make it a properly functioning diffusion barrier for the advanced copper metallization seem to be essential. In this dissertation, we have applied different types of modifications in Ru thin film, and the performance of the copper diffusion barrier has been studied.
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CHAPTER 3

OBJECTIVE AND RATIONALE OF THE PRESENT WORK

In the previous chapters (Introduction and Literature Review), it has been mentioned how features sizes of the device structure are downscaling and what the requirement is for the diffusion barrier at BEOL of transistors, to be in tune with the future technology road map. These also mention the transition in the selection of the barrier materials, and research works performed on Ru for the potential barrier, its bottleneck, and the ways of modification to make it a better functioning barrier. The literature review on Ru-based diffusion barriers shows that the columnar microstructure has been the dominant cause of poor performance of the barrier. Many research works have dealt with this situation, and for introducing more desirable barrier. Most of the studies have been performed on thicker Ru film, and quite a bit of research is being performed with thickness in the 5 nm range. The literature review chapter summarizes the works carried out by many researchers and also indicates the merits and demerits.

The work performed for this dissertation is also about solving the problem of columnar microstructure of Ru for copper diffusion barrier. But the ways of solving the problem are innovative and different from the studies reported. This research work has improved the performance of Ru film to use as a diffusion barrier for advanced copper interconnects by resolving the problem of grain boundaries. Three different ways have been evaluated for the modification of the Ru film of around 5 nm thickness.

3.1 Plasma Surface Amorphization and Nitridation

This work introduces the shallow surface modification of Ru film by means of nitrogen plasma processing, which also adds the nitrogen in the top layer of the film. Since few monolayers of the film are modified with the plasma, the underneath of the film is still the bulk
metal. Compared to the nitrogen dissolving in whole thin film in the work done by Damayanti et al.,\textsuperscript{1} and Li et al.,\textsuperscript{2} the resistivity of the surface nitrided film should be lower as the conductivity of unprocessed bulk film underneath the processed surface is unchanged. This is one of the great advantages of shallow surface modification of the film, which still preserves its good conductivity. Nitrogen plasma surface modification in the present study has been conducted by using physical vapor deposition (PVD) system with the nitrogen ions accelerated by means of the different bias voltages applied to the substrate film. Though there are many applications of plasma treatments reported for many systems of metals and ceramics, this kind of shallow surface treatment by using PVD plasma processing has not been realized yet. This treatment would be worth performing to reveal the effect of the modification of a few monolayers of Ru film in the performance of the barrier capability. In the present study, this surface nitridation has modified the top surface, making it a dense amorphous structure, and it has also introduced nitrogen in the top surface of the film.

3.2 Low Energy Carbon Irradiation Induced Amorphization

This work introduces the concept of modifying the whole Ru film without adding any elements to Ru lattice. This modification has been carried out to disrupt the columnar structure of the Ru film by making it amorphous. The purpose of this ion beam modification is for the fundamental study to realize how effective the barrier is when an as deposited columnar structured Ru film is made nearly amorphous without adding any elements to its crystal lattice. Until now, no one seems to be applying this concept of modification to improve the barrier performance of the materials. In this modification, Ru film is irradiated with the carbon ions. The energy of the ions has been specifically chosen so that the irradiating C ions do not stay in the Ru lattice, but cross the Ru/SiO\textsubscript{2} interface. In many works, people have introduced the different
elements by means of co-sputtering to disrupt the crystallinity. This effect increases the resistivity of the film. But the ion beam irradiated Ru does not contain other elements, due to which the resistivity should be lower than the film modified with co-sputtering. In this ion beam modification, high energy ions make the nuclear interaction with the lattice atom of the film. This causes the dislodging of the atoms from their periodicity and increases the defect density. This phenomenon makes the crystal unstable thereby transforming it to nearly amorphous or amorphous phase. This solves the grain boundary problem and improves the barrier capability.

3.3 Aluminum Doping Induced Near Amorphous Nitrided Ru Thin Film Growth

Plasma nitridation only modified the surface. In ion beam irradiation, the whole film has been modified without adding elements to Ru lattice. Finally, this work is about the modification of Ru film with the addition of small amount of other elements by means of reactive co-sputtering. This allows an opportunity to perform the comparative study of the performance of the barriers subjected to different kinds of modifications. Many research works have been reported with the co-sputtering, reactive co-sputtering, and ALD of Ru with other different elements to suppress the crystallization of Ru. In the multi component films, the amount of added elements to disrupt the Ru lattice is large (10% to even 77%). Since the added elements are similar to the addition of impurities, these behave as the scattering centers for the conducting electrons, due to which the resistivity is higher. Further, most of the works have been performed in the thicker films and will not be able to follow the industrial road map requirements. In this work, Al and N have been introduced in the Ru lattice by means of reactive co-sputtering for the same purpose, but the added Al is in a very low amount like in the doping scale. Al is chosen because of its high conductivity and different crystalline structure from that of Ru. The addition of nitrogen again helps to reduce the crystallization kinetics. The work by
Damayanti et al.\textsuperscript{1} to dissolve N in Ru to make RuN film shows that the film was stable until the low annealing temperature of 275 °C. After this temperature, nitrogen was unstable in the film.

In the present study, the purpose of the addition of Al is not only to disrupt the lattice but also to increase the stability of nitrogen during thermal processing due to Al and N bonding in the film. The recrystallization temperature related to the stability of N in the film will be revealed in this work. The original plan for this study was to relate the stability of nitrogen at different Ru to Al ratios in the film and to carry out their effectiveness in the suppression of crystallization as well as in the performance as the diffusion barrier for copper metallization. But for this dissertation, only one Ru to Al ratio has been studied. The study of different Ru to Al ratios in the RuAlN film has been left as future work, and these other ratios can be another good topic for the research.

Finally, due to the shrinking of the feature size of the device, the deposition of the barrier material with the physical vapor deposition (PVD) technique is difficult in vias and trenches, and PVD causes the shadowing effect when deposition is made in the small featured via and trench of the real device structure. Atomic layer deposition (ALD) is required for the future technology beyond 32 nm node to make a conformal barrier layer deposition. In this dissertation, because two dimensional thin film structures have been used, it was possible to work with PVD. The similar modification techniques carried out in this work may also be adopted in ALD prepared films in real device structures with vias and trenches.

The results related to the above mentioned modifications will be presented in this dissertation.

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CHAPTER 4
EXPERIMENTAL TECHNIQUES

4.1 Physical Vapor Deposition (Magnetron Sputtering)

The physical vapor deposition process for the thin films is the atomistic deposition process in which material is vaporized from the solid source in the form of the atoms or molecules. These atoms or molecules are transported in the form of a vapor through a vacuum or low pressure gases and plasma environment to the substrate, where they condense.\(^1\) There are several methods of deposition of thin films by means of PVD process, which include ion planting, thermal evaporation (vacuum evaporation), electron beam evaporation, and sputter deposition.\(^1\) These processes of physical vapor deposition are conducted in a vacuum or low pressure gaseous environment. The reason of performing film deposition at a reduced pressure or vacuum is that low pressure, or a vacuum provides the long mean free path for the collision of the particles between the source material and substrate material where particles are deposited. Also, the vacuum environment helps for the control and minimization of contamination in the films and system.\(^1\) Contaminations affect the film properties or influence the stability as well as the reproducibility of film. The contaminations consist of gaseous impurity, adsorbed water vapor, and debris, and such.

In the present study, we have carried out thin film deposition by means of magnetron sputtering physical vapor deposition. In the magnetron sputtering process, atoms of a solid target are ejected with the momentum transfer from the bombarding particles (ions) impinging on the surface of target. The atoms vaporized from the target material condense and coat on the substrate material. This kind of sputtering is performed by using gaseous ions in the plasma state, which are accelerated and directed to the target. A magnetron sputtering system consists of
a vacuum chamber, magnetron guns, and plasma environment. The schematic of the sputtering system is shown in the Fig. 4.1.

Fig. 4.1 Schematic of magnetron sputtering

Magnetron guns provide the combination of electric and magnetic fields to confine the electron path in the manner that it always remains near to the surface of cathode. The cathode is the target material, and being the negative terminal, it behaves as an electron emitting surface. The electrons are normal to the magnetic line of forces, and due to the Lorentz force, these electrons spiral around the magnetic field. The radius of the spiral depends on the magnitude and direction...
of the electric and magnetic fields. These electrons form a circulating current which may be several times the current measured in the external electrical circuit. The high flux of electrons trapped near to the target surface creates the high density plasma by means of electron-atom collisions and ionizations. Plasma is a gaseous environment that contains enough ions and electrons that serves as a good electrical conductor. For the process of physical vapor deposition, the plasma is usually established in “low pressure gases”, and it contains more neutral gas atoms than the ions. In most of the deposition system, Ar gas is used to generate the plasma. The positive ions in the plasma are directed towards the negative cathode by the electric field, and these ions bombard on the surface of the cathode to cause the sputtering effect. The sputtered atoms fly from the target and coat on the substrate. Plasma can also emit ultraviolet radiation, which can help for the chemical reaction and surface energetics by photo-absorption. In the PVD process, the uniformity of the plasma is important. Uniform plasma allows a more controlled and reproducible deposition environment. Plasma uniformity depends on the system geometry and the way plasma has been produced. Magnetron sputtering configurations take different shapes. Electromagnetic field is generated by either electromagnets or permanent magnets. In the planar magnetron as shown in Fig.4.1, the magnets are used internal to the target and this is the simplest and most common design of the magnetron sputtering system.

Magnetron sputtering can also be used for the purpose of reactive deposition to make compound films. In this method, a mixture of gas with Ar is used. The reactive gases can be O₂, N₂, and others. These gases can be in the molecular state or in an active state. Activated gases are partially ionized or in an alternative chemical state, which can react more readily (e.g. ozone). The plasma environment near the target surface is sufficient to activate the reactive species. These reactive gases are of lower atomic number and are not involved in the energetic
bombardments to the target. In the mixture, a heavier gas such as Ar is called working gas and it is used at a higher partial pressure, and a reactive gas is a lighter gas at a lower partial pressure. When the Ar ions sputter out the atoms from the target material, the reactive gas species react with the sputtered atoms and generates the compound film.

Co-deposition of different elements or compounds can also be carried out by using two or more magnetron guns. The different guns contain the different target materials. The electromagnetic field is generated in all required guns, and the plasma is produced on the surface of each gun. Simultaneous sputtering of all targets is performed, which generates a compound film with different elements.

In the present study, we have used AJA sputtering systems with the facility of 5 guns available at University of Texas at Dallas (UTD) and Kert J. Lesker’s PVD 75 with facility of 3 guns available at Center for Advance Research and Technology (CART) facility, UNT.

4.2 Accelerator for Ion Beam Irradiation

A particle accelerator is used for the purpose of ion implantation or ion irradiation in the materials. When an energetic ion passes through the material, the ion-solid interactions cause the different processes such as scattering, sputtering, and implantation. Implantation is the process in which ions get incorporated into the materials, losing all their energies in the range of several KeV to few MeV. The ion beam implantation technique is a very powerful technique for modifying the surface and near surface of materials with the accurate and predictable control of the doping ions. This technique is established as a primary technique in the semiconductor industry for introducing the impurities in the semiconductor materials to form the devices and IC circuits.
A particle accelerator for the ion beam implantation consists of five main components: (1) ion source to generate appropriate ion species; (2) analyzer magnets to filter the unwanted ions; (3) ion beam accelerator column, which gives energy to the selected ion species; (4) horizontal and vertical scanning electrodes to deflect the beam electrostatically to raster across the wafer; and (5) target holding the wafer. A greatly simplified schematic diagram of an ion implanter is shown in Fig. 4.2 (a). All these units are housed inside the vacuum chamber, and wafers are transferred into and from the implanting chamber.

The ion source is the SNICS (Source of Negative Ions by Cesium Sputtering) source shown in Fig. 4.2 (b). The SNICS source can produce the negative ions of all possible elements having the suitable electron affinity. The National Electrostatics Corporation (NEC) SNICS ion source manual 4 provides information about the operation of SNICS source, and the Roy Middleton Negative Ion Cookbook 5 provides the choice of the types of the cathode materials and the expected amount of current from the ion source.

The material from which the ion beam is desired is crushed into a powder form and loaded in the cathode. The powder is made either from the pure element or from the closely related compounds. The reservoir containing cesium is heated to evaporate the cesium. The vapor form of the cesium rises up into the ion source and cathode. Some of the cesium adheres to the tip of the cathode, and it is cooled. Some of the cesium hits on the hot surface of the ionizer.
Fig. 4.2 (a) Schematic diagram of ion beam implanter, (b) Schematic diagram of SNICS ion source
The cesium atoms reaching the ionizer get ionized, and the electric field focuses the cesium ions to strike the tip of the cathode. This causes the sputtering of the material out of the powder. The sputtered material leaves the cathode tip and passes through the cold cesium on the surface. While passing through the cold cesium surface, the sputtered materials grab the electrons from the cesium and become negatively charged. These negatively charged particles are extracted from the source and accelerated towards the target.

In the present study, the low energy ion implantation beam line facility available in the Ion Beam Modification and Analysis laboratory (IBMAL) at UNT was used. This can provide the implant energy range from 10 KeV to 80 KeV. Commercially available graphite powder was used to make the cathode source with carbon. The ion beam of carbon after the mass analyzer magnet was accelerated towards the target chamber. By using the high voltage electrostatic X-Y raster scanner, the ion beam to be implanted was scanned across the sample in the range (X-Y) of about 2.5 cm. This gives the uniform implantation over the area of interest.

The amount of ions to be implanted, which is called fluence, is calculated by means of current integration technique. In this technique, a BNC cable connects the target holder to an Ortec digital current integrator. In the current integration, a high voltage power supply of 300 V is used for the electron suppression. The output pulses of the current integrator are sent to the counter/timer. The fluence is calculated by using the formula given by

\[ F = \frac{NC}{eA} \]  \hspace{1cm} (4.1)

where \( F \) is the total implanted ions called fluence and measured in atoms/cm\(^2\), \( N \) is the total number of pulses in the counter, \( C \) is the total charge in coulomb per pulse, \( e \) is the electronic
charge in coulombs, and A is the surface area of the implanted region on the sample measured in Cm².

4.3 X-Ray Diffraction (XRD)

X-ray diffraction has been a powerful and nondestructive technique over the past several decades for the characterization of materials. Determination of crystalline phase and orientation, structural properties such as lattice parameter, residual stress, strain, grain size, epitaxy, and preferred orientation, as well as the thickness of films and multilayers can be achieved by using this technique.

In this technique, X-ray photons are produced by striking the electron beam to a very high speed to a metal target. The electrons are generated from the hot filament cathode by thermionic emission, and these are accelerated towards the target by a high electric field. The X-ray generating tube consists of a filament source, a high voltage source, and an angled metal target called anode all sealed together in a vacuum required for the operation. The point on the target where the electron beam hits is called the focal point, where most of the kinetic energy of electrons is converted to heat. Only around 1% of the electron energy is converted to X-rays. The heat is dissipated via a heat sink with the circulation of water. X-rays are produced in all directions from the focal point with maximum intensity being around 60-90° from the direction of the electron beam. A small round beryllium window inside the X-ray tube allows the X-ray to exit the tube. Copper, aluminum, cobalt, chromium, magnesium, and molybdenum are the most widely used metals as the target materials to produce X-rays. The schematic diagram for the production of X-rays is shown in Fig. 4.3.1.
The wavelength of the X-ray produced depends on the characteristic energy levels of the target metal and differs from metal to metal.

When X-rays are produced, they are made to focus on the sample to be characterized. The X-rays striking the sample get scattered in all directions. The different phenomena such as X-ray reflection and diffraction occur there. Since the crystalline materials are composed of different lattice planes oriented in different directions, these parallel planes act like the diffraction grating. The scattered X-ray beam will be out of phase in some directions and completely in phase in other directions. The beams meeting each other in phase can interfere constructively and give rise to the diffracted beam. The phenomenon of X-ray diffraction from the crystals can be explained on the basis of a relation formulated by British physicists W.H. Bragg and W.L. Bragg in 1912 for which they were awarded the Nobel Prize in physics in 1915. They determined the crystal structures beginning with NaCl, ZnS, and diamond.

Fig. 4.3.1 Schematic diagram of X-ray production
Bragg’s law can be derived by taking the condition of constructive interference of the scattered wave. The condition for constructive and destructive interference of the waves as well as the schematic of Bragg’s reflection is given in Fig. 4.3.2, and in Fig. 4.3.3, respectively.

Fig. 4.3.2 Conditions for constructive and destructive interference
Fig. 4.3.3 Bragg’s law of diffraction in two parallel planes of a crystal

The two X-rays are in phase and parallel. One X-ray gets scattered from the top plane whereas the other X-ray gets scattered from the parallel lower plane of a crystal. These two X-rays will be in phase after striking the crystalline planes, when the X-ray striking the lower plane travels an extra distance \( AB+BC \), which is called the path difference. Constructive interference will take place only when the path difference is equal to the integral multiple of wavelength of X-ray. \(^{11}\)

Mathematically,

\[
AB+BC = n\lambda,
\]

where \( \lambda \) is the wavelength of X-ray, and \( n \) is an integer

From \( \triangle ABZ \), \( AB = BZ \sin \theta = d \sin \theta \), where \( d \) is the inter-planar distance

From \( \triangle BCZ \), \( BC = BZ \sin \theta = d \sin \theta \)

Therefore, \( AB+BC = d \sin \theta + d \sin \theta = 2d \sin \theta \)
Thus, $2d \sin \theta = n\lambda$; this is known as Bragg’s law of diffraction.

When we know the wavelength of X-ray and the Bragg angle of diffraction, we can measure the inter-planar spacing ‘$d$’ of the planes involved in the diffraction phenomena. By using the value of interplanar distance, lattice parameter can be determined using the known miller indices (hkl) of the diffracting planes. For the case of a cubic crystal, lattice constant ‘$a$’ is determined by using the following relation 11

$$d^2 = \frac{a^2}{h^2 + k^2 + l^2}$$

As shown in Fig.4.3.3, the incident beam and the diffracted beam lie in the same plane, so the angle between the incident and diffracted beam becomes $2\theta$. Thus for the XRD measurement of the samples, diffracted angle $2\theta$ is used in the scan. The peak identification in the XRD measurements is performed by using the reported data base in the powder diffraction file of the International Center for Diffraction Data (ICDD). 8 In this ICDD file, most of the standard powder diffraction parameters such as diffraction angle ($2\theta$), plan spacing (d), Miller indices (hkl) of diffracting planes, integrated peak intensities, the crystal system, and the corresponding phase are reported. The experimentally observed peaks for the given sample are compared with the complete entries from the ICDD file 13 and determined whether most of the intense experimental peaks matched with the data base.

The grain size of the polycrystalline materials can also be determined by the X-ray diffraction measurements. For the known value of the angle of diffraction ($2\theta$), peak broadening at the half of the maximum intensity known as full width half maxima ($\beta$), and the wavelength of the X-ray used, the size of the grain can be obtained by the Scherrer formula 14.
This formula is generally used for a grain size lesser than 100 nm.\textsuperscript{11}

In the present study, we have used the XRD equipment, the Rigaku Ultima-III with Cu K$_\alpha$ 1.542 Å available in the Center for Advance Research and Technology (CART) facility at the University of North Texas (UNT).

4.4 X-ray Photoelectrons Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS) is a powerful characterization technique for the surface science of the materials. This technique is used to determine the elemental composition from the surface of the materials,\textsuperscript{15} elements contaminating the surface of the materials,\textsuperscript{16} chemical and electronic state of the materials,\textsuperscript{17} elemental composition across the surface, and elemental composition along the depth of the materials assisted with ion beam etching.\textsuperscript{18} As the XPS technique is used to characterize the materials on the basis of their chemistry, this technique is also known as spectroscopy for chemical analysis (ESCA).

The XPS system consists of many components such as \textsuperscript{19} a source of X-ray, an ultrahigh vacuum (UHV) chamber connected with various UHV pumps, an electron collection lens, an electron analyzer, a Mu-metal magnetic field shielding, an electron detector system, a moderate vacuum chamber for sample introduction, stage, sample mounts, and set of manipulators. A schematic diagram of an XPS measurement is shown in Fig. 4.4.1 below.
X-ray photoelectron spectroscopy is based on the photoelectric effect.²⁰ It was developed by Kai Siegbahn and his research group at the University of Uppsala, Sweden, for which he was awarded the Noble Prize in Physics in 1981.²¹ In this technique, a solid sample is irradiated with monochromatic X-ray photons in an ultra-high vacuum (UHV), and electrons are made to eject from the core levels of atoms. The requirement for the ultra-high vacuum is because the analytical signal of low energy electrons of range 20-2000 eV from the solid are easily scattered.
from the residual gas molecules in case the vacuum is poor. These electrons are prevented from reaching to the electron analyzer and then the spectral intensity decreases, and noise level becomes dominant.\textsuperscript{22} The electrons excited by X-ray photons from the solid are of short range. Therefore, this technique is highly surface sensitive, and the depth of analyzing stands around 1-10 nm from the surface of the sample.\textsuperscript{22} The energy of the electrons leaving from the sample gives rise to a spectrum with a series of photoelectron peaks. The analytical method in the XPS study is shown schematically in Fig. 4.4.2.

Fig. 4.4.2 Schematic for electron emission from sample in XPS measurement
The kinetic energy (KE) of the photoelectrons is the experimental quantity measured by spectrometer, which is related to the binding energy of the electrons and is given by the relation,

$$\text{KE} = h\nu - \text{B.E.} - \Phi_{\text{sample}}$$

$$- (\Phi_{\text{spec}} - \Phi_{\text{sample}}) = h\nu - \text{B.E.} - \Phi_{\text{spec}}$$

where $h\nu$ is the energy of X-ray, KE is the kinetic energy, and $\Phi_{\text{spec}}$ is the work function of the spectrometer. By knowing the physical quantities such as photon energy, kinetic energy of the photoelectrons, and the work function of the analyzer, we can determine the binding energy of an electron for the given orbital of the sample. The binding energy of the XPS peak is the characteristic of each element. As the electron environment with respect to the given electrons in the orbital changes, there is a shift in the peak position in the binding energy curve. This shift corresponds to the particular chemical state of the given element. There is also peak broadening.
with the shape change when the chemical state of the element changes. In the peak deconvolution, the broadened peak is fitted with a number of peaks with different chemical states. This gives the information about the bonding of the sample. The area under the peaks and the sensitivity factor of the given elements are utilized to calculate the chemical composition of the sample. The process of electron emission in XPS is shown in Fig. 4.4.3. The photoelectrons involved in the XPS process are given the spectroscopic notation such as n (principal quantum number), l (orbital quantum number), and j (total angular quantum number). The principal quantum number takes the integral values 1, 2, 3, …, n. The orbital quantum number takes such values as s = 0, p = 1, d = 2, …, n-1. The total angular momentum quantum number j takes the values of |l+s| where s is the spin quantum number with value either +1/2 or -1/2. The peaks related to p, d, and f orbitals are split into two peaks. The separation between the two peaks is named as spin orbital splitting. The relative intensities of the doublet formed due to spin orbit coupling is given by the ratio of (2j+1). This means the ratio of intensities of the doublets of p, d, and f orbitals are 1:2, 2:3, and 3:4, respectively.

XPS is not only used for the surface analysis of a sample, but it is also used for the determination of composition as a function of depth. The non-destructive technique for the depth composition can be applied for a few nanometers of the sample, usually 1-10 nm, and this technique is called angled resolved XPS.17 For the thick sample, the compositional depth profile can be obtained by means of a destructive technique in which alternate Ar sputtering and the XPS probing of the sample are performed.

In the present study, we have used PHI 5000 Versa probe X-ray photoelectron Spectrometer available in the UNT CART system. This uses Al Kα X-ray of energy 1486.6 eV.
4.5 Rutherford Backscattering Spectrometry (RBS) Technique

Rutherford backscattering spectrometry (RBS) has emerged as one of the simplest and widely used ion beam analysis methods for the thin film analysis.\textsuperscript{23} Rutherford, in 1911, used the backscattering of alpha particles from a gold film to determine the fine structure of atoms, resulting in the discovery of an atomic nucleus. Rubin \textit{et al.}\textsuperscript{24} firstly described the RBS as a method for materials analysis. Modern applications of RBS are described by Tesmer and Nastasi.\textsuperscript{25}

RBS involves the elastic collision between the light ions of high energy with the rest nuclei of the target atoms. In RBS, lighter ions (like He\textsuperscript{+} and H\textsuperscript{+}) with the energy range of 0.5 to 3 MeV are used to impinge on the target. The number and energy distribution of energetic ions backscattered from the target atoms is measured by using an energy sensitive solid state detector, which gives the information about the atomic mass and concentration of elements in the target as a function of depth below the surface.\textsuperscript{26} RBS is a non-destructive technique with a good depth resolution of the order of several nanometers, and it has a very good sensitivity for heavy elements of the order of parts per million. For the incident He ions, the analyzed depth is about 2 µm whereas for the incident protons it is about 20 µm. RBS has a poor sensitivity for the lighter elements with atomic number (Z) less than 10. This is because of the small value of scattering cross section for backscattered ions, which is proportional to the square of the atomic number. In this case, backscattered ions have lower energy and are difficult to separate for spectrum background noise.

In RBS, since the collision between atomic nuclei is elastic, by using the law of conversation of energy and momentum we can determine the mass of scattering ions. Fig. 4.5.1
shows the schematic representation of elastic collision between the projectile ion and target mass.

![Schematic representation of an elastic collision](image)

**Fig. 4.5.1** Schematic representation of an elastic collision

In the figure, $M_1$ and $E_0$ represent the mass and energy of the projectile ion before collision, $M_2$ and $E_2$ represent the mass and energy of the target nucleus after collision, and $M_1$ and $E_1$ represent the mass and energy of the backscattered ion. $\theta$ is the backscattered angle. During the collision, a portion of energy of the projectile is transferred to the rest nuclei of the target atoms.

This kind of interaction is described by means of Coulomb force of repulsion between the nuclei,\textsuperscript{27} and the energy fraction is represented by the term kinematic factor denoted by $K$. The kinematic factor $K$ is the ratio between the energy of the projectile ion after collision and before the collision,\textsuperscript{23} and it is determined by using the laws of conservation of energy and momentum. The mathematical expression for kinematic factor is given as
\[ K = \frac{E_1}{E_0} = \left[ \sqrt{\frac{M_2^2 - M_1^2 \sin^2 \theta + M_1 \cos \theta}{M_1 + M_2}} \right]^2 \]  

In the case of light elements in the target material, a significant momentum is transferred from the projectile particles, and backscattered particles can have adequate energy separation. If two different elements in the target material have mass difference \( \Delta M_2 \), the energy separation \( \Delta E_1 \) of the backscattered particles is given by \(^{28}\)

\[ \Delta E_1 = E_0 \frac{dK}{dM_2} \Delta M_2 \]  

For the lighter elements, the derivative \( \frac{dK}{dM_2} \) is steeper due to which energy separation \( \Delta E_1 \) is larger, whereas for heavier elements the derivative is smaller, which makes the poor energy resolution of backscattered particles.

The number of backscattered particles from the target material for a given solid angle and for the given number of incident particles depends on the differential scattering cross-section. The differential cross-section defines the probability of the occurrence of interaction between the projectile and target nuclei. For the given masses of projectile and target particles and for the given backscattered angle, the differential scattering cross-section is directly proportional to the square of atomic numbers of target and projectile particles but inversely proportional to the incident energy of projectile particles. For the given atomic numbers \( Z_1 \) and \( Z_2 \) for the incident and target atoms, the differential scattering cross-section on the basis of geometry shown in Fig.4.5.1 is given as
\[
\frac{\partial \sigma}{\partial \Omega} = \left[ \frac{Z_1 Z_2 e^2}{4E} \right]^2 \times \frac{4}{\sin^4 \theta} \times \frac{\sqrt{1 - \left[ \frac{M_1 \sin \theta}{M_2} \right]_2 + \cos \theta}^2}{\sqrt{1 - \left[ \frac{M_1 \sin \theta}{M_2} \right]^2}}
\]

Most of the charged particles undergo inelastic collisions with orbital electrons when they pass through the target material. Each interaction causes very little scattering, as only a small fraction of incident particles reach the close proximity of the target nuclei and back scatter. Most of the incident particles are implanted in the target material. The projectile particles lose the energy by means of electronic stopping due to the interaction with electrons and nuclear stopping due to glancing collision with the target nuclei. Thus the energy of the backscattered particles is less than the energy of the incident particles. For the given target material, the energy loss of the projectile particles is different at different depths from the surface of the target. The energy lost at the target surface is less than the energy lost at any depth from the surface. The amount of energy lost by projectile particles for the given target material and for the given depth depends on the velocity of the projectile, on the elements, and on the density of the target material. Most of the energy loss is governed by the electronic stopping. Energy loss due to nuclear stopping is significant when the projectile particles possess low energy.\(^{23}\)

A typical backscattering geometry and the energy loss in the target material of thickness “t” is shown in Fig. 4.5.2.
When the projectile particles impinge on the target material, the backscattered energy from the surface (or from the thin film) becomes \( E_3 = K E_1 \), where \( K \) is the kinematic factor. The projectile particle penetrating through the solid target loses the energy both along the incident path (\( \Delta E_1 \)) prior to scattering and along the exit path after backscattering (\( \Delta E_3 \)). Hence backscattered energy becomes \( E_3'' = (E_1 - \Delta E_1) - \Delta E_3 \). This energy difference in the RBS spectra, which provides the depth profile of target constituents, can be used to identify scattering depths.\(^{26}\)

In the present study we have carried out the RBS measurements by using 2 MeV He\(^+\) ions with the detector position at 160° from the direction of incident ions.

Fig. 4.5.2 Schematic illustration of the parameters of RBS
4.6 Stopping and Range of Ions in Matter (SRIM) Simulations

Stopping and range of ions in matter (SRIM) is a computer program developed by James F. Ziegler and Jochen P. Biersack to calculate the interaction of ions with matter. This simulation program is based on the Monte Carlo simulation method with binary collision approximation (BCA) (influence of neighboring atoms neglected when there is collision between ion and atom). In ion irradiation physics, BCA enables the efficient computer simulation of the penetration depth and defect in a solid produced by energetic ions. The energy range of the energetic ions for the SRIM simulation is from 10 eV to 2 GeV. A comprehensive program called TRIM (Transport of Ions in Matter) is included in SRIM. TRIM can calculate the distribution of ions and the kinetic phenomena associated with ions stopping, damage produced, sputtering of target material, ionization, phonon production, and radiation damage. These calculations are made on the basis of full quantum mechanical treatments of ion-atom collisions where moving particle are ions and the rest particles are atoms in the target. Use of statistical algorithms makes the calculation efficient by allowing the ion to make jumps between calculated collisions and then averaging the collision results over the intervening gap. In these collisions, ion and atom have screened coulomb collisions with the interactions between overlapping electron shells. The ion can make long range interactions, which create electron excitations and plasmons in the target. The charge state of the ion within the target is considered to be the effective charge including velocity dependent charge state and long range screening, due to the sea of electrons of the target. In the TRIM simulation, we can even use a complex targets with up to 8 layers of different materials. It can calculate the 3D distribution of ions, ions range, damage, sputtering, ionization, and phonon production. This program has been made easy in the sense that it can be
interrupted at any time, and can be resumed later. The plots for the calculation can be saved and displayed when needed.

We will use this simulation to find out the ion range in surface nitrogen plasma treatment and carbon ion irradiation of the ultrathin Ru film.

4.7 Four Point Probe

A four point probe is used to measure the resistivity of a material. In the resistivity measurement of a thin film, it is required that the film is separated by some insulating layer. In case of the semiconducting materials, the junction between n-type and p-type materials itself acts as the insulating layer. This allows us to measure the resistivity of a p-type or an n-type material. But, in the case of metals or ceramics, the resistivity measurement requires the thin film deposition on some insulating substrate such as silicon dioxide.

Fig. 4.7 shows the schematic of resistivity measurement of a metal or ceramic thin film by using a four point probe. The four point probe contains four thin collinear tungsten wires which are made to contact the sample under test. These four probes are separated by an equal distance denoted by ‘S’. Current is made to flow between the outer probes, whereas voltage is measured between the two inner probes.

For a thin film of thickness ‘t’, which satisfy the condition of \( t/S \leq 0.5 \), the bulk resistivity of the thin film measured in the unit Ω-cm is given by

\[
\rho = 4.53 \, t \, \frac{V}{I}
\]

where, \( V/I \) is the slope of the current versus voltage plot obtained in the four point probe measurement.
4.7 Schematic of a four point probe resistivity measurement

4.8 References


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CHAPTER 5
PLASMA SURFACE AMORPHIZATION AND NITRIDATION

5.1 General Introduction: Plasma Modification in Metals and Ceramics

For the technological advances in different fields of applications, materials with unusual combinations of structural and functional properties not obtainable in monolithic bulk materials are often required.\(^1\) Thin films are an attractive alternative to bulk materials due to their significantly different properties owing to their physical dimensions, geometry, and non-equilibrium microstructures.\(^2\) Further uniqueness in the properties of thin films can be introduced by means of different modifications. Plasma assisted processes for thin film deposition and modification enable film properties to be varied over a wide range with the control of plasma conditions.\(^3\) In material processing and thin film technology, different plasmas have been increasingly used for modifications.\(^3\) Plasma consists of a source of activated gas and energetic ionic species, which can be used to promote various physical and chemical processes that can influence the properties of thin films.\(^3\) In the various plasma assisted processes, the main roles of the plasma are \(^4\) to activate and enhance the reactions necessary for the deposition of compound films and to modify the structure, morphology, and growth kinetics of the deposits.

There are many applications of plasma treatment of thin films. Plasma surface treatment is now considered one of the principle methods of improving the performance in the metal-mechanical industry to achieve the increased wear resistance of the materials.\(^5\) Surface nitriding to the titanium and its alloys has improved the wear and friction properties by means of microstructure modification.\(^6,7,8,9,10,11\) The similar nitriding treatments have also enhanced the corrosion and fatigue resistance in titanium and its alloy.\(^7\) F. M El-Hossary et al.\(^12\) have systematically studied the nitrogen plasma processing on a titanium surface by RF inductively
coupled plasma. Their result shows the increase in surface hardness of Ti with the increase in plasma processing time until 40 min. They report that during nitrogen plasma processing, the active nitrogen species (nitrogen ions) penetrate faster through surface grain boundaries as well as through micro-cracks of samples. With the further plasma processing, the rate of nitridation decreases because the nitrogen species already trapped in the sample block the grain boundaries and micro-cracks.\textsuperscript{12}

Keng-lian Ou \textit{et al.}\textsuperscript{13} have studied the thermal stability and electrical properties of plasma treated TaN films for the diffusion barrier applications in the Cu/TaN/Si system. N\textsubscript{2} and O\textsubscript{2} plasmas have been used to post-treat the tantalum nitride diffusion barriers. Both oxygen and nitrogen plasmas introduced microstructural modifications with the top layers being amorphized as confirmed by glancing angle XRD and TEM cross-sectional images.\textsuperscript{13} The grain size was found to decrease with the increase in plasma treatment time. For the equal times of plasma treatments, oxygen plasma was found to be more effective than nitrogen plasma. The as deposited TaN film was polycrystalline in nature with a grain size of about 20 nm. With the oxygen plasma treatment for 30 min, the grain size of TaN film reduced to about 2 nm.\textsuperscript{13} Thus, plasma processing to the TaN thin film caused the nanocrystalline effect, which is due to the reactions and bombardment of energetic radicals and ions. The nanostructured amorphous diffusion barrier is highly attractive due to its relatively higher thermal stability against copper diffusion.\textsuperscript{14} An increase in resistivity of the nitrogen irradiated TaN was observed. The resistivity was found to be stable after 10 min of plasma processing with a 6\% increase in value than the resistivity of as deposited TaN.\textsuperscript{13} The increased resistivity is attributed to the nitridation and nanocrystalline effects due to the plasma treatment.\textsuperscript{13} The failure temperature of nitrogen plasma treated TaN diffusion barrier to copper metallization was found to be about 150 °C higher
than non-irradiated TaN barrier. This proves that the thermal stability of the TaN diffusion barrier can be enhanced by means of nitrogen plasma processing.

5.2 Plasma Modification in Ru Film in the Present Work

As mentioned above, the plasma processing introduces the modification to the film in terms of its surface chemistry and micro or nanostructure. We have performed the nitrogen plasma irradiation to the 5 nm ruthenium (Ru) thin films. The N-plasma was generated by using radio frequency (RF) power with research grade nitrogen in a PVD system with a graphite target. Different bias voltages have been applied to the substrate (Ru film) to accelerate the nitrogen ions and bombard the film surface for a fixed time. As the bias applied in this study is not of sufficiently high power, this kind of plasma results the shallow surface processing of the few monolayers from the surface of the film. The purpose of this nitrogen plasma irradiation to Ru is twofold. The first is to cause microstructural modifications on the top surface. The second is to incorporate nitrogen in the film which prevents the diffusion of copper atoms during annealing and improves the barrier capability of the film. The results related to the nitridation and the barrier stability will be presented in this chapter.

5.3 Experimental Procedures

Ruthenium thin film was deposited on Silicon dioxide [Ru/\text{SiO}_2 (1000 \text{ A})/\text{Si}] by using magnetron sputtering physical vapor deposition (PVD). The target was 99.999% pure Ru material, and research grade Ar gas was used for the sputtering process. The thickness of ruthenium was confirmed to be around 5 nm by Rutherford backscattering spectroscopy (RBS) measurement using He+ beam at 2 MeV energy. RBS was performed by using the facility of the Ion Beam Modification and Analysis Laboratory (IBMAL) at the University of North Texas.
Six samples of dimensions 1cm×1cm each were irradiated with nitrogen plasma separately. Each sample was loaded in the chamber and base pressure was 5×10^-6 Torr. Nitrogen plasma was generated by introducing research grade nitrogen into the chamber at a pressure of 10 mTorr and by applying RF (Radio Frequency) power of 15 Watt. Negative DC bias voltage of -100V, -150V, -200V, -250V, -300V, and -350V were separately applied on the six samples. The time of nitrogen plasma irradiation for all samples at different bias voltages was kept fixed at 10 min.

X-ray photoelectron spectroscopy (XPS) measurements were performed on the samples to probe the ruthenium peak, nitrogen peak, and oxygen peak. XPS was done by using a PHI 5000 Versa probe at Center for Advance Research and Technology (CART) at University of North Texas. For the XPS measurements, Al monochromatic radiation (1486.6 eV) was used as the x-ray source and was focused to a spot size of about 200 µm. The pass energy for the measurement was 23.5 eV. Ar sputter clean was performed on the samples prior to the acquisition. Beam voltage and the current for the Ar ion were 1 kV and 0.5 µA. The size of the beam was 4 mm × 4 mm.

X-ray diffraction measurements were performed on the samples by using Rigaku Ultima III high resolution XRD at CART. The diffraction patterns were obtained using two-theta scans. The angle of incidence was fixed at 0.5°. The scan speed was 0.5°/min, and the step size was 0.05°.

About 40 nm copper was deposited on the non-irradiated Ru sample and N-plasma irradiated sample at the bias voltage -350 V by using the magnetron sputtering physical vapor deposition method. The copper deposited samples were annealed at different temperatures from 350 °C to 450 °C in a nitrogen atmosphere for 10 min. RBS measurements were carried out on
the annealed and non-annealed samples by using 2 MeV beam energy with the detector position at 160°.

5.4 Result and Discussion

Fig. 5.1 and fig. 5.3 show the Ru 3d and Ru 3p$_{3/2}$ signals respectively from the XPS measurements performed on as-deposited Ru thin film. The purpose of this measurement is to figure out the right sputtering conditions in order to clean carbon from the surface of the Ru samples. Since the carbon peak at around 284.5 eV overlaps with Ru 3d$_{3/2}$ peak at 284.3 eV, it is not possible to obtain independent C 1s spectra. Therefore, a different trick needs to be adopted here to ensure the sample surface becomes free from carbon contamination. Here we are considering a constant area ratio between Ru 3d$_{5/2}$ and Ru 3d$_{3/2}$ or a constant area under the Ru 3p$_{3/2}$ peak as the evidence for the carbon cleaned surface after an interval of sputtering time. The Ar sputtering used for the XPS measurements consists of the Ar ion accelerating voltage of 1 kV, and the ion current of 0.5 µA focused on the spot size of 4 mm × 4 mm. Ru 3d and Ru 3p$_{3/2}$ signals have been probed at different times of Ar sputtering. For Ru 3d signals, the area ratios under the 3d$_{5/2}$ and 3d$_{3/2}$ peaks have been calculated, whereas for Ru 3p$_{3/2}$ signals, the areas under curves have been calculated at different times of sputtering. Fig. 5.2 and fig. 5.4 reveal the plots for area ratio versus sputtering time and area versus sputtering time, respectively. For the Ru surface free from carbon contamination, the intensity ratio between 3d$_{5/2}$ and 3d$_{3/2}$ peaks should be greater than 1.5.$^{15}$ After 0.9 min. of sputtering, the area ratio has been found to be greater than 1.6 and remains almost constant until the sputtering time of 1.5 min. Similarly, the area under Ru 3p$_{3/2}$ curves remains constant after 0.9 min of sputtering. The area ratio greater than 1.6 for the Ru 3d peaks and the constant area under the Ru 3p$_{3/2}$ peaks after 0.9 min of Ar sputtering confirms the carbon contamination free surface of Ru film. So, in all XPS measurements related
to Ru samples, the carbon contamination cleaning was carried out with Ar sputtering with 1 kV and 0.5 µA for 1 min.

Fig. 5.1 Ru 3d signals from XPS measurements for as-deposited Ru films at different Ar sputter clean time

Fig. 5.1 Ru 3d signals from XPS measurements for as-deposited Ru films at different Ar sputter clean time
Fig. 5.2 Area ratio between Ru 3d$^{5/2}$ and Ru 3d$^{3/2}$ versus Ar sputter time from XPS measurements.

Fig. 5.5 shows the Ru 3d signals for nitrogen plasma irradiated Ru films before and after 1 min of Ar sputter clean. The area ratio between 3d$^{5/2}$ and 3d$^{3/2}$ peaks is greater than 1.6 after 1 min of Ar sputter clean. This indicates that for the nitrogen plasma irradiated Ru sample also carbon cleaning time with Ar sputter is 1 min.
Fig. 5.3 Ru 3p$_{3/2}$ signals from XPS measurements for as-deposited Ru films at different sputtering times
Fig. 5.4 Area under curves versus Ar sputter time for Ru 3p signals from XPS measurements
Fig. 5.5 Ru 3d signals from nitrogen plasma irradiated sample before and after Ar sputter clean.

Fig. 5.6 shows the SRIM simulation on nitrogen plasma irradiated Ru at different ion energies (a) 100 eV, (b) 150 eV, (c) 200 eV, (d) 250 eV, (e) 300 eV, and (f) 350 eV. From the simulation, it is clear that the nitrogen ion range in 5 nm Ru film for the above mentioned ion energies is 1.2 nm to 2.2 nm. This clearly indicates that the nitrogen plasma in the energy range we used processes only the top surface of the film.
Fig. 5.7 shows the N 1s signals in XPS measurements from the nitrogen plasma irradiated Ru samples at different negative dc bias voltages such as -100V, -150V, -200V, -250V, -300V, and -350V. This shows that we could successfully incorporate nitrogen on ruthenium film by means of nitrogen plasma irradiation. This nitrogen is incorporated at different ranges in Ru films irradiated at different bias voltages as shown in SRIM simulation.

Fig. 5.8 shows the area under N 1s peaks for the samples irradiated at different bias voltages. The area of nitrogen incorporated at bias voltage -100 V seems to be less, whereas for other bias voltages, the area is almost similar. This may be due to the competition between nitrogen incorporation in the film and the nitrogen sputtering out due to bombardment with the ions above the bias voltage of -150 V.
Fig. 5.7 N 1s signals from nitrogen irradiated Ru films at different negative dc bias voltages
Fig. 5.8 Area under N 1s curves from N-plasma irradiated Ru samples at different negative dc bias voltages.

Fig. 5.9 and Fig. 5.10 demonstrate the XPS signals of Ru 3d and Ru 3p₃/₂ respectively for as-deposited and nitrogen plasma irradiated ruthenium samples at different negative bias voltages. XPS signals from ruthenium before and after nitrogen irradiation at different bias voltages were found to be quite similar as shown in Ru 3d and Ru 3p₃/₂ peaks in figures. This indicates that there is no loss of Ru due to ion irradiation. Further, we observed the same centroid position of Ru 3d₅/₂ at 280.1 eV in Ru 3d spectra and Ru 3p₃/₂ at 461.3 eV between as-deposited and N-plasma irradiated samples, which means the Ru film is showing metallic...
character even after irradiation due to processing on the surface only and the weak bonding to the nitrogen.

Fig. 5.9 Ru 3d signals from N-plasma irradiated Ru samples at different negative dc bias voltages
Fig. 5.10 Ru 3p\textsubscript{3/2} signals from N-plasma irradiated Ru samples at different negative dc bias voltages.

Fig. 5.11 shows the XPS signals of O 1s for the as deposited Ru sample with (a) no Ar sputter clean, and Ar sputter cleaned for (b) 0.3 min., (c) 0.6 min., (d) 0.9 min., and (e) 1.2 min. Argon sputter clean was performed by using low energy file of 1 keV and 0.5 µA, and its sputter rate calibrated with silicon dioxide was 0.5 nm/min. The oxygen peak on as deposited Ru sample is from the native oxide layer. The broad peak in O 1s spectra before the Ar sputter clean may be due to the presence of C in the network of oxygen in the native oxide layer. Since chemical analysis on the specimens of interest is carried out after the removal of C from the sample, the analysis of oxygen spectrum on native Ru oxide in the presence of carbon contamination is not
known. Fig. 5.11 shows that oxygen remains in Ru film until the Ar sputter clean time of 1.2 min.

Fig. 5.11 XPS signals for O 1s for (a) as deposited ruthenium sample, and Ar sputter cleaned ruthenium sample for (b) 0.3 min., (c) 0.6 min., (d) 0.9 min., and (e) 1.2 min.

Fig. 5.12 exhibits the XPS signal of O 1s for the nitrogen irradiated Ru sample with (a) no Ar sputter clean, and Ar sputter clean for (b) 0.3 min., and (c) 0.6 min. The O 1s signal in fig. 5.12 marked as (a) is from the native oxide formed on the surface of the sample when it is exposed to air after taking it out from the nitrogen plasma irradiation chamber. Our not having observed oxygen after 0.3 min. of Ar sputter cleaning as marked (b) in fig 5.12, indicates that nitrogen plasma removed the native oxygen from the as deposited Ru sample during the irradiation. Further, we can see the native oxygen level until 1.2 min. of Ar sputter clean in the as
deposited Ru sample as shown in fig. 5.11. But in the nitrogen irradiated Ru sample, we could not observe oxygen after 0.3 min. of Ar sputter clean as shown in fig. 5.12. This proves that a nitrogen irradiated Ru film prevents oxygen intrusion, therefore, acts as the oxygen diffusion barrier. An oxygen diffusion barrier consisting of Ru-TiN thin film for dynamic random access memory (DRAM) capacitors has been reported by Jeong Sj et al.\textsuperscript{16}

Fig. 5.12 XPS signals for O 1s for nitrogen irradiated ruthenium (a) with no Ar sputter clean, and Ar sputter cleaned for (b) 0.3 min., and (c) 0.6 min.

Fig. 5.13 shows the x-ray diffraction measurements on (a) as deposited, and (b) nitrogen plasma irradiated Ru sample at -350V dc bias. The Ru peaks in the diffraction patterns were matched and verified by the JCPDS data card # 021258.\textsuperscript{17} We observed the reduction in intensity
of the XRD peaks for N-plasma irradiated Ru which is due to the nitridation and amorphization of the top surface of the film. A calculation showed that there is a reduction of crystallinity of around 18.6% in the N-plasma irradiated Ru film compared to the crystallinity of the as deposited Ru film. This calculation was performed on the basis of a ratio of the areas under (002) peaks in the XRD measurement under similar conditions for the as deposited and N-plasma

Fig. 5.13 X-ray diffraction patterns for (a) as deposited ruthenium film, and (b) nitrogen irradiated ruthenium film at -350 V dc bias
irradiated films. XPS study showed that the solubility limit of nitrogen in the N-plasma irradiated Ru film at the bias voltage of -350 V is 26% in the range of around 2 nm. In this calculation, the areas under Ru 3d peak and N 1s peak were calculated for the 2 nm region. The areas were divided by the respective sensitivity factors of ruthenium and nitrogen related to XPS measurement. The ratio between areas corrected by sensitivity factors was used to calculate the amount of nitrogen in the modified region.

Fig. 5.14 shows the resistivity of the as deposited Ru film and the N-plasma processed Ru films at different bias voltages. The resistivity of the as deposited Ru film was found to be 24 µΩ·cm, whereas the resistivity of the surface plasma treated Ru films varied from 41.3 to 98.7 µΩ·cm for the bias voltage that varied from -100 V to -350 V. The increase in resistivity of Ru films with the increase in N-plasma irradiation energy is due to the combined effect of top surface amorphization and different ion ranges of nitrogen in the films. In general, to meet the functional demand of the technology road map for the barrier materials, the resistivity of the barrier materials should be less than 300 µΩ·cm. The resistivity of the processed films in the present study is fairly below 300 µΩ·cm, so these films can fulfill the resistivity requirements for the barrier materials.
Fig. 5.14 Resistivity of the as deposited Ru film and the N-plasma processed Ru films at different bias voltages

Fig. 5.15 (a) reveals the RBS measurements on (a) not annealed, and (b) annealed at 350 °C Cu/Ru/SiO₂ samples with non-plasma irradiated Ru. Similarly, Figure 5.15 (b) shows the RBS measurements on (a) not annealed, and (b) annealed at 400 °C Cu/Ru/SiO₂ samples with non-plasma irradiated Ru. The measurement shows that copper reveals a growth of a distinct tail towards the lower energy channel number for the sample annealed at 400 °C. This observation is due to the diffusion of copper atoms to SiO₂ because of the failure of the Ru barrier. Also, Ru is
observed to slightly grow the tail towards the higher energy channel number at a temperature of 400 °C. This is due to the Ru film moving towards the surface when copper atoms diffuse down to SiO₂. This observation indicates that 5 nm Ru is safe for the diffusion barrier for copper interconnect at a temperature below 350 °C.

Fig. 5.15 (a) RBS measurements on (a) not annealed, and (b) annealed at 350 °C, Cu/Ru/SiO₂ samples with non-plasma irradiated Ru
Fig. 5.15 (b) RBS measurements on (a) not annealed, and (b) annealed at 400 °C, Cu/Ru/SiO$_2$ samples with non-plasma irradiated Ru

Fig. 5.16 (a) shows the RBS measurements on (a) not annealed, and (b) annealed at 400 °C, Cu/Ru/SiO$_2$ samples with N-plasma irradiated Ru at -350 V bias. Because nitrogen has a lower atomic weight than Si, the RBS peak of it superimposes in the Si region not shown in the plot. Until the annealing temperature of 400 °C, there is no sign of diffusion of copper to SiO$_2$ as displayed by the overlapping spectra of the as deposited sample to the sample annealed at 400 °C.
Fig. 5.16 (a) RBS measurements on (a) not annealed, and (b) annealed at 400 °C, Cu/Ru/SiO₂ samples with N-plasma irradiated Ru

Fig. 5.16 (b) shows the RBS measurements on (a) not annealed, and (b) annealed at 450 °C, Cu/Ru/SiO₂ samples with N-plasma irradiated Ru at -350 V. At the annealing temperature of 450 °C, the copper peak barely started growing a tail towards a lower energy channel number and Ru towards a higher energy channel number, which means copper is starting to diffuse towards SiO₂. Since diffusion is just beginning, it may still work for a diffusion barrier until 450
83°C annealing. This demonstrates that the nitrogen plasma treatment to the Ru film improved the barrier performance for copper metallization with an increase in the failure temperature by 100°C.

![Graph showing RBS measurements](image)

Fig. 5.16 (b) RBS measurements on (a) not annealed, and (b) annealed at 450°C Cu/Ru/SiO₂ samples with N-plasma irradiated Ru at -350 V

Fig. 5.17 shows the N 1s signal in XPS measurement on N-plasma irradiated Ru films at negative bias voltage of -350V, (a) not annealed sample, (b) annealed at 400°C, and (c) annealed
at 450 °C. From the figure, it can be observed that a small amount of nitrogen remained in the film until the annealing temperature of 400 °C. But, at the annealing temperature of 450 °C, nitrogen completely lost. This is the reason why the barrier started to fail and copper diffusion started at the annealing temperature of 450 °C.

Fig. 5.17 N 1s signal in XPS measurement for the N-plasma irradiated Ru film at -350 V bias and annealed at different temperatures
5.5 Summary of the Work

Nitrogen plasma post-treatment to the magnetron sputtered physical vapor-deposited ruthenium thin film of about 5 nm was carried out to improve the effectiveness of Ru as a diffusion barrier for advance copper interconnects. Nitrogen plasma could modify the microstructure of the top surface, making it amorphous as shown by XRD measurements. The XPS study showed that nitrogen was successfully incorporated in the Ru film. Because nitrogen is a good diffusion inhibitor to the diffusing species, the barrier was improved. Nitrogen plasma irradiated Ru film at bias voltage -350 V was studied to test the effectiveness of the diffusion barrier for copper and was found to have a superior performance over non-irradiated Ru film with an increase of failure temperature by around 100 °C, as shown in the RBS measurements. N1s signal in XPS measurement for annealed samples showed that nitrogen was unstable at the annealing temperature of 450 °C, which is the reason of failure of barrier to prevent copper diffusion.

5.6 References

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6.1 General Introduction: Ion Beam Modification in Materials

Ion beam technology has emerged as a very powerful and versatile tool in the field of research and industrial application. This technology has been widely used for the materials modifications, device making, and materials characterization. In the field of materials science and technology, the use of energetic ions is found to have unique applications. The ion beam analysis technique allows the precise determination of structural and compositional properties without any damage to the sample.1 Moreover, the process of ion beam implantation, or ion beam irradiation offers a wider range of possibilities for changing or modifying the structural, electronic, and optical properties of materials.2,3

In ion implantation or ion beam irradiation, there is ion-atom interaction, and such kinds of interactions are controlled by the velocity and energy, ion and atomic size, atomic number, mass, and distance of closest approach.4 Two forces, namely coulomb force and the nuclear force are involved in the ion-atom interaction process, and such an interaction involves elastic atomic collisions, inelastic atomic collision with atomic excitation, elastic nuclear collisions, and inelastic nuclear collision with nuclear interaction.4 When an ion impinges on the target and interacts with the target atom, the atom attempts to slow down the energetic ion, and its trajectory gets perturbed. This phenomenon is called the minor interaction. In the case of major interactions, there are large angle scattering, atomic displacements, sputtering, and inner shell ionization, or nuclear reaction.4 The energy of the ions, species of the ions, and the composition of the target determine how much modification is carried out in the material. Ion beam modifications in the material are performed by the major interactions. In the nuclear collision,
when a heavy ion with low energy interacts with the target atoms, many atoms are displaced from their original lattice positions. The target atoms recoiling from these collisions can carry sufficient energy to cause other atomic displacement, thereby causing the collision cascade, which causes the many atoms to be displaced from the ion path. A single Ar ion of energy 50 KeV can make hundreds of atoms displace in a volume nearby the ion trajectory. Ion beam irradiation causes point defects such as vacancy and interstitial. Ion impinging on the material causes the transfer of energy to the lattice atom and makes it dislodge from the crystal site. The removed atom may take an interstitial position in the crystal. The lattice point left by the atom behaves as the vacancy.

Solid state amorphization by means of ion irradiation was first observed on the experiments in intermetallic compounds. Some of the important properties like low magnetic loss, high corrosion and wear resistance, high strength, and improved catalytic properties are the useful and unique properties that the amorphous metallic alloy reveals over the crystalline alloy. The work performed by the researchers have experimentally shown that amorphization of a metallic alloy is possible with ion implantation with elements such as P, B, Si, As, and so on. When the energy per atom in the collision cascades due to the implanted ions in the crystal lattice reaches to $10^{-2}$ to 10 eV and the time required to cool the cascade (energy dissipation) is $\tau \leq 10^{-10}$ sec, then the final state of material in the cascade is considered similar to the quenching of the material from the liquid state. In this time interval of quenching, the quenching rate reaches $10^{12}$-$10^{14}$K/sec, which introduces the possibility of an amorphous state for both alloys and pure metals with self-implantation or implantation by inert gases. However, the works published on show the doubt about the amorphization of metals and alloys by means of microquenching from the melt in cascades. The works reported in introduce the concept
of solid-phase reaction for the amorphization of metals and alloys by means of ion implantation. This kind of solid-phase reaction consists of two stages, which are (i) a stage of attainment of a high energy state in the crystal, and (ii) a stage of nucleation and development of the amorphization process. In these phenomena, a physical picture of amorphization under ion beam includes the solution of thermodynamic, structural, and kinetic aspects.

The amorphization of metals thin films of sputtered aluminum\textsuperscript{19} and iron, cobalt, nickel, and such\textsuperscript{20,21} has been reported specifically for the high dose (10\textsuperscript{17}/cm\textsuperscript{2}) implantation of different ions such as P\textsuperscript{+}, As\textsuperscript{+}, B\textsuperscript{+}, and Sb\textsuperscript{+}. The amorphization process for these metal-metalloid systems is divided into two stages\textsuperscript{22}: the stage of accumulation of distortions or deformations of the lattice due to growth of concentration of implanted ions where lattice parameter increases linearly with the concentration of impurity to a value of about 0.6-0.8\%, and the stage of rapid development of amorphization in a narrow concentration region where the lattice parameter starts to decrease and is considered the relaxation of internal stress of the lattice. The amorphization occurs when the critical energy for lattice distortion is attained by means of implantation\textsuperscript{23} as the thermodynamic non-equilibrium of the high energy of crystal is the necessary condition for amorphization. Also, attainment of high atomic mobility in the regions connected with cascades or in the region of overlap is the kinetic process of amorphous phase formation. In these cascades, there are atomic disordering,\textsuperscript{24,25} formation of the regions enriched in vacancies and vacancy clusters, and interstitial atoms in the surrounding of the cascade.\textsuperscript{26,27} These are the factors that introduce the thermodynamic instability of the crystal lattice driving towards amorphization. Also, critical energy/defect density model considers that the crystalline to amorphous transformation is related to an increase in crystal lattice energy above the critical value.\textsuperscript{28,29} The increase in energy in the crystal lattice is due to the part of nuclear-stopping of
implanted ions during the collisions with lattice atoms. For the sufficiently high value of this
energy transfer, the defective crystalline lattice has an energetically favorable condition for the
transformation to amorphous state. The model assumes that the energy deposition per unit
volume should exceed the value $5 \times 10^{23}$ eV/cm$^3$ for the amorphization.$^{30}$ Since the energy
imparted is responsible for atomic displacement or defects, amorphization can also be considered
as a phase transformation due to the accumulation of critical defect concentration,$^{31}$ and in the
case of Si lattice, the defect concentration should exceed 0.02 atomic fractions for the
amorphization. This model is also considered to be a homogenous amorphization mechanism as
amorphous state is assumed to nucleate due to the interaction of many defects within the
different collision cascade and distributed uniformly in the irradiated region.

6.2 Carbon Ion Irradiation in Ru Film in the Present Work

From the above study, it is clear that ion beam irradiation modifies the microstructural
properties of the materials. In this work, we have modified the nanostructure of about 5 nm
ruthenium thin film on SiO$_2$ by means of ion beam irradiation. The ion beam constitutes
negatively charged carbon ion. We have used C-ion as it is easy to get an ion beam from the ion
source; we can get more ion current, which saves the processing time; and because the C atom is
lighter than the Ru atom, there is less sputtering effect. The energy of the ion beam used is 60
KeV, which is calculated by SRIM simulation. C-ions with this energy cross the Ru/SiO$_2$
interface, modifying the film. The irradiation was performed with the different fluences of
$2 \times 10^{16}$ atoms/cm$^2$, $5 \times 10^{16}$ atoms/cm$^2$, and $1 \times 10^{17}$ atoms/cm$^2$. In this ion beam modification,
high energy ions make the nuclear interaction with the lattice atom of the Ru film. This
interaction distorts the lattice periodicity and causes the defects accumulations. This process
invites the thermodynamic instability in the film and transforms to near amorphous or
amorphous phase. This process reduces or removes the grain boundary problem in the Ru film due to which the barrier performance gets enhanced. The results related to the Ru film processed with C-ion beam and its barrier capability for copper interconnects will be discussed in this chapter.

6.3 Experimental Procedures

Ruthenium thin film was deposited on Silicon dioxide [Ru/SiO₂ (1000 Å)/Si] by using magnetron sputtering physical vapor deposition (PVD). The target was 99.999% pure Ru material, and research grade Ar gas was used for the sputtering process. The thickness of the Ru was around 5 nm as determined by Rutherford backscattering spectrometry (RBS). RBS measurement used He⁺ beam at 2 MeV energy. X-ray diffraction measurements were performed on the samples by using a Rigaku Ultima III high resolution XRD at CART. The diffraction patterns were obtained using the two-theta scans. The angle of incidence was fixed at 0.5°. The scan speed was 0.5°/min, and the step size was 0.05°. The samples were irradiated with different carbon ion doses of 2×10¹⁶ atoms/ cm², 5×10¹⁶ atoms/ cm², and 1×10¹⁷ atoms/ cm². The irradiation was performed by using the facility of the Ion Beam Modification and Analysis Laboratory (IBMAL) at the University of North Texas. It uses a National Electrostatics Corporation Source of Negative Ions by Cesium Sputter (SNICS-II) to produce the ions for the implantation. The beam energy required for the purpose was determined by using SRIM simulation ³² and was found to be 60 KeV. The simulation showed that the C- ions with this energy would cross the Ru/SiO₂ interface, causing the modification on Ru film. The ion current during irradiation was 2 µA. The base pressure in the irradiation chamber was 5×10⁻⁶ Torr. Copper film was deposited on the non-irradiated Ru sample and the carbon irradiated Ru by using magnetron sputtering (PVD). The thickness of the copper was around 40 nm. The copper
deposited samples were annealed at a temperature range from 400 °C to 450 °C for 10 min in the nitrogen atmosphere. RBS measurements on these annealed and as deposited samples were performed to study the performance of the Ru diffusion barrier for copper metallization. RBS was done at IBMAL using He+ at 2 MeV energy. The detector position was kept at 160°.

6.4 Result and Discussion

Fig. 6.1 shows the SRIM simulation for 60 KeV C-ions irradiation on the multilayer structure Ru/SiO₂/Si. From the figure, it is seen that the carbon ions are implanted far from the
Ru/SiO₂ interface in the Si region. This ensures that C-ions are not staying in the Ru lattice. This has provided us the situation in which we could modify the Ru film without adding anything in its crystal lattice.

Fig. 6.2 shows the X-ray diffraction patterns for (a) as deposited sample, and the carbon irradiated samples at a fluence of (b) 2×10¹⁶ atoms/cm², (c) 5×10¹⁶ atoms/cm², and (d) 1×10¹⁷ atoms/cm². The Ru peaks in the diffraction patterns were matched and verified by the JCPDS data card # 021258.³³ It is clear from the figure that carbon irradiation with a fluence of 5×10¹⁶ atoms/cm² could greatly reduce the crystallization of Ru thin film by making it near amorphous, and that the fluence of 1×10¹⁷ atoms/cm² amorphized the film. The term near amorphous in the present study has been used for the microstructure of the film which shows a broad peak with a reduced intensity in the XRD spectrum. The critical energy and defect density model predicts that this kind of modification is related to the increase in crystal lattice energy above the critical value,³⁷,³⁸ which can also lead the crystalline to amorphous transformation for a sufficiently high value of energy transfer. The increase in energy in the crystal lattice is due to the part of nuclear stopping of implanted ions during the collisions with lattice atoms, and the effect of ion induced defects.³⁷,³⁸ Works by the researchers ⁷, ⁸, ⁹ have experimentally shown that amorphization of metals and alloys is possible by ion implantation. Since C-ion irradiation to Ru has made it amorphous, the film should be effective in blocking the copper diffusion.

Fig. 6.3 shows the resistivity of the as deposited Ru film; and C-ion irradiated Ru films at a fluence of 2×10¹⁶ atoms/cm², and 5×10¹⁶ atoms/cm². The resistivity of the as deposited Ru film was found to be 24 µΩ-cm, whereas for the C-ion irradiated Ru films with the doses of 2×10¹⁶ atoms/cm², and 5×10¹⁶ atoms/cm², resistivities were found to be 33.4, and 49.2 µΩ-cm,
respectively. The increase in resistivity of Ru films with the carbon irradiation is due to the amorphization effects.

Fig. 6.2 X-ray diffraction patterns for (a) as deposited Ru film, and carbon irradiated Ru film at a fluence of (b) $2 \times 10^{16}$ atoms/cm$^2$, (c) $5 \times 10^{16}$ atoms/cm$^2$, and (d) $1 \times 10^{17}$ atoms/cm$^2$. 

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Fig. 6.3 Resistivity of the as deposited Ru film and C-ion irradiated Ru films

Fig. 6.4 shows the RBS measurement on copper deposited on C-irradiated Ru film at the fluence of $5 \times 10^{16}$ atoms/cm$^2$ (a) not annealed, and (b) annealed at 400 °C. Until the annealing temperature of 400 °C, the Cu and Ru peaks overlap exactly on the Cu and Ru peaks of the as deposited samples, thereby indicating no sign of diffusion of copper into SiO$_2$. 
Fig. 6.4 RBS measurement on copper deposited on C-irradiated Ru film at a fluence of $5 \times 10^{16}$ atoms/cm$^2$ (a) not annealed, and (b) annealed at 400 °C

Fig. 6.5 shows the RBS measurement on copper deposited on C-irradiated Ru film at the fluence of $5 \times 10^{16}$ atoms/cm$^2$ (a) not annealed, and (b) annealed at 450 °C. At the annealing temperature of 450 °C, copper starts to grow a small tail to a lower energy channel number and Ru does to a higher energy channel number as compared to the as deposited sample, which means Ru barrier barely started to fail to block the diffusion of copper towards SiO$_2$. This indicates that C-ion modification to the Ru film improved the performance of the diffusion barrier properties by increasing the failure temperature of the barrier.
Fig. 6.5 RBS measurement on copper deposited on C-irradiated Ru film at the fluence of $5 \times 10^{16}$ atoms/cm$^2$ (a) not annealed, and (b) annealed at 450 °C.

Fig. 6.6 shows the XRD measurements performed on the (a) as deposited Ru film, and carbon irradiated Ru film at $5 \times 10^{16}$ atoms/cm$^2$ (a) not annealed and (b) annealed at 450°C. In the plot, it is observed that the C-ion irradiated near amorphous Ru film again recrystallized at an annealing temperature of 450 °C. This explains why the C-irradiated Ru barrier started to fail in blocking the copper diffuse at a temperature of 450 °C. This result shows that the failure of the Ru barrier for copper diffusion is related to the microstructure of the film. With an increase in C-ion irradiation dose to a certain limit, more damage is carried out in the film, and a defect density
in the film increases. This will increase the recrystallization temperature of the film, and the barrier performance will also enhance.

![XRD measurements](image)

Fig. 6.6 XRD measurements performed on (a) as deposited Ru film, and carbon irradiated Ru films at a fluence of $5 \times 10^{16}$ atoms/cm$^2$ (b) not annealed and (c) annealed at 450°C.
6.5 Summary of the Work

Carbon irradiation on around 5 nm Ru thin film on silicon dioxide at fluence of $5 \times 10^{16}$ atoms/cm$^2$ at energy of 60 keV caused the reduction in crystallinity by making the film near amorphous whereas irradiation with the fluence of $1 \times 10^{17}$ atoms/cm$^2$ almost amorphized the film. C-ion modified Ru thin film showed the superior performance over non-modified Ru film for the diffusion barrier for copper interconnects. Microstructure modification in Ru delayed the diffusion of copper until the temperature of 400 °C and barely started to fail for blocking copper diffusion at the annealing temperature of 450°C. Thus the failure temperature was increased by 100 °C more than that of the non-irradiated Ru film. The XRD measurements show that the reason copper barely started to diffuse at a temperature of 450°C is due to the recrystallization of the Ru film. This study shows that the failure of Ru film as a diffusion barrier for copper metallization is related to the microstructure of the film.

6.6 References


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CHAPTER 7
ALUMINUM DOPING INDUCED NEAR AMORPHOUS NITRIDED RUTHENIUM FILM GROWTH

7.1 Introduction: Effect of Co-sputtering in the Microstructure of the Films

Near amorphous alloys with disordered atomic arrangement have various unique and attractive properties different from the regular crystalline metals. These film structures are dense and free of grain boundaries, which lead to the improved performance of thin a film. In the absence of amorphous structures, thin films are impaired by porous columnar grains.

Transition metal (Ta, W, Ti, etc) based binary or ternary alloy films used for the diffusion barrier for copper metallization are mostly polycrystalline in nature. In these barriers, grain boundaries act as the dominant path for the diffusion of copper atoms. However, barrier layers consisting amorphous or near amorphous alloy films are free of grain boundaries and normally have a dense structure, and these are expected to effectively block the fast diffusion of copper into a silicon-based dielectric. Stable amorphous barrier layers such as Ta-Si-N, W-Si-N, and Ti-Si-N have already been reported, but the resistivity of these barriers is greater than 300 µΩ cm. Because of relatively high resistivity, these barriers are no more applicable in the manufacture of high speed operation devices following the trend of downscaling node technology. Studies have focused on exploring the possibility of the amorphization of films. From the theory of thin film growth, it is known that geometrical shadowing effect for the incident atoms is the main reason for the formation of a porous columnar structure. This kind of structure consists of a lower density void network surrounded by an array of parallel rods of a higher density, and such structures are observed in the film where the adatoms have limited atomic mobility. These columnar structures are more nearly perpendicular to the substrate than the vapor beam direction in the
film deposition process, and a simple logic of geometrical shadowing of the atomic vapor beam is sufficient to explain the features of these structures. Other investigations showed that the formation of columnar structures also depends on the deposition conditions such as substrate temperature, deposition rate, angle of incidence of vapor atoms, the vacuum ambient, and, as well, on the material itself. Besides the well-known processes for getting amorphous or near amorphous alloy structures such as rapid quenching and mechanical alloying, co-sputtered deposition of two or more elements has also emerged as the effective method. If two elements with dissimilarly sized atoms are deposited by co-sputtering technique, the process of forming columnar structures can be disrupted due to the increased atomic mobility and reduced shadowing effect. Also, during the co-sputtering process, bias can be applied to make energetic particles bombard on the film surface, which can alter the phase formation. Bias on the substrate also plays the role for amorphization tendency, and the properties such as stress on films, resistivity, and adhesion, all of which physically depend on the microstructure, can be changed by means of energetic particles bombardment.

Phase formation in the non-equilibrium material processing is carried by the interplay between thermodynamics and transformation kinetics. From the thermodynamics point of view, an amorphous structure of alloy thin film can be formed if a) heat of mixing is highly negative, b) atomic size difference is greater than 10%, c) deep eutectic point exists, and d) electronegativity difference is large. But Z.Z. Tang et al. reports the amorphization in Ta-Zr alloy film even when heat of mixing is positive (6 KJ/mol), the radius difference is 3.4%, and the eutectic temperature is 1820 °C, which contradicts the thermodynamic requirement for amorphization. This indicates that in some of the alloys like Ta-Zr, the kinetics might play a dominant role over thermodynamics. In such kinds of co-deposited alloys, formation of
amorphous phase is attributed to the suppression of crystallization due to limited surface diffusion. When the crystallization is forbidden kinetically, the solution phases would compete in the basis of thermodynamic stability.\textsuperscript{12} The surface diffusion coefficient is the well accepted dominant parameter that affects the phase competition kinetics at a low temperature physical vapor deposition (PVD).\textsuperscript{13} The effective surface diffusion length defined by Cantor and Cahn \textsuperscript{13} is given as

\[ X = \frac{D_s \alpha}{\sqrt{R}} \]  

(1)

where \(D_s\) is the surface diffusion coefficient, \(\alpha\) is the atomic spacing, and \(R\) is the deposition rate. The amorphous phase formation possibility in the alloy thin film by means of PVD can also be predicted on the basis of surface diffusion length.\textsuperscript{14} It is assumed that when effective diffusion distance reaches the value of distance to the nearest neighbor and crystal embryos reach the critical size, crystal growth is possible. In the case of Ta-Zr alloy film, an increase in energetic particles bombardment by means of increased bias voltage increased the surface diffusion distance. Because of this, amorphous structure forming range decreased.\textsuperscript{6}

Introducing the nitrogen in the co-sputtered alloy thin film can affect the amorphization because of its small atomic size and compound formation ability. Nitrogen can play the role of amorphous phase stabilizer in the films.\textsuperscript{15} When nitrogen is added in the alloy films, the atomic mobility and the activation energy of the atoms are reduced.\textsuperscript{15} This means the velocity of crystallization is reduced. Thus the addition of nitrogen acts as the diffusion inhibitor for the moving species during the crystallization phenomenon due to which nucleation temperature increases. This indicates that the addition of nitrogen in co-sputtering has an effect on the crystallization kinetics.\textsuperscript{15} J.H Hsieh et al. \textsuperscript{2} show the effect of addition of nitrogen in the amorphization of co-sputtered Ta-Cr alloy thin film. Ta-Cr-N thin films were found to have a
near amorphous structure, and introducing nitrogen also enhanced the range of formation of the near amorphous structure with different atomic % of Ta and Cr. Their work also shows that the addition of excessive nitrogen may lead to the formation of stable nitride, which in turn creates the possibility of a formation of columnar structure.

7.2 Reactive Co-sputtering of Ru and Al in the Present Work

From the study above, we know that co-sputtering of differently crystalline materials with different electronegativity and different atomic sizes produces the near amorphous or amorphous thin film due to the interplay between thermodynamics and transformation kinetics. We have also modified Ru film by means of reactive co-sputtering of Ru and Al with the addition of nitrogen. We have chosen Al metal in a small amount to incorporate to Ru lattice as it is a high conductive metal. Al has fcc crystalline structure, which is different than the hcp crystalline structure of Ru. Co-sputtering of Al with Ru to make alloy film generates the disrupted lattice. This phenomenon resists the crystallization, and the crystallization temperature is enhanced. Again, when nitrogen is introduced during co-sputtering, it acts as the amorphous phase stabilizer by inhibiting the activation energy and the atomic mobility of the diffusing species. The purpose of the addition of Al is not only to get the disrupted thin film but it is also to increase the stability of nitrogen at higher temperatures. Recrystallization of the film is suppressed for longer when nitrogen is stable in the film. We have prepared many thin films with the interplay between the gun power of Ru and Al, where Al was kept at fixed gun power and Ru was subjected to different power, keeping the fixed Ar to N ratio at 2.5 at 5 mTorr. The time of the deposition was varied with the variation of Ru gun powers so as to maintain the similar thickness of the films. Out of many thin films, one with the fixed Ru to Al ratio was studied for this dissertation.
7.3 Experimental Procedures

Clean SiO2 wafers were used as the substrate for the deposition of barrier films for this study. The co-sputtered depositions of Ru and Al were done by using the AJA sputtering system at the clean lab facility of University of Texas at Dallas (UTD). The sputtering system has a facility of 5 gun sources. The base pressure of this sputtering system was as good as 7 x 10^-8 Torr. Many test samples were prepared by varying the power between Ru and Al guns to match the right conditions of sputtering. Ar gas was used at 20 sccm flow to maintain 5 mTorr pressures in the chamber. Some co-sputtered samples were prepared without introducing N2 gas. The Al gun power was kept fixed at 20 W, whereas Ru gun power was varied to 50, 70, 100, and 200 W. With the increase in Ru gun power, the time of deposition was decreased so as to produce the similar thickness of the films. The other samples were prepared by means of reactive co-sputtered deposition by introducing N2 gas with Ar gas. The flow for Ar and N2 gases were maintained at 20 and 8 sccm, respectively, whereas the chamber pressure during sputter deposition was maintained at 5 mTorr. Many samples were prepared by keeping the Al gun power at 20 W and varying the Ru gun power to 50, 70, 100, and 200 W, and also varying the time of deposition.

X-ray diffraction measurements were performed on the samples by using Rigaku Ultima III high resolution XRD at CART. The diffraction patterns were obtained using two-theta scans. The angle of incidence was fixed at 0.5°. The scan speed was 0.5°/min, and the step size was 0.05°.

X-ray photoelectron spectroscopy (XPS) measurements were performed on the samples. XPS was done by using PHI 5000 Versa probe at the Center for Advance Research and Technology (CART) at the University of North Texas. For the XPS measurements, Al
monochromatic radiation (1486.6 eV) was used as the x-ray source and was focused to a spot size of about 200 µm. The pass energy for the measurement used was 11.75 eV. Ar sputter clean for hydrocarbon was performed on the samples prior to the acquisition. Beam voltage and the current for the Ar ion were 1 kV and 0.5 µA. The size of the beam was 2 mm×2 mm.

An energy dispersive X-ray (EDX) measurement was performed on the samples by using FEI Quanta environmental scanning electron microscope (ESCM) to determine the Ru to Al ratio in the sample. The electron beam voltage used was 5 kV. Since the film thickness was smaller, to reduce the interaction volume of the electron beam in substrate (SiO₂), the angle between beam direction and the sample surface was maintained at 10° by tilting the sample stage to 80°.

Around 40 nm of copper was deposited in around 5 nm Ru-Al-N films by using the physical vapor deposition (PVD) method. The copper deposited samples were annealed at different temperatures from 450 °C to 500 °C in a nitrogen atmosphere for 10 min. RBS measurements were done on the annealed and non-annealed samples by using 2 MeV beam energy with the detector position at 160°.

7.4 Result and Discussion

Fig. 7.1 shows the XRD measurements performed on the Ru film and the reactive co-sputtered Ru with Al films at different Ru gun powers and the time of deposition. These deposition parameters have been selected so as to have almost similar thickness of the films. For this purpose, before the real deposition of the films, the test films with different parameters were deposited on the Si substrate. A standard 5 nm Ru film was taken as reference, and the Si signal at 80° take of angle in XPS was probed. Test samples were prepared so as to get similar Si signals at 80° take off angles in XPS. These samples were assumed to have an almost similar thickness to that standard Ru sample. Now, using these parameters, the thin films were prepared
on the SiO₂ substrate. From the XRD measurements, it is clear that co-sputtering of Ru and Al in the Ar and N₂ gas flow has greatly reduced the crystallinity of the films. However, in different films prepared at different sputtering times with Ar to N₂ ratio fixed at 2.5 and varied gun power such as Ru gun power 200 W and Al gun power 20 W, Ru gun power 70 W and Al gun power 20 W, and Ru gun power 45 W and Al gun power 30 W show the oxide peaks. Since our purpose is to make oxygen free nitride thin film and study its performance in term of nitrogen stability and diffusion barrier capability, we dropped off the samples showing oxygen peaks in the XRD measurements. Now, the possibility remains to work with the thin film prepared with Ru gun power 100 W, Al gun power 20 W, Ar to N₂ ratio 2.5, and Ru gun power 70 W, Al gun power 20 W, Ar to N₂ ratio 5. XRD measurements in these two thin films show the near amorphous structure without any oxide peak. But the Al content in the film with Ru gun power 100 W should be lesser than that in the Ru gun power 70 W. For the similar crystallinity of the films, we want the film with comparatively low Al content. Therefore, for the further study, we are choosing the film prepared with Ru gun power 100 W, Al gun power 20 W, Ar to N₂ ratio 2.5.
Fig. 7.1 XRD measurements on the Ru film and the reactive co-sputtered RuAlN films at different Ru gun powers, Ar to N₂ gas ratio, and the time of deposition.

The composition of the film was determined by using XPS and RBS. For RBS measurement for composition determination, similar Ru-Al-N film was prepared on a vitrous carbon substrate. This is because for the film deposited in SiO₂, the Al and N peaks overlap with the Si peak, and it is difficult to separate them. The composition from RBS and XPS for the film on vitrous carbon was compared, and the necessary correction on the film on SiO₂ was made.
The composition of the film deposited for 2 min. with Ru gun power 100 W, Al gun power 20 W, and Ar to N₂ ratio 2.5 was found to be 82% Ru, 3.9% Al, 14% N and 0.1% O. This composition shows that the Ru to Al ratio is 21:1.

Fig. 7.2 shows the EDX spectra for the film deposited for 2 min with Ru gun power of 100 W and Al gun power of 20 W at Ar and N₂ gas ratio 2.5 (gas flow of 20 and 8 sccm respectively). This measurement was done to cross check the Ru to Al ratio in the film. The EDX peak for Al consists of Kα line and for Ru peak it consists of Lβ line. These spectra were measured with the 80° tilt of the stage to reduce the electron interaction volume and minimize the signal from the SiO₂ substrate. From this EDX measurement, the composition ratio between Ru and Al was found to be approximately 24:1. The Ru to Al ratio obtained for the RBS and XPS measurements and the measurement done with EDX are almost similar. This shows that a small amount of Al has been incorporated in Ru during co-sputtered deposition.

The thickness of the film was measured by using profilometer and SIMNRA simulation on the RBS measurement data. The profilometer shows the thickness of the film to be around 5 nm. Most of the composition in the film is Ru and there is only 3.9% of Al. So, for the thickness calculation using RBS and SIMNRA simulation was performed by taking the Ru peak only. The SIMNRA simulation also showed that the thickness of the film is around 5 nm.
Fig. 7.2 EDX measurement for the film deposited with Ru gun power 100 W and Al gun power of 20 W; and at an Ar to N₂ gas ratio of 2.5

Fig. 7.3 shows the XRD measurements performed on (a) Ru thin film (b) Ru₀.₈₂₄₄₃₈Al₀.₀₄₄₄₃₈N₀.₁₄ film. The Ru peaks in the diffraction patterns were matched and verified by the JCPDS data card #021258.¹⁶ From the fig. 7.3 in (b), it can be observed that the introduction of nitrogen and a small amount of Al to the Ru lattice by means of reactive co-sputtered deposition greatly reduced the crystallinity of the film by making it near amorphous. For Ru₀.₈₂₄₄₃₈Al₀.₀₄₄₄₃₈N₀.₁₄ films in (b), there is a broad peak at a diffraction angle of around 41.2°. Under the investigation, we found that for the phase Ru₅Al₂, there is a peak position at 41.1° matching to the observed peak in the samples. But, for the observation of Ru₅Al₂ phase, the percentage composition range for Al should be
65%-75% as verified in the Ru-Al phase diagram.\textsuperscript{17, 18, 19} In our sample, Al composition is fairly lower than this value.

![XRD measurements](image)

**Fig. 7.3 XRD measurements on (a) Ru thin film (b) Ru\textsubscript{0.82}Al\textsubscript{0.04}N\textsubscript{0.14} film**

Moreover, since we have introduced nitrogen in the Ru and Al system, we do not know yet how the nitrogen plays the role for phase evolution. The ternary phase diagram consisting of Ru, Al, and N systems is not known yet. This should be the single broad peak due to the disrupted lattice and near amorphous structure of the film. The peak shift to the lower diffraction angle should be because of strain on the film due to the incorporation of Al and N. This kind of peak shift due to stress in palladium because of incorporation of hydrogen (hydrogenation) in the film has been
reported by R. Juskenas et al.\textsuperscript{20} The presence of Al and N in the Ru lattice makes the lattice parameter of Ru increase due to which XRD peak shifts to a lower diffraction angle.

Fig. 7.4 shows the XPS signals for (a) Ru 3d, (b) Al 2p, (c) N 1s, and (d) O 1s for the thin film Ru\textsubscript{0.82}Al\textsubscript{0.04}N\textsubscript{0.14}. The XPS signals were probed after the carbon contamination cleaning on the surface of samples by Ar ion sputtering. The beam voltage and current of Ar ion used are 1k and 0.5 µA, respectively. The size of the beam used is 2mm × 2 mm, and time of sputter clean is about 25 sec. These signals from XPS measurements indicate that the co-sputtered film composition consists of Ru, Al, and N. In the figure (b) and (c), we have also shown the de-convolution for Al 2p, and N 1s peaks. The de-convolution has been carried out for the chemical analysis of the film to show the contribution of electrons with different binding energy to give the XPS peak profile of Al 2p and N 1s. Before doing de-convolution of the peak, for each sample B.E. correction was done by taking SiO\textsubscript{2} peak position corresponding to 103.3 eV as standard. Since the most dominant component of the film is Ru as shown by composition, it does not show the peak broadening with other elements. This was confirmed by comparing the FWHM in the Ru 3d \textsubscript{5/2} XPS signal on the pure Ru film and the Ru\textsubscript{0.82}Al\textsubscript{0.04}N\textsubscript{0.14} film prepared in the present study. XPS measurements on both films showed the FWHM to be equal to around 0.7 eV for Ru 3d \textsubscript{5/2}. The peak de-convolution parameters such as centroid and full width half maxima (FWHM) for Al-Al, Al-N, and N-Al bonding have been taken from the references.\textsuperscript{21, 22, 23, 24} The centroid and FWHM for Al 2p (Ru-Al-N), and N 1s (N-Al-Ru) bonding have been chosen so as to fit the curve.
In the present study, the centroid for Al-Al, Al-N, and N-Al were found to be 72.8, 74.3 eV, and 397.2 respectively, and FWHM were found to be 1.1, 2.1 eV, and 1.0 eV respectively, which matches the references 23, 224, 25, 26. The centroid and FWHM of Al 2p (Ru-Al-N), and N 1s
(N-Al-Ru) were found to be 76.2 eV, 4 eV and 398.3 eV, and 1.5 eV, respectively. The de-
convolution parameters from the references and from the present study have been listed in Table
7.1. The XPS measurements performed by Fuggle et al. 25 for Al in different alloys such as Al-
Cu, Al-Ag, and Al-Au show the significant shift to the higher binding energy due to alloying.
Piao et al. 26 report 2 eV shift of binding energy of the gold Au 4f7/2 spectra in Al2Au alloy (85.95
eV) as compared to the pure gold (83.9 eV). They also report that the oxidation of the Al2Au
alloy reveals the shoulder peak for gold Au 4f7/2 spectra even to the higher energy of around 86.5
eV [26].

<table>
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<th>FWHM (eV)</th>
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<td>From present study</td>
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<tr>
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Table 7.1 XPS peaks de-convolution parameters for Al 2p and N 1s in Ru0.82Al0.04N0.14 film

The increase in binding energy due to alloying is assumed due to the decreased electron density
of an atomic site. 27 Also, in the alloy system, the charge distribution is more complex than in a
simple ionic compound, and such a kind of binding energy shift comes from several facts such as
(i) differences in the chemical potential of the electrons in the different materials, 25 (ii) shifts of
charge to the region between the atoms, 28 and (iii) polarization effects. 29 The higher binding
energy peak of Al 2p spectra in our Ru0.82Al0.04N0.14 sample exhibits the similar trend of the Al and Au alloy as reported in the literatures.25, 26

Fig. 7.5 shows the resistivity measurements on the Ru film and the Ru-Al-N film by using a four point probe method. The resistivity of the Ru-Al-N film was found to be 129 µΩ-cm. This resistivity of the Ru-Al-N film meets the functional demand for use as the barrier material.

Fig. 7.5 Resistivity measurements on Ru film and Ru-Al-N film

Fig. 7.6 shows the RBS measurement on (a) not annealed, and (b) annealed at 450 °C, Cu/ Ru0.82Al0.04N0.14 /SiO2 samples for 10 min. in a nitrogen atmosphere. As Al and N are lower atomic weight elements than Si, the RBS spectra of them superimpose in the Si spectra and are not shown in the plot. Until the annealing temperature of 450 °C, the RBS spectra for the as
deposited and the annealed sample are perfectly overlapping without any tail of copper to a lower energy channel number and tail of Ru to a higher energy channel number. This indicates that there is no diffusion of copper to SiO₂ till the annealing temperature of 450 °C.

Fig. 7.6 RBS measurement on (a) not annealed, and (b) annealed at 450 °C, Cu/ Ru₀.₈₂Al₀.₀₄N₀.₁₄ /SiO₂ samples.

Fig. 7.7 shows the RBS measurement on (a) not annealed, and (b) annealed at 500 °C, Cu/ Ru₀.₈₂Al₀.₀₄N₀.₁₄ /SiO₂ samples for 10 min. in nitrogen atmosphere. From the plot it can be observed that at the annealing temperature of 500 °C, copper barely started growing a tail to lower energy channel and Ru to the higher energy channel. This indicates that the copper barely began to diffuse through the barrier at the annealing temperature of 500 °C, and the film may still
be used as a barrier for copper diffusion to this temperature. The introduction of a small amount of Al and N into Ru to disrupt the lattice, making it a near amorphous structure improved the barrier performance against the copper diffusion.

![Graph showing RBS measurement](image)

Fig. 7.7 RBS measurement on (a) not annealed, and (b) annealed at 500 °C, Cu/Ru$_{0.82}$Al$_{0.04}$N$_{0.14}$/SiO$_2$ samples

Fig. 7.8 shows the XRD measurement on (a) not annealed, (b) annealed at 450 °C, and (c) annealed at 500 °C Ru$_{0.82}$Al$_{0.04}$N$_{0.14}$ film for 10 min in a nitrogen atmosphere. Until the annealing temperature of 450 °C, we found no change in crystallization peak, which is similar to the as deposited sample. But at the temperature of 500 °C, again the crystallization peak Ru (100) reappeared, and Ru (002) and Ru (101) peaks started to grow up. The presence of Al and N in Ru
lattice delayed the growth of crystallization in the film until 450 °C. This is the reason why there is no diffusion of copper through the barrier film until this temperature. At 500 °C, the film became more crystalline, and copper atoms started diffusing through the grain boundaries.

Fig. 7.8 XRD measurement on (a) not annealed, (b) annealed at 450 °C, and (c) annealed at 500 °C Ru$_{0.82}$Al$_{0.04}$N$_{0.14}$ film

Fig. 7.9 shows the N 1s signal for XPS measurement on (a) not annealed, (b) annealed at 450 °C, and (c) annealed at 500 °C Ru$_{0.82}$Al$_{0.04}$N$_{0.14}$ film for 10 min in a nitrogen atmosphere.
The plot shows that the film contains nitrogen until the annealing temperature of 450 °C. But at a temperature of 500 °C, the nitrogen was completely lost from the film. In comparing the XRD measurements in Fig. 7.8 to the N1s signal in XPS measurements in Fig. 7.9, it is clear that crystallization growth was inhibited until nitrogen remained in the film. When the film became deprived of nitrogen at 500 °C, the crystallization growth began. This confirms that in the Ru$_{0.82}$Al$_{0.04}$N$_{0.14}$ film, nitrogen has played a great role in the crystallization kinetics.

Fig. 7.9 XPS measurement on (a) not annealed, (b) annealed at 450 °C, and (c) annealed at 500 °C Ru$_{0.82}$Al$_{0.04}$N$_{0.14}$ film
Nitrogen is behaving as a crystallization inhibitor by reducing the velocity of atomic rearrangement during the crystallization. This situation has led to the better performance of the film as the diffusion barrier for copper metallization.

7.5 Summary of the Work

A low amount of Al and nitrogen was introduced in the Ru lattice by means of reactive co-sputtering to make Ru-Al-N film. The addition of 4% Al and 14% nitrogen in Ru greatly reduced the crystallinity of the film, making it near amorphous compared to the pure Ru film. Nitrogen remained stable until the annealing temperature 450 °C for 10 min in N₂ atmosphere as shown in the XPS measurement. This is the improvement of the stability of nitrogen in the Ru film compared to the work done by Damayanti et al., in which nitrogen remains stable until the annealing temperature of 275 °C. This increase in stability of nitrogen is due to the introduction of a small amount of Al in the film. Nitrogen was completely lost from the film at the annealing temperature of 500 °C. Crystallization growth of the film was inhibited until the annealing temperature of 450 °C. At 500 °C, the crystallization growth commenced. The crystallization phenomenon in this work revealed the relation with the nitrogen content in the film. Until there is nitrogen, the crystallization appears inhibited. In the absence of nitrogen in the film, crystallization started to increase. This result verifies that nitrogen is acting as the crystallization inhibitor. The Ru-Al-N film perfectly worked as the diffusion barrier for copper until the annealing temperature of 450 °C, but began slightly to fail at 500 °C. The failure of the barrier is related to the crystallization growth and the nitrogen content of the film. In this work, we successfully improved the performance of the Ru film as a diffusion barrier by adding a low amount of Al and nitrogen.
7.6 References


16 JCPDS Data Card 74-2307 1998 (Swarthmore, PA: International Centre of Diffraction Data)


CHAPTER 8
CONCLUSION OF DISSERTATION

A study on the ultrathin Ru film was carried out to address the effect of surface modification and nanostructure modification on the performance of the diffusion barrier capability for the copper metallization. A comparison between the as deposited nanostructured film and the film modified with different techniques shows that the modified film has superior resistance in blocking the copper diffusion to that of the as deposited film.

Nitrogen plasma for surface modification of Ru film was performed using PVD with substrate bias at different voltages. SRIM simulation showed that the modification was a shallow surface modification which altered the top surface of the film. The N-plasma processing using a DC bias voltage -350 V transported the ions only to the depth of around 2.2 nm from the surface. This plasma modified the microstructure of the top surface, making it amorphous as shown by the decreased intensity of the XRD peaks in the XRD measurements. The N 1s signal in the XPS study from the plasma processed Ru film at different bias voltages showed that nitrogen has been incorporated in the film. Ru 3d and Ru 3p signals in the XPS measurements for the processed and as deposited films revealed no formation of strong chemical bonding between Ru and nitrogen. The resistivity of N-plasma processed Ru film was within an acceptable limit for the functional demands of chip manufacturing (below 300 $\mu$Ω·cm). Nitrogen plasma irradiated Ru film at substrate bias voltage of -350 V was studied to test the effectiveness of the diffusion barrier for copper, and it showed superior performance over non-irradiated Ru film with the increase of failure temperature being 100 °C as shown in the RBS measurements. This improvement in the diffusion barrier that resisted the copper diffusion is owing to the nitrogen being a good diffusion inhibitor to the diffusing species, and top surface of the film being
amorphized. Nitrogen was diffused completely out from the film at the annealing temperature of 450 °C which is the reason for the failure of the barrier at this temperature.

Also, ion beam modification on Ru thin film on silicon dioxide was carried out by means of carbon ions using the ion beam implanter. As shown by the SRIM simulation, the 60 KeV carbon ions could cross the Ru/SiO₂ interface. This modified the whole Ru film. 60 KeV carbon ions at the fluence of 5×10¹⁶ atoms/cm² reduced the crystallinity of the Ru film by disrupting the columnar structure, and made it near amorphous. The fluence of 1×10¹⁷ atoms/cm² almost amorphized the film as shown in the XRD measurement. The resistivity of C-ion irradiated Ru film was found to be within an acceptable limit for the functional demands of chip manufacturing (below 300 µΩ·cm). RBS measurements showed that the capacity of resisting the diffusing copper atoms by the ion beam modified Ru film is better than that of non-modified film. A nanostructure modification in Ru delayed the diffusion of copper until the temperature of 400 °C, and the failure temperature was increased by 100 °C. XRD measurements showed that the failure of the modified barrier at the temperature of 450 °C is due to the recrystallization. The performance of N-plasma irradiated Ru and C-ion irradiated Ru was similar for the diffusion barrier for copper metallization.

Finally, suppression of the crystallinity of the Ru film was also executed by introducing a low amount of Al and nitrogen in the Ru lattice by means of reactive co-sputtering. Producing a Ru-Al-N film by adding 4% of Al and 14% of nitrogen in Ru greatly reduced the crystallinity of the film and generated a near amorphous structure. XPS measurements with the de-convolution of Al 2p and N 1s peaks showed the bonding information in the film. Nitrogen in the film remained stable until the annealing temperature of 450 °C for 10 min in N₂ atmosphere. Thus a small amount of Al doping stabilized the nitrogen in the film until 450 °C, which is an
improvement against nitrogen stabilization in Ru film itself. Nitrogen was completely lost from the film at the annealing temperature of 500 °C. Crystallization growth of the film inhibited until the annealing temperature of 450 °C. At 500 °C, the crystallization growth initiated. Crystallization of the film in this work showed the relation to the nitrogen content in the film. Until the film contained nitrogen, the crystallization was inhibited. In the absence of nitrogen in the film, crystallization started to increase. Thus the nitrogen acted as the crystallization inhibitor. The Ru-Al-N film perfectly worked as the diffusion barrier for copper until the annealing temperature of 450 °C, but it started failing at 500 °C, as shown in the RBS measurements. The failure of the barrier is connected with the crystallization growth and the nitrogen content of the film. In this work, we could successfully improve the performance of the Ru film as a diffusion barrier by adding a low amount of Al and nitrogen. Low aluminum doped nitrided Ru thin film showed the superior performance as a diffusion barrier for copper metallization over N-plasma irradiated and C-ion irradiated Ru films.