SURFACE CHEMICAL DEPOSITION OF ADVANCED ELECTRONIC MATERIALS

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As interconnect features continue to shrink, new and challenging issues arise in the fabrication of advanced electronic materials. The focus of this work was to examine the direct plating of Cu on Ru diffusion barriers for use in interconnect technology and the substrate mediated growth of graphene on boron nitride for use in advanced electronic applications. The electrodeposition of Cu on Ru(0001) and polycrystalline substrates (with and without pretreatment in an iodine containing solution) has been studied by cyclic voltammetry (CV), current–time transient measurements (CTT), in situ electrochemical atomic force microscopy (EC-AFM), and X-ray photoelectron spectroscopy (XPS). The EC-AFM data show that at potentials near the OPD/UPD threshold, Cu crystallites exhibit pronounced growth anisotropy, with lateral dimensions greatly exceeding vertical dimensions.

XPS measurements confirmed the presence and stability of adsorbed I on the Ru surface following pre-treatment in a KI/H$_2$SO$_4$ solution and following polarization to at least −200 mV vs. Ag/AgCl. CV data of samples pre-reduced in I-containing electrolyte exhibited a narrow Cu deposition peak in the overpotential region and a UPD peak. The kinetics of the electrodeposited Cu films was investigated by CTT measurements and applied to theoretical models of nucleation. The data indicated that a protective I adlayer may be deposited on an air-exposed Ru electrode as the oxide surface is electrochemically reduced, and that this layer will inhibit reformation of an oxide during the Cu electroplating process.
A novel method for epitaxial graphene growth directly on a dielectric substrate of systematically variable thickness was studied. Mono/multilayers of BN(111) were grown on Ru(0001) by atomic layer deposition (ALD), exhibiting a flat (non-nanomesh) $R30(\sqrt{3} \times \sqrt{3})$ structure. BN(111) was used as a template for growth of graphene by chemical vapor deposition (CVD) of $C_2H_4$ at 1000 K. Characterization by LEED, Auger, STM/STS and Raman indicate the graphene is in registry with the BN substrate, and exhibits a HOPG-like 0 eV bandgap density-of-states (DOS).
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By

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CHAPTER 1

INTRODUCTION

As interconnect features continue to shrink, new and challenging issues arise in the fabrication of integrated circuits (IC). Cu, the interconnect material of choice, has been shown to have compatibility issues with interlayer dielectrics such as SiO₂. Problems including adhesion of Cu with SiO₂ and diffusion of Cu into substrates via electromigration can lead to unstable interfaces during fabrication processes. To overcome these obstacles, various metals such as Ta and Ti and their nitrides have been investigated as diffusion barriers for Cu metallization due to their immiscibility with Cu and relatively good electrical conductivity. Unfortunately, Cu does not wet these surfaces and a PVD layer of Cu must first be deposited. This PVD Cu is prone to dissolution in acidic solutions and difficult to apply uniformly over high aspect features. These problems have lead to investigation of direct plating on semi-noble diffusion barriers such as Ru. Electrodeposition of high quality, conformal Cu films on diffusion barriers is of direct importance to the semiconductor industry in the near future.

According to the international technology roadmap for semiconductors (ITRS), the features on semiconductor chips is expected to reach 15 nm by 2020. This will lead to a number of critical issues related to materials currently being used. In order to continue in advancement, a replacement for Si will have to be found. The discovery of isolated graphene in 2004 has shown to be a promising candidate for future CMOS and interconnect structures. Graphene has many exciting characteristics such as high electron mobility even at room temperature and it behaves like a zero-gap semiconductor. One of the key issues with the adaptation of graphene into devices is the development of techniques that will form large area,
single-layer films. The use of Ir(111) as a template for graphene growth indicates that the surfaces of seminoble surfaces such as Ru(0001) can be used as a template for graphene growth \textsuperscript{13}.

The first part of the research presented in this dissertation focuses on the kinetics of electrodeposited Cu on polycrystalline and Ru(0001) substrates. These studies included: 1) Growth kinetics and nucleation behavior of electrochemically deposited Cu on Ru(0001) in sulfuric acid solution and 2) The stability of an adsorbed iodine layer and its effects on nucleation behavior of electrodeposited Cu. Benchtop electrochemical experiments and those performed in a combined ultrahigh vacuum/electrochemistry system (UHV-EC) were used to study the nucleation behavior of Cu on the Ru substrates. Surface analytical techniques including x-ray photoelectron spectroscopy (XPS) and electrochemical atomic force microscopy (EC-AFM) where used to study iodine stability on the surface and growth modes of Cu nuclei on the surface respectively.

The second half of this dissertation concentrates on the chemical vapor deposition (CVD) growth of graphene on atomic layer deposited (ALD) hexagonal boron nitride (h-BN) films using Ru(0001) as a template. This method allows for the deposition of graphene films on a dielectric substrate of systematically variable thickness. The graphene and boron nitride films were characterized by low energy electron diffraction (LEED), Auger spectroscopy (AES), scanning tunneling microscopy/spectroscopy (STM/STS), and Raman.

1.1 Current Interconnect Processing

In 1997 IBM announced that it was replacing aluminum with copper in interconnects.
Because Cu is difficult to etch, a process was developed where vias and trenches were etched directly into an insulator known as a damascene or dual damascene (vias and trenches etched simultaneously). In this process an insulator, which is made of SiO₂ or other low-k materials, is patterned with conventional wet or dry etching techniques. Next, a diffusion barrier is deposited followed by a Cu seed layer that is deposited via PVD. The Cu seed layer is required due to poor adhesion of electrochemically deposited Cu to the materials used in the diffusion barrier (Ta, TaN, etc.). Electrochemically deposited Cu is then used to fill the trenches. Excess Cu and the diffusion barrier on the top horizontal surface are removed via chemical-mechanical planarization (CMP). By adding successive layers of insulator and Cu, a multilayer interconnection structure is created.

1.2 Diffusion Barriers in Cu Metallization

As mentioned previously, the poor adhesion of Cu to SiO₂ and the migration of Cu into the surrounding dielectric, necessitates the use of diffusion barriers in copper interconnects (Fig 1.1). An ideal diffusion barrier should exhibit several properties: good adhesion to copper and interlayer dielectric, high melting point, good electrical conductivity, immiscible to Cu and dielectric, and chemically stable with Cu and dielectric. Currently, diffusion barriers such as Ta and TaN are used in Cu interconnects ¹⁴,¹⁵. Thin barriers comprised of TaN are too resistive to deposit Cu electrochemically ¹⁶ so a Cu seed layer is needed to obtain good Cu electrofill. The copper seed layer is deposited via sputtering or PVD.
Fig 1.1. Diagram of Cu interconnect structure. ILD is the interlayer dielectric – SiO₂ or other low-k material.

As the feature size continue to shrink, so does the seed layer making it susceptible to etching in the open circuit condition of the plating bath. Because the electroplating process is carried out in ambient conditions, the copper seed layer can become oxidized which will affect the adhesion between Cu and the substrate ¹⁷. Decreased feature size also means that barrier materials are occupying an increasing portion of the cross-sectional area of the conductors. This becomes a problem because electrical and thermal conductivity of Ta is almost an order of magnitude lower than Cu ¹⁸. Ru and other semi-noble metals have been proposed as possible replacement barrier materials for Ta/Ta₂N ¹⁸, ¹⁹. Ru is particularly attractive option because Ru is stable in the ambient, bulk Ru and Cu are immiscible even at elevated temperatures ¹⁷, Cu has been shown to adhere strongly ¹⁹, and the thermal and electrical conductivities are almost twice that of Ta (7.6 µΩ cm and 13 µΩ cm respectively) ¹⁸.

1.3 Direct Plating of Cu

As devices continues to shrink down to 32 nm and below, overhang of the PVD Cu seed
layer will cause seed pinch off and sidewall coverage issues that will result in void formation during Cu electrofill as shown in Fig. 1.2. Chemical vapor deposition (CVD) of Cu has attracted some interest as a replacement for PVD Cu due to its superior step coverage. The high cost of the Cu precursor and formation of TaC and TaF limit the application of this approach.

Electroless deposition of Cu has also been explored for high aspect ratio features. Although electroless deposition allows for conformal films, the instability of the plating bath and slow film growth hinder this method. Therefore, the ability to directly plate Cu on a Ru barrier allows for the possibility of a seedless superfilling process.

Fig 1.2. Overhang of PVD Cu on feature.

1.4 Underpotential Deposition (UPD) of Cu

By studying underpotential deposition (UPD) reactions on electrode surfaces, one can gain insight into the electroactive area and the effect of various electrode pretreatments. UPD is defined as the electrochemical deposition of a metal (typically a metal cation) on an electrode surface at potentials more positive than predicted by the Nernst equation. The
Nernst equation is the equilibrium reduction potential of the half-cell in an electrochemical cell and is given by:  

$$E = E^\circ - \frac{RT}{nF} \ln Q$$  

(1.1)

where $E^\circ$ is the cell potential, $R$ is the universal gas constant ($R = 80314 \text{ JK}^{-1} \text{ mol}^{-1}$), $T$ is the absolute temperature, $F$ is the Faraday constant ($F = 9.65 \times 10^4 \text{ C mol}^{-1}$), $n$ is the number of electrons transferred in the cell reaction or half-reaction, and $Q$ is the reaction quotient. UPD occurs when the interaction of the metal with the electrode is thermodynamically more favored than metal-metal interactions. In cyclic voltammetry (CV), UPD appears as a small peak at a potential more positive than bulk deposition of the metal.

The underpotential deposition of sub-monlayer to multilayer quantities of Cu on Ru(0001) has been studied previously via combined electrochemical and UHV techniques. They observed the deposition of an initial, epitaxial layer formed via UPD followed by bulk deposition at more cathodic potentials. The appearance of the UPD peak is extremely sensitive to surface conditions. Cu UPD does not occur on the 3D oxide that forms on Ru due to exposure to the ambient or by electrochemical oxidation. Therefore, the presence or lack thereof of a Cu UPD peak can be used qualitatively to determine the effectiveness of surface pretreatment in the removal of ruthenium oxide. The Cu UPD process also offers an opportunity to study the interaction Cu and the Ru electrode that have been modified with additives used in superfilling applications without the measurement challenges associated with bulk Cu deposition.
1.5 Why Graphene?

As technology is quickly approaching the limits of how small transistors can be made in a chip, a replacement for silicon based electronics is highly sought after. Graphene holds the potential to play a role in the move away from traditional Si based microelectronics due to its exceptional electronic properties \(^{27,28}\) and spintronic applications \(^{10,29,30}\). Graphene consists of a single plane (2D) of hexagonally arranged, sp\(^2\) hybridized carbon atoms. While other crystallographic forms of carbon have been known for time (0D – fullerenes, 1D – carbon nanotubes, and 3D - graphite and diamond), graphene was only isolated recently \(^{11,31}\). Graphene is also one of the thinnest and strongest materials known.

1.6 Electronic Properties of Graphene

Graphene is a two-dimensional zero-band gap semiconductor with a band structure shown in Fig. 1.3. Charge carriers that propagate through the lattice are described by a Dirac-Like Hamiltonion: \(^{31}\)

\[
\hat{H}_0 = -i\hbar v_F \sigma \nabla
\]

where \(v_F\) is the Fermi velocity (~10\(^6\) m s\(^{-1}\)) and \(\sigma = (\sigma_x, \sigma_y)\) are the Pauli matrices. This is a direct consequence of graphene’s crystal structure, which consists of two equivalent sublattices \(^{32-34}\). Quantum mechanical hopping between the two sublattices leads to the formation of two energy bands. Where the two bands meet near the edges of the Brillouin zone generates the conical energy spectrum near the “Dirac” points K and K’ \(^{31}\). The linear nature of the spectrum of graphene causes its electrons to behave differently than those of metals and semiconductors whose spectrum is approximated by a parabolic dispersion relation \(^{35}\). Electrons in graphene act
as if they are massless relativistic quasiparticles (Dirac fermions) that travel close to the speed of light ($v_F \approx c/300$) even in ambient conditions $^{36}$.

Electron waves in graphene move through a layer that is only one atom thick and are sensitive to the proximity of other materials such as high-K dielectrics, ferromagnets, and superconductors. This property is similar to that observed for a 2D electron gas (2DEG) in semiconductors $^{29}$. Another exciting property of graphene is that unlike a metal where impurities in the crystal scatter electrons causing a loss in energy, the electrical resistance in graphene is independent to the number of impurities $^{37}$. As result of this, electrons can traverse microns without scattering even on samples placed on atomically rough substrates, covered in adsorbates, and at room temperature $^{35}$. This makes graphene a promising material for construction of high speed switching device called a “ballistic transistor.”

1.7 Fabrication of Graphene

The first and still most common method to obtain graphene is though micromechanical cleavage of bulk graphite $^{11,38}$. A freshly cleaved graphite crystal is gently rubbed across the

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Fig. 1.3. Band structure of graphene near the Fermi level. The conductance band touches the valence band at K and K’ points.
surface of an oxidized silicon wafer with an oxide layer of a specific thickness (300 nm)\textsuperscript{11,38}. Single sheets of graphene are visible in an optical microscope due to thin film interference effects. An alternative method is to place a graphite flake on a piece of adhesive tape and repeatedly peel the flake until the thinnest flakes are found (scotch-tape technique)\textsuperscript{11}. The isolated graphene sheets are then transferred to another substrate for experimentation as shown in Fig. 1.4. Both of these methods can produce high quality graphene films of up to 1 mm in size, but are delicate and time-consuming. Graphene films can also be grown on catalytic metal surfaces and then transferred to a pre-patterned substrate\textsuperscript{13,39,40}.

Epitaxial growth of graphene offers the most viable route towards electronic applications. Recently thermal decomposition of SiC has garnered significant interest because SiC provides an insulating substrate. In this method, a SiC(0001) substrate is heated to temperatures above 1500 K causing Si to evaporate leaving behind epitaxial graphene layers (Fig. 1.4)\textsuperscript{27,28,41}. The limited choice of substrate, high temperatures involved, and material processing issues connected with SiC has hampered development of this process\textsuperscript{42}. The use of Ir(111) as a template for growth of graphene flakes via the thermal decomposition of ethylene\textsuperscript{43} demonstrates the ability of (111) surfaces as templates for direct graphene growth.

![Diagram of graphene growth](image)

**Fig. 1.4. Conventional methods of graphene growth.**
1.8 Doping of Graphene Films

While graphene is of great interest due to its high electron mobilities in nanoelectronic or spintronic devices, in order to create useful components the electronic properties of graphene must be customizable via doping or by interactions with adjacent layers. Silicon based devices are doped by replacing some of the atoms in the crystal lattice with various dopant atoms or molecules. In graphene, however, the electronic structure of graphene is modified by adsorbed molecules on the surface or interaction with adjacent layers. Hwang et al. found that adsorbed NH$_3$ and NO$_2$ increased the Hall mobility and decreased the existing charged impurity density$^{44}$. Graphene films grown on SiC(0001) exhibit intrinsic n-type doping$^{35}$. Recently, charge neutrality was achieved in this system by noncovalently functionalizing graphene with the strong electron-acceptor tetrafluorotetracyanoquinodimethane (F4-TCNQ)$^{45}$. Alkali metals such as potassium are known to act as electron donors in graphene$^{37}$. The work presented in this dissertation demonstrates that an intermediate boron nitride layer enhances Ru to graphene charge transfer.

1.9 References


CHAPTER 2

EXPERIMENTAL METHODOLOGY

2.1 Film Deposition Techniques

2.1.1. Chemical Vapor Deposition (CVD)

Chemical vapor deposition (CVD) in its simplest form involves the flowing of precursor gas or combination of gases into a reaction chamber containing a heated substrate in order to initiate the growth of thin films. CVD has become an essential technique in ultra large-scale integrated circuit (ULSI) manufacturing. One advantage CVD has over types of film growth is the ability to grow conformal films of high purity even in high aspect ratio features \(^1\). This is in sharp contrast to deposition techniques such as physical vapor deposition (PVD) which requires line of site between the source and the surface of interest. Other advantages of CVD include relatively high deposition rates and it doesn’t require as high a vacuum as PVD.

For any given material there exists a number of precursors and processes that can be employed to deposit it. A precursor generally consists of the element of interest (metal, semiconductor, oxide, etc.) chemically bonded to a variety of atoms or groups of atoms. During the CVD process these atoms/groups of atoms react with the heated substrate leaving behind the species of interest. CVD starts from an initial vapor phase and then progresses through a series of physico-chemical steps. First, the reactive gas has to be supplied to the surface. Next, the reactive species are adsorbed on the surface, migrate, chemically react with the substrate, and form nuclei on the surface leading to the formation of a film. This is followed by desorption of the reaction by-products and diffusion of those by-products from the surface. This process is illustrated in figure 2.1.
Fig. 2.1. An illustration of the complex CVD process occurring on the substrate surface leading to film growth.

The reaction is typically endothermic and the energy required drive the reaction can be supplied via several sources such as thermal, photons, and electrons. Thermal energy is the most common form of energy used. In the following chapters graphene growth was achieved through the thermal decomposition of ethylene (C₂H₄) at 1000 K at 1.5 Torr.

2.1.2. Atomic Layer Deposition (ALD)

Atomic layer deposition (ALD) is a type of thin film deposition similar to CVD that uses sequential doses of typically two precursors to build up a film as shown in figure 2.1. As feature sizes on electronic devices continue to shrink, ALD is an attractive method of thin film deposition. One of the key advantages of ALD is the self-limiting nature of the process that provides atomic level control of film growth. In addition to the ability to grow films on high aspect ratio features, ALD techniques have been shown to grown conformal films on ultrafine
particles. ALD has been used to grow several types of films including metal sulfides (ZnS) \(^2,^3\), various oxides (Al\(_2\)O\(_3\), TiO\(_2\), etc.) \(^4,^5\), and metal nitrides (TiN, TaN) \(^6,^7\).

The ALD process used for the deposition of BN films was adapted from the literature \(^8\).

The overall binary reaction for BN growth is based on the CVD reaction: \(\text{BCl}_3 + \text{NH}_3 \rightarrow \text{BN} + 3\text{HCl}\). The binary reaction can be divided into the two \(\text{BCl}_3\) and \(\text{NH}_3\) half-reactions:

\[
\begin{align*}
\text{BNH}_2^* + \text{BCl}_3 & \rightarrow \text{BNBCl}_2^* + \text{HCl} \\
\text{BCl}^* + \text{NH}_3 & \rightarrow \text{BNH}_2^* + \text{HCl}
\end{align*}
\]

where * indicates a surface species. Each surface reaction is self limiting and sequential doses.

Fig. 2.2. An illustration of the ALD process.
of BCl$_3$ and NH$_3$ deposit approximately one monolayer of BN per AB cycle (~1.1 Å). Each precursor was dosed at a pressure of 1.5 Torr at 550 K for 12 min. Films of varying thickness can be deposited by controlling the number of AB cycles.

2.2 Electrochemical Techniques

2.2.1. Cyclic Voltammetry (CV)

Cyclic voltammetry (CV) is a form of potentiodynamic electrochemical measurement similar to linear sweep voltammetry (LSV) that can be used to study kinetics and thermodynamics of redox reactions on the surface of an electrode. In a CV experiment, the electrode potential is ramped linearly with time in a triangular waveform at a fixed rate known as the scan rate (V/s). The current response is measured continuously as the potential is swept and then plotted as current (i) versus potential (E). A typical triangular waveform and resulting CV is shown in figure 2.3. The scan is normally started at open circuit potential (OCP)/V$_1$, where no current flows, and then is swept negative towards the second potential (V$_2$). There is an initial rise in current as the oxidized species contained in the bulk solution are reduced at the electrode surface (e.g. Cu$^{2+}_{\text{aq}}$ + 2e$^- \rightarrow $ Cu$_{\text{metal}}$). As the equilibrium is shifted further to the right side, a peak occurs (E$_{pc}$) due to a diffusion layer that forms over the surface because the flow of oxidized species is limited by their diffusion through the electrolyte. There is a drop in current until the second potential is reached and the potential is swept in the opposite direction. As the scan is reversed, the species that were reduced at the electrode surface are oxidized and diffuse back into the solution until a second peak (E$_{pa}$) occurs. There is a decrease in current as
the oxidized molecules diffuse away from the surface until all of the molecules are removed and the potential returns to the OCP.

Fig. 2.3. a) Triangular wave form and b) corresponding cyclic voltammogram (CV) techniques.

2.2.2. Chronoamperometry (CA)

Chronoamperometry (CA), also known as potential step voltammetry, is an electrochemical technique where the potential of the working electrode is stepped to another potential for a given amount of time and the resulting current is measured over time. The potential wave form and resulting current-transient are shown in figure 2.4. The initial potential \( V_1 \) starts at a potential where no reduction takes place and then is stepped to a second potential \( V_2 \) where reduction of the molecule of interest occurs. There is an instantaneous rise in current due to the charging of the double layer followed by an increase of current due to electron transfer reaction with an electroactive species \(^{10}\). The current decays quickly as all of the molecules near the electrode surface are depleted and a diffusion layer forms above the
surface. Further reduction only occurs as the molecules of interest diffuse though the solution.

Chronoamperometry can be used to determine rate of diffusion of a species through the solution, the thickness of an electrochemically deposited film and determine the kinetics of nucleation.\(^9\)

![Fig. 2.4. a) The potential wave form and the b) corresponding current-time response.](image)

2.3 Characterization Techniques

2.3.1. Auger Electron Spectroscopy (AES)

Auger electron spectroscopy (AES) is a surface specific technique that utilizes the emission of low energy electrons in the Auger process to determine the composition of the surfaces, thin films, and interfaces. An Auger electron spectroscopy system consists of an ultrahigh vacuum system, an electron gun for sample excitation, and an energy analyzer for the detection of Auger electron peaks. In AES the sample is bombarded by an electron beam of 1-10 keV energy that forms a vacancy due to the ejection of a K shell (core level) electron. X-rays
can also be used to induce Auger emission in a process called X-ray-excited Auger electron spectroscopy (XAES). Because the ionized atom is an unstable state, the core hole is filled by electron from a higher level within the same atom (e.g., L₁). The electron transitioning to a lower energy level loses an amount of energy equal to the difference between the two energy levels in the form of a photon. This photon can either escape from the solid via fluorescence or react with a lower energy electron within the atom (L₂,₃) which can be emitted if the transferred energy exceeds the orbital binding energy. A diagram of the Auger process is shown in Fig. 2.5. The emitted electron is called an Auger electron after Pierre Auger who first observed the process in the mid-1920’s. The final state is a doubly-ionized atom with core holes in the L₁ and L₃ levels.

Fig. 2.5. Diagram of the Auger process showing a) the ejection of a core electron followed by b) emission of an Auger electron.
Auger electrons are labeled according to energy level involved in their production. The initial hole location is given first, followed by the locations of the two final holes in order of decreasing binding energy. Thus in the example in figure 2.5 the Auger transition would be labeled as KL\textsubscript{1}L\textsubscript{2,3}. The kinetic energy (KE) of the ejected Auger electron is approximated by:

\[
KE = E_K - (E_{L1} + E_{L2,3}) \tag{2.1}
\]

where \(E_K\) is the binding energy of the core electron and \(E_{L1}\) and \(E_{L3}\) are the binding energies of the two higher energy level electrons involved in the Auger process. Due to the dependence of the Auger electron on the three energy levels involved in the Auger process and since the binding energies are unique, the Auger electrons will have a kinetic energy characteristic of the parent atom. Auger spectroscopy has a high sensitivity to most atoms especially atoms with low atomic number except H and He, which do not have 3 electron and therefore cannot undergo the Auger process.

Auger spectroscopy is extremely surface sensitive due to low the energies of Auger electrons (10 – 3000 eV). At these energies, the depths at which electrons can escape the solid without losing all of its energy are on the order of a few monolayers. The low escape depth of an Auger electron is a direct result of the inelastic scattering process an Auger electron undergoes in a solid. The inelastic mean free path (IMFP) is the average distance an electron travels between successive inelastic collisions. In an Auger experiment the intensity of the Auger electrons are plotted as a function of energy (N vs. eV). The Auger peaks appear as smaller features on a large, continuous secondary electron background as shown in Fig 2.6.a. In order to obtain a better sensitivity for detection and to emphasize the Auger fine structure the Auger spectra is typically plotted in derivative mode (dN/dE) as shown in Fig. 2.6.b. The total
Auger electron intensity is directly proportional to the concentrations of the various elements that comprise the sample volume. The surface concentration of a particular element can therefore be derived from measuring the peak-to-peak heights in the Auger spectrum. In addition some information on the chemical environment of the element can be determined from the peak position, shape, or fine structures.

Fig. 2.6. Auger spectrum of BN film on Si(111) in a) integrated and b) derivative mode.

2.3.2. X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), is a technique used to determine the elemental composition and
electronic state of the surface region of a sample. An XPS system consists of ultrahigh vacuum system, a source of X-rays, electron energy analyzer, electron detector, and a recorder. In XPS the sample is illuminated with soft x-rays (with a photon energy of 1253.6 eV (Mg Kα) or 1486.6 eV (Al Kα)) that result in the emission of photoelectrons from the surface. The photoemission process is shown schematically in Fig. 2.7. Because the energy of the incident x-rays are known, the electron binding energy of the emitted photoelectrons can be determined by measuring the kinetic energy of the emitted electrons and inputting it into the following equation:

\[ E_b = h\nu - E_k + \phi_s \]  

(2.2)

where \( E_b \) is the binding energy of the emitted photoelectron, \( h\nu \) is energy of the incident photon, \( E_k \) is the photoelectron’s kinetic energy, \( \phi_s \) is the work function of the spectrometer. In addition to the photoelectrons emitted in the photoelectric process, Auger electrons may be emitted due to relaxation of the excited atoms after photoemission.

For each element there is a characteristic binding energy associated with each core atomic orbital. This gives rise to a characteristic set of peaks for each element determined by the incident photon energy and the binding energy of the core electron. Therefore the presence of peaks at characteristic energies indicates the presence of a specific element in the sample. The intensity of the peaks is related to the concentration of a given element within the sample. Chemical shifts (variations in the elemental binding energies) due to differences in chemical potential, oxidation state and polarizability of compounds can be used to determine the chemical state of the materials being studied. The ability to discern between different oxidation states and chemical environments is one of the major advantages of XPS as an analytical technique.
The thicknesses of native oxides and deposited thin films were quantified by measuring the attenuation of the substrate intensity by an overlayer of interest. The signal of substrate B covered by an overlayer A with thickness \(d_A\) is: \(^{11}\)

\[
I_B = I_B^\infty \exp\left(-\frac{d_A}{\lambda_A(E_B)} \cos \theta \right)
\]  
(2.3)

where \(I_B\) and \(I_B^\infty\) are the intensity and atomic sensitivity factors for the substrate respectively, \(\lambda_A(E_B)\) is the IMFP for a photoelectron from substrate B passing through overlayer A, and \(\cos \theta\) is the angle between the surface normal and the axis of the analyzer. The signal of the overlayer A with thickness \(d_A\) is: \(^{11}\)

\[
I_A = I_A^\infty \left[1 - \exp\left(-\frac{d_A}{\lambda_A(E_A)\cos \theta} \right) \right]
\]  
(2.4)

where \(I_A\) and \(I_A^\infty\) are the intensity and atomic sensitivity factors for the overlayer respectively, \(\lambda_A(E_A)\) is the IMFP for a photoelectron from overlayer A. Equations 2.3 and 2.4 are plotted vs. thickness with the point at which the two line cross equal to the thickness of the overlayer A.

The IMFPs (\(\lambda\)) used in the thickness measurements were calculated using the TPP-2M equation: \(^{11,13}\)
\[ \lambda = \frac{E}{E_p^2 \left[ \beta \ln(\gamma E) - \left( \frac{C}{E} \right) + \left( \frac{D}{E^2} \right) \right]} \quad (2.5) \]

\[ \beta = -0.10 + 0.944 \left( E_p^2 + E_g^2 \right)^{1/2} + 0.069 \rho^{0.1} \quad (2.6) \]

\[ \gamma = 0.191 \rho^{-1/2} \quad (2.7) \]

\[ C = 1.97 - 0.91U \quad (2.8) \]

\[ D = 53.4 - 20.8U \quad (2.9) \]

\[ U = N_v \rho / M = E_p^2 / 829.4 \quad (2.10) \]

\[ E_p = 28.8 \left( N_v \rho / M \right)^{1/2} \quad (2.11) \]

where \( E_p \) is the free-electron plasmon energy (eV), \( \rho \) is the bulk density (g/cm\(^3\)), \( N_v \) is the number of valance electrons per atom or molecule, \( E_g \) is the band gap energy (eV), \( \gamma \) is a parameter that describes the dependence of energy-loss function on momentum transfer, \( \beta \) is a parameter that describes the dipole matrix effect for all available inelastic scattering process, and \( M \) is the atomic or molecular weight.

2.3.3. Low Energy Electron Diffraction (LEED)

Low energy electron diffraction (LEED) is a technique used for the determination of the surface structure of crystalline materials. LEED is used in one of two ways: 1) qualitatively – analysis of the spot positions is used to determine information on the size, symmetry, and rotational alignment of adsorbates with respect to the substrate, or 2) quantitatively – the intensities of the spots are recorded as a function of electron beam energy to generate I-V curves which can provide information on atomic positions. LEED experiments use a collimated beam of low energy electrons (usually in the range of 20 – 200 eV) that are directed normally.
on the sample. LEED takes advantage of the wave-particle duality nature of electrons –
electrons may be regarded as a series of waves incident normally on the surface. These waves
will be scattered by regions of high electron density (the surface atoms), which can be
considered to behave as point scatterers. The wavelength (λ) of the incident electrons is given
by the de Broglie relation:\textsuperscript{14}

\[ \lambda = \frac{h}{p} \approx \sqrt{\frac{150}{V}} \text{Å} \tag{2.12} \]

where \( p \) is the momentum of the electrons and \( V \) is the accelerating voltage of the electron gun
(eV). For an electron with a kinetic energy of 150 eV, the wavelength is \( \sim1 \) Å, which corresponds
to the interatomic distances in a solid.

Unlike x-ray diffraction, low energy electrons are strongly back-scattered by the
electrons of the surface atoms. A simple model for the scattering of surface atoms is a one
dimensional (1-D) chain of atoms with an atomic separation \( a \) and an electron beam at right
angles to the chain as shown in Fig. 2.8. For backscattered electrons from two adjacent atoms
at a well-defined angle, \( \theta \), there is a path difference \( (d) \) the electrons have to travel from the
scattering centers back to the detector. The path difference between beams is \( d = a \sin \theta \). For
constructive interference to occur the path difference must be an integral multiple of the
wavelength of the incident electron beam. This constructive interference can be described by
Bragg’s law of diffraction:

\[ a \sin \theta = n \lambda \quad \text{where } n = 1, 2, 3... \tag{2.13} \]

For two isolated scattering centers the diffracted intensity varies slowly between zero
(complete destructive interference) and its maximum value (complete constructive
interference). For a large periodic array of scatterers the diffracted intensity is only significant when the Bragg condition is met. For a surface with a two dimensional (2-D) array of atoms of interatomic distance $a$ and $b$, the Bragg condition requires that for constructive interference to occur both $a\sin\theta = n\lambda$ and $b\sin\theta = m\lambda$ must be true $^{14}$.

![Diffraction of electrons from a 1-D chain of atoms.](image)

Fig. 2.8. Diffraction of electrons from a 1-D chain of atoms.

A LEED system is comprised of two main components: 1) an electron gun that produces a collimated beam of electrons and 2) a display system, usually a hemispherical fluorescent screen on which the diffracted pattern is observed directly. A typical LEED system is shown in Fig. 2.9. The sample must be a crystalline, well-ordered, and planar surface in order for a diffraction pattern to be observed. In a LEED experiment a narrow beam of electron strikes the sample surface with an energy between 20 and 200 eV. A series of diffracted beam of electrons with the same energy as the incident beam are produced in the backward direction and strike the detector. The detector consists of four metal grids at different voltages and a hemispherical
fluorescent screen. The first and last grids are held at ground potential to ensure a field free region around the sample. The next two grids are set to the retarding potential, which is slightly lower than the kinetic energy of the electrons produced by the electron gun. These grids repel all inelastically scattered electrons. The elastically scattered electrons are accelerated towards the hemispherical fluorescent screen which is set to a high positive voltage (on the order of a few keV). The diffracted electrons that strike the screen result in bright spots whose pattern are the reciprocal of the ordered atoms of the surface. The LEED spots are then either photographed or captured digitally for analysis.

Fig. 2.9. A diagram of a LEED system.

2.3.4. Electrochemical Atomic Force Microscope (EC-AFM)

Electrochemical atomic force microscope (EC-AFM) is a technique used to image in-situ the topography of an electrode surface with a resolution of nanometers through an adsorbed fluid layer on the surface. An EC-AFM instrument consists of a cantilever and tip, piezoelectric motor, fluid cell, potentiostat, diode laser, and split photodiode detector. The tip, attached to
the end of a cantilever made from SiN, is scanned across the surface of the sample in contact mode. The sample is mounted on a piezoelectric tube that is used to raster the sample in the x and y direction and move the sample in the z direction to maintain contact with the tip. When the tip is brought into contact with the surface, forces between the tip and sample lead to deflection of the cantilever according to Hooke’s Law: 15

\[ F = -kx \]  

(2.14)

where \( F \) is the force, \( k \) is the spring constant, and \( x \) is the cantilever deflection. Forces range from nN to µN 15. The deflection is measured using a laser spot on the top surface of the cantilever reflected into a split photodiode detector. An EC-ATM also has a fluid cell made from machined glass with an O-ring to form a seal between the fluid cell and the sample surface. The fluid cell is a closed system where the injected electrolyte and sample surface are not exposed to ambient air. A diagram of a fluid cell for AFM is shown in Fig. 2.10.
2.3.5. Scanning Tunneling Microscope (STM) and Spectroscopy (STS)

Scanning tunneling microscopy (STM) is a common technique for obtaining atomic-scale images of surfaces. The STM uses the concept of quantum tunneling to monitor the separation between the sample and a sharp metal tip. When an atomically sharp metal tip is brought in close proximity (a few angstroms) to the surface to be studied, an applied bias can cause electrons to tunnel from the tip to the sample or vice versa. The direction of the tunneling current is determined by the polarity of the applied bias: when the sample is biased negatively relative to the tip, electrons will tunnel from occupied states of the sample into empty states or conduction band of the tip; alternatively when the sample is biased positively, electrons will tunnel from occupied states of the tip into empty states of the sample. This process is illustrated in Fig. 2.11.

![Diagram](image-url)

**Fig. 2.11** Quantum tunneling from the tip that has been biased negative into a metal substrate.
As tip-sample separation decreases and increases due to feature height, the corresponding tunneling current \( I_t \) increases and decreases exponentially according to the following relationship:\textsuperscript{16}

\[
I_t \propto e^{-2\kappa d}
\]

(2.15)

where \( d \) is the tip-sample distance and \( \kappa \) is the wave functions in the barrier. \( \kappa \) is given by:

\[
\kappa = \sqrt{\frac{2m\Phi}{\hbar}}
\]

(2.16)

where \( \Phi \) is the local barrier or the effective local work function. Work functions are usually on the order of 4 to 5 keV which gives a value for \( \kappa \) of \( \sim 1 \text{ Å}^{-1} \). As a direct result of this, for every one angstrom that the separation distance decreases, the tunneling current increases by almost an order of magnitude. The exponential decay of tunneling current with tip-sample distance is what makes STM such an important technique for imaging surface topography on an atomic level.

To a first approximation in STM, the electron density across a surface corresponds to the positions of atoms or atomic steps of the surface. To be more precise, the STM measurements are actually based on the electron density of states (DOS). Because the tunneling current reflects the DOS of the sample’s surface, the STM can be used to perform scanning tunneling spectroscopy (STS). STS gives details about which electron energy states are occupied as well as unoccupied. In addition, STS provides information on chemical composition, bonding, and the band gap of the surfaces being studied. There are several ways to perform STS experiments including topography imaging at varied applied potentials, current imaging at different heights, and local measurements of the tunneling current versus tip-sample bias (I-V or dI/dV) curve.
In the following chapters, the I-V and dI/dV (tunneling current is measured versus the bias voltage in constant height mode and its derivative) curve are the method of choice for probing the DOS. STS measurements can be averaged over a large region or obtained for a single point. In order to obtain an I-V curve while imaging the surface, a sample-and-hold circuit freezes the voltage applied to the z piezo. This fixes the tip-sample distance without the feedback system responding. The tip-sample bias is swept between the specified values and the resulting tunneling current is recorded. The recorded I-V curve can be used to probe the local electronic structure and the band gap of the material. By taking the derivative of the I-V curve, a plot of conductance (dI/dV), versus the tip-sample can be obtained. The structure of the dI/dV curve is associated with the local DOS.

2.4 References


CHAPTER 3
GROWTH KINETICS AND NUCLEATION BEHAVIOR OF ELECTRODEPOSITED COPPER ON RU(0001)
IN SULFURIC ACID SOLUTION

3.1 Introduction

Interest in the electrodeposition of Cu on various substrates for use in Cu interconnects arises from the increasingly aggressive architecture—and constantly shrinking feature sizes of modern integrated circuits\textsuperscript{1,2}. To prevent contamination caused by Cu diffusing through interlayer dielectrics, a diffusion barrier, such as Ta/Ta\textsubscript{2}N, is required. This is deposited on the patterned dielectric by physical vapor deposition. Typically a Cu seed layer is first deposited via PVD and then followed by Cu electrodeposition to fill the feature. This seed layer is thin and susceptible to etching in the open circuit conditions in the plating bath. As features continue to shrink—this leads to thinner Cu seed layers as well as poorer step coverage from sputter deposition. These problems have sparked the interest in direct plating of Cu on a more stable, semi-noble diffusion surface, particularly Ru\textsuperscript{3}. Previous work from our group\textsuperscript{4} has shown that a partial monolayer of absorbed iodine can inhibit oxide formation on a Ru substrate in ambient or in solution, but did not examine the mode of Cu nucleation. We report here the use of cyclic voltammetry (CV), current time transient (CTT) measurements, and electrochemical atomic force microscopy (EC-AFM) to study the electrodeposition of Cu on a clean Ru(0001) surface in 0.1 M CuSO\textsubscript{4} and 0.5 M H\textsubscript{2}SO\textsubscript{4}.

Electrodeposition of Cu on a Ru(0001) electrode via combined electrochemical-UHV methods has been previously reported\textsuperscript{5}. Stuve et al. studied sub-monolayer to multilayer quantities of Cu on a Ru(0001) substrate. They observed the formation of an initial, epitaxial
layer formed via underpotential deposition (UPD) on the Ru(0001) surface followed by bulk deposition at more cathodic potentials. The demonstrated potential region for the UPD process was in agreement with earlier electrochemical studies of Cu UPD on polycrystalline Ru electrodes. Recent results of the electrochemical deposition of Cu on polycrystalline Ru demonstrated a predominately progressive nucleation of Cu on the Ru surface. Investigations of electrodeposited Cu on other semi-noble or noble electrodes have demonstrated Cu nuclei that exhibit significant growth anisotropy with growth rates that were much greater in lateral than vertical dimensions. This type of growth would be of practical importance for the electrodeposition of Cu on Ru, because the anisotropic growth would be adventitious in the bottom-up, void free filing of trenches and interconnects in semiconductor processing.

3.2 Experimental

Cyclic volatammetry (CV) and current-time transient (CTT) studies were carried out in a flat three-electrode cell (K0235 flat cell, EG&G) fitted with a Luggin capillary and a Pt-Rh counter-electrode. All potentials reported here are referenced to the saturated Ag/AgCl electrode. The cell was configured so that the area of the electrode accessible by the electrolyte was 0.28 cm². The solutions used consisted of 0.1 M CuSO₄ in 0.5 M H₂SO₄ (Mallinckrodt, ACS). Solutions were purged with N₂ for 1.5 hour prior to each experiment. A Ru(0001) single crystal (Mateck, Germany; dimensions by 10 mm x 0.5 mm, oriented to within ± 0.1°) was annealed for 2 hr at 1000°C in a programmable furnace that was purged with an Ar (95%)/H₂ (5%) gas mix. The annealed sample was allowed to cool to room temperature under the Ar/H₂ stream while in the furnace prior to analysis. While still under Ar/H₂ atmosphere, the sample was quenched
with a drop of dilute, purged electrolyte prior to transport to the three-electrode
electrochemical cell or AFM electrochemical cell. This procedure has been previously been
demonstrated to yield well-defined, reproducible Ru(0001) surfaces. Electrochemical
measurements were carried out with a commercially available potentiostat (EG&G 263 A) with
270 Electrochemistry software by EG&G. AFM images were acquired with a commercially
electrochemical atomic force microscope (EC-AFM: Nanoscope E, Veeco Metrology Inc.)
operating in direct contact mode, using a high purity platinum wire as a reference electrode
(RHE). Correlation of RHE-referenced potentials with Ag/AgCl referenced potentials was made
by comparison of UPD feature potentials in the AFM cell versus flat cell.

3.3 Results
3.3.1 CV and CTT Data

A cyclic voltammogram (CV) of Ru(0001) in purged 0.1 M H₂SO₄ bath with 0.5 M CuSO₄
is shown in Fig. 3.1. The scan was started at open-circuit potential (OCP) (+530 mV/Ag/AgCl),
swept in the cathodic direction to just short of the onset of hydrogen evolution (-525 mV),
anodically to +600mV, and then back to OCP at a rate of 10mV/s. Repeated potential cycling on
the same surface did not produce any significant changes to the CV. The CV is similar to
previously reported results on polycrystalline Ru. The deposition of Cu started around 0.0 mV
and displayed a diffusion-limited deposition peak centered ~280 mV and a Cu stripping peak at
300 mV. A small UPD was observed in Fig. 1 at 117 mV. When the electrode potential was
swept from OCP to the initial onset of Cu deposition and then back anodically again, a small
feature can be in the scan which is associated with the stripping of the UPD Cu as well as a
smaller anodic stripping peak (Fig 3.1, inset). The features observed in the CVs (UPD, bulk deposition, and UPD stripping peak) obtained on Ru(0001) are similar to those reported by Stuve et al. for a Ru(0001) electrode prepared under ultrahigh vacuum (UHV) conditions. The observation of the UPD related features are indicate a clean, well prepared electrode and validate the preparation methods employed in this study.

Fig 3.1. CV of Cu deposition and anodic stripping in 0.1 M CuSO₄/0.5 M H₂SO₄. The scan rate was 10 mV/s (Ag/AgCl). A UPD peak and it corresponding stripping peak are evident in the inset.

In order to examine the nucleation behavior of Cu on Ru(0001) current-time transient (CTT) measurements were used. The sample was held at OCP, where no Cu deposition occurs, and then stepped to a negative potential in the range of -50 to -550 mV and held for 5 s to initiate the Cu deposition process (Fig 3.2). As expected, the maximum in the Cu ion reduction current, I_{max} (plotted in Fig 3.2 as negative) increases in magnitude as the potentials stepped to increasingly cathodic values. At times longer than that corresponding to the current maximum (t_{max}), the current decays as t^{-1/2} indicating the point at which the diffusion zones of the Cu
nuclei begin to overlap and the deposition becomes diffusion-limited.

Fig. 3.2 Current-time transient curves for Cu deposition on Ru(0001) in 0.1 M CuSO₄/0.5 M H₂SO₄. The potential was stepped from OCP (+540 mV) to various potentials (mV) at (a) -550, (b) -450, (c) -350, (d) -250, (e) -150, (f) -100, and (g) -50.

The data in Fig 3.2 was plotted in reduced variable form $\left[ \frac{I}{I_{\text{max}}} \right]^2$ versus $\left[ \frac{t}{t_{\text{max}}} \right]$ in Fig. 3.3 for selected deposition potentials. The reduced parameter plots were then compared to theoretical models developed by Scharifker et al. for three-dimensional (3D) instantaneous and progressive nucleation. This model states that at longer times a depletion zone of cation concentration forms above the surface relative to that of the bulk concentration and diffusion controlled growth of hemispherical nuclei is the dominate mechanism. Instantaneous nucleation describes the situation where all available nucleation sites are activated instantly when $t = 0$ and

the $\frac{I}{I_{\text{max}}}$ varies according to the equation:
\[
\frac{i^2}{i_{\text{max}}^2} = 1.9542 \left( \frac{t_{\text{max}}}{t} \right) \left[ 1 - \exp \left( -1.2564 \frac{t^2}{t_{\text{max}}^2} \right) \right]^2
\]  
(1)

In the case of progressive nucleation, where the nucleation is slow and the number of separate nuclei increases with time, the relationship is

\[
\frac{i^2}{i_{\text{max}}^2} = 1.2254 \left( \frac{t_{\text{max}}}{t} \right) \left[ 1 - \exp \left( -2.3367 \frac{t^2}{t_{\text{max}}^2} \right) \right]^2
\]  
(2)

Fig. 3.3 shows the deviation from the instantaneous 3D nucleation models of the kinetic data at higher cathodic overpotentials. At -150 mV the data fits closely to the 3D instantaneous model for \(t/t_{\text{max}}<3\). When the applied potential is stepped to -250 mV a good fit is only obtained for \(t/t_{\text{max}}<2\). At -550 mV, however, the 3D nucleation model does not fit the experimental data at any time scale.

Fig 3.3 Current-time transient data plotted in reduced-variable form and compared to behavior expected for three dimensional progressive and instantaneous nucleation for Cu deposition on Ru(0001) in 0.1 M CuSO4/0.5 M H2SO4. The potential was stepped from OCP (+540mV) to various potentials. The data was from Fig 3.2.
3.3.2 EC-AFM Results

A freshly prepared Ru(0001) electrode is shown in the wide area (3 μm x 3 μm) EC-AFM scans at open circuit potential (Fig. 3.4a) and after polarization to +210 mV (Fig. 3.4b) in 0.1 M CuSO₄/0.5 M H₂SO₄. The Ru(0001) surface consisted of broad terraces of up to 0.5 μm wide with step heights between 3 and 10 Å. Several small features are observed in the freshly prepared sample as bright dots in Fig 3.4a and are removed after stepping the electrode to more cathodic potentials that are still positive relative to the Cu deposition region as shown in Fig 3.4b. The bright spots are indicative of a small amount of surface oxide that is reduced upon polarization below OCP without altering the topography of the surface.

![AFM image of oxide clusters on Ru(0001) at OCP in 0.1 M CuSO₄/0.5 M H₂SO₄.](image)

Fig 3.4. (a) AFM image of oxide clusters on Ru(0001) at OCP in 0.1 M CuSO₄/0.5 M H₂SO₄. (b) Potential was stepped to +210mV in order to reduce oxide clusters on surface.

The EC-AFM data in Fig. 3.5 demonstrates the relationship between Cu film morphology and deposition potential. There are significant differences to each of the films grown at the various potentials. Each of the AFM images of the Cu films (Fig. 3.5b-d) was acquired in a 120 s time span within several seconds of polarization to the deposition potential (+193, +93, -7, and -207 mV/Ag/AgCl) in 0.1 M CuSO₄/0.5 M H₂SO₄. The AFM images in Fig 3.5a and b are at the same
spot on the sample. After each deposition, the Cu film was electrochemically stripped from the surface and the Ru(0001) sample was cleaned according to the established procedures outline above. At +93 mV, which is near the OPD/UPD boundary, large Cu nuclei with pronounced growth anisotropy were observed. The in-plane dimensions of the nuclei in general were an order of magnitude larger than the vertical dimensions. As the overpotential was increased (-7 mV, Fig 3.5c), the deposited Cu films were significantly rougher and the film topography became more irregular. At -207 mV, several large nuclei ( < 0.3 μm in diameter) and a high density of small nuclei indicating more isotropic rather than anisotropic growth.

The EC-AFM images in Fig 3.6a-e display the continued growth and merger of the large Cu nuclei formed at low overpotentials (+93mV, Fig. 3.5a). The boundary between the two large
grains observed in Fig. 3.6a continues to shrink in the series of subsequent images. There is little change in the overall height of the grains indicating that lateral growth occurs more quickly than vertical growth under these conditions.

Fig 3.6. (a)-(e) AFM images of Cu films on Ru(0001) deposited at +96 mV vs. Ag/AgCl (0.1 M CuSO₄/0.5 M H₂SO₄). Each image was acquired for 120 s.

3.4 Discussion

The data shown in Figs 3.1 and 3.4 demonstrate that the sample preparation procedures described above resulted in the formation of well-ordered terraced surfaces that displayed UPD-related features that were in agreement with those observed on single crystal surfaces prepared under UHV conditions. The kinetics of nucleation (Figs. 3.2 and 3.3) vary significantly with the applied potential. The nucleation at low overpotentials follows the model of
instantaneous 3D nucleation at reasonably long time scales. At higher overpotentials, however, the nucleation data is inconsistent with and lying above the theoretical models for 3D or 2D nucleation. The fit becomes progressively poorer as the overpotential is increased.

Deviations of the kinetics plots from the calculated 3D nucleation behavior for Cu deposition on TiN under acidic conditions has been previously reported. In those reported cases the departure of the current from the instantaneous nucleation model decreased with increasing overpotential – the opposite trend as that observed in Fig. 3.3. A possible theory for the increasing departure at higher overpotentials is due to increased hydrogen evolution, but the CV data in Fig. 3.1 demonstrate that the applied potentials are all positive of the hydrogen evolution region. An alternate explanation is that the deviation from 3D instantaneous nucleation is due to kinetic factors. The Scharifker-Hill model of nucleation assumes that growth is diffusion-limited, however, the AFM data (Fig 3.5) indicate significant changes to the nucleation density and morphology with increasing overpotential. Kinetics modeling has shown that the arrangement of nuclei hemispheres on the plane has a clear influence on the current and therefore the nucleation kinetics. The AFM data (Fig 3.5) and models of kinetics indicate that the behavior displayed in Fig 3.3 results from the significant changes in the film nuclei density and morphology at increasing overpotentials.

Previously reported results for Cu electrodeposition on in 0.5 M H₂SO₄ demonstrated a close relationship between the experimental kinetic behavior to that calculated for 3D progressive nucleation for \( \frac{t}{t_{\text{max}}} < 3 \). In addition, there was no significant change in the reduced parameter plot based upon the deposition potential. Possible explanations for the differences for the data shown here and the previous report include the use of a single crystal versus
polycrystalline substrate or differences in how the electrodes were prepared. The Cu concentration of the solution was different (0.1 M CuSO$_4$ in this study) than that used in the previous report (0.5 M CuSO$_4$), however, it is unlikely that would lead to the differences in the results if the two studies.

The EC-AFM data displayed in Figs. 3.5 and 3.6 indicates that changes in deposition potential has a profound effect on the topography of the deposited Cu film over large expanses and long times. The AFM images in Fig. 3.5 show a transition from a few large, relatively flat nuclei at low overpotentials to a higher nucleation density with a rougher topography at larger overpotentials. The correlation between increasing nucleation density and increasing overpotentials has been reported for TiN $^{2,13}$, W $^{15,16}$, and Ru $^3$. Similar Cu growth anisotropy (more rapid growth laterally than vertically) has been demonstrated on other noble or seminoble substrates $^{7,9,10,17}$.

The ability to control the Cu film morphology by controlling the applied deposition potential is of great import for interconnect fabrication in microelectronics. Current industrial practice utilizes galvostatic deposition – where the current is fixed and the deposition potential varies during the course of deposition. The results shown here demonstrate the use of potentiostatic control of deposition to control Cu topography and roughness as an effective method for Cu electrodeposition.

3.5 Conclusion

Cyclic voltammetry, current-time transient, and EC-AFM measurements were used to characterize the Cu electrodeposition from a purged 0.1 M CuSO$_4$/0.5 M H$_2$SO$_4$ electrolyte onto
a clean Ru(0001) electrode with broad terraces prepared under non-UHV conditions. The kinetic data fits the model for 3D instantaneous nucleation for \( t/t_{\text{max}} < 3 \) at low overpotentials. At higher overpotentials there is significant deviation from the theoretical model for 3D instantaneous or progressive nucleation. It is evident in the EC-AFM data that Cu deposition at low overpotentials results in the formation of smooth, large-grained nuclei with lateral dimensions an order of magnitude larger than the vertical dimensions. In addition, at larger overpotentials the Cu nucleation density increases and the nucleus size decreases.

3.6 References


CHAPTER 4

STABILITY OF IODINE ON RUTHENIUM DURING COPPER ELECTRODEPOSITION AND ITS EFFECTS ON COPPER NUCLEATION

4.1 Introduction

Current interconnect technology involves deposition of a Ta$_2$N/Ta diffusion barrier, followed by the physical or chemical vapor deposition of a Cu seed layer to enhance nucleation of subsequently electrodeposited Cu, which fills the via or trench $^{1,2}$. As feature sizes continue to shrink, the Cu seed layer must also shrink. As Cu is unstable at open circuit in conventional plating baths, this can result in significant or even complete dissolution of the seed layer prior to plating.

Ruthenium is a promising candidate for replacing the seed layer because bulk phase Ru and Cu are immiscible $^3$. Ru is electrochemically stable in H$_2$SO$_4$-based plating solutions $^4$, and Ru has better resistance to oxidation in the ambient than does Ta. Direct Cu electrodeposition on Ru(0001) and polycrystalline Ru has been reported previously $^5$-$^7$. The ability to directly plate conformal Cu films on Ru provides the potential for a seedless superfilling process. Ru is susceptible to oxidation if exposed to the ambient or water at room temperature $^3$, $^7$-$^9$. Some groups have suggested that the presence of Ru oxide is advantageous due to the fact that the oxide plugs the grain boundary diffusion passageways, enhancing the diffusion barrier performance of the Ru liner $^{10}$. Previous studies, however, have shown that the presence of a Ru oxide surface layer during Cu electrodeposition will result in Volmer-Weber (island) type

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$^1$ Entire chapter is reproduced from Bjelkevig, C., Kelber, J. Stability of iodine on ruthenium during copper electrodeposition and its effects on the nucleation behavior of electrodeposited copper, *Electrochimica Acta* 2009 54(15), 3892-3898, with permission from Elsevier.
growth, poor trench filling, and poor adhesion between Cu and Ru\textsuperscript{3}. The reduction of this surface Ru oxide, and/or the inhibition of oxide growth on the Ru surface prior to plating is therefore of considerable practical interest.

It has also been shown that electrochemical reduction of the oxidized Ru layer in a purged sulfuric acid solution, followed by rapid transfer to a Cu plating bath, allows for superfilling of trenches and improved adhesion between Cu and Ru\textsuperscript{3}. Previous XPS/electrochemistry studies\textsuperscript{7} have demonstrated that an iodine adlayer formed on Ru remains stable during exposure to ambient air and water (pH = 7) at 300K, and effectively passivates the surface against significant RuO\textsubscript{2} formation. XPS and electrochemical data have also demonstrated that the iodine adlayer remains on top of the Cu film after continued cycles of overpotential electrodeposition and dissolution of Cu on Ru(0001)\textsuperscript{7}. A similar tendency has been demonstrated for underpotential deposition at various I-modified electrodes\textsuperscript{11-13}.

If iodine passivation of Ru is to be of practical use, however, then the electrochemical conditions under which I may be adsorbed on a reduced Ru surface, and the potential range at which I is stable on Ru, need to be explored. This is particularly true for Cu electrodeposition in production environments, where galvanic, rather than potential control, is usually employed. We have therefore probed the stability of an iodine adlayer deposited by reducing the as-received Ru electrode surface in a purged sulfuric acid/KI solution, and the effects of this adlayer on Cu nucleation kinetics, using XPS and electrochemical methods in a UHV-electrochemical transfer system (UHV-EC), as well as electrochemical measurements involving intermittent ambient exposure (“benchtop” environments).
4.2 Experimental

UHV-EC experiments were performed in a combined ultrahigh vacuum/electrochemistry transfer system permitting sample transfer between liquid and UHV environments under controlled conditions. This system, as well as the methods of XPS data acquisition and analysis, has been described previously \(^7\), \(^13\). Briefly, the system consisted of a main analytical chamber (base pressure \(<5\times10^{-10}\) Torr) that included a hemispherical analyzer, a dual anode X-ray source for XPS, and an Ar ion sputter gun; and an electrochemical chamber (base pressure \(<2\times10^{-6}\) Torr) with the ability to carry out electrochemical measurements under an inert gas atmosphere. XPS spectra were acquired with the electron energy analyzer operated in the constant pass energy mode at 23.5eV using a polychromatic Mg Kα source operated at 15 kV and 300 W. Binding energies were calibrated by comparing the binding energies of Ru metal to previous results \(^14\) and literature values \(^15\). The Ru surface was characterized by XPS under UHV conditions and then transferred to the electrochemical chamber. The electrochemical chamber was brought to \(>1\) atm by backfilling it with dry N\(_2\). The electrochemical cell filled with electrolyte was then introduced into the electrochemical chamber through a gate valve in proximity to the sample, allowing the meniscus to wet the electrode surface. Thickness calculations used to estimate surface coverage were based upon the integrated intensities of XPS core level transitions normalized by atomic sensitivity factors appropriate to the analyzer (PHI Model 10-360). Shirley background subtraction and Gaussian-Lorentzian functions were used for peak fitting.

Some electrochemical measurements were also carried out in a bench-top flat three-electrode cell (K02235 flat cell, EG&G) fitted with a Luggin capillary and a Pt-Rh counter-
electrode. All potentials reported here are referenced to the saturated Ag/AgCl electrode. The cell was configured so that the area of the electrode accessible by the electrolyte was 1cm$^2$. Electrochemical measurements were carried out using a commercially available potentiostat (EG&G 263A) and software. Samples consisted of 100 Å Ru films deposited via PVD on TaN/SiO$_2$ wafers. The solutions used for these studies consisted of 50mM CuSO$_4$/1M H$_2$SO$_4$. Solutions were purged with N$_2$ for 1.5 hours prior to each experiment. In order to treat the surface with iodine, a solution consisting of 1mM KI/1M H$_2$SO$_4$ was used. The sample was rinsed in N$_2$-purged DI water to prevent contamination of the plating bath.

The oxide coverage was estimated from XPS core level intensities by the following equation

$$\frac{1 - \exp[-d / \lambda_a(E_A)]}{\exp[-d / \lambda_b(E_B)]} = \frac{N_A}{N_B}$$

(4.1)

where $N_A$ and $N_B$ are the atomic concentrations of the oxygen overlayer and Ru substrate, respectively, $E_A$ and $E_B$ represent the XPS electron kinetic energy for O (1s) and Ru (3d$_{5/2}$) electrons, and $\lambda_a$ , $\lambda_b$ are the corresponding inelastic mean free path (IMFP) values. The IMFPs were determined from the TPP-2M predictive formula published by Tanuma et al. $^{17}$ The IMFP of Ru (3d$_{5/2}$) electrons ($\lambda_b$) = 14.1 Å. In order to estimate the IMFP of O(1s) electrons in the Ru oxide overlayer, the overlayer composition was assumed to be RuO$_2$, yielding a calculated IMFP ($\lambda_A$) = 15.1 Å. For adsorbed I atoms, an IMFP value of 16.3 Å was obtained.

As-received Ru samples consisted of films ~ 100 Å thick, on TaN/SiO$_2$ wafers. Samples 1cm x 1 cm in size were used, and were sonicated in methanol and deionized water prior to insertion into the vacuum chamber.
4.3 Results

4.3.1 Benchtop Studies: Effects of Ru Electrode Pre-treatment on Cu Electrodeposition

The as-received Ru samples were covered with a thin ruthenium oxide film of 6 Å average thickness, as determined by XPS. Moffat et al. have shown that polarizing a Ru sample in 1.8M H$_2$SO$_4$ + 1mM NaCl to potentials near the hydrogen evolution region is an effective method for removing the surface oxide from ruthenium. Guo et al. observed complete reduction of ~ 1 nm thick RuO$_2$ at -200 mV vs. Ag/AgCl in a more dilute (0.2 M) H$_2$SO$_4$ solution. More cathodic reduction potentials with more dilute acidic solutions are reasonable in relation to the reduction of oxide by the formation of surface hydrogen. It was determined that a treatment of stepping the potential to -100 mV for 30 seconds was sufficient to reduce the surface oxide in a solution of 1 M H$_2$SO$_4$, as shown by CV data (Fig. 4.1).

![Cyclic voltammograms of the air-exposed Ru film (solid line) and after reduction of the air-formed oxide by polarization to -100 mV for 30 s (dashed line), in 1M H$_2$SO$_4$. Scan rate = 50mV/s.](image)

For each CV, the scan was started at +50 mV (where no oxidation/reduction occurs) and swept negative until the onset of hydrogen evolution, then swept anodically at a scan rate of 50 mV/s. A peak due to Ru oxide reduction was observed centered at -100 mV for the as-received
The absence of a peak corresponding to RuO$_2$ reduction after cathodic polarization is apparent.

Figure 4.2 shows a series of cyclic voltammograms (CVs) in 0.05M CuSO$_4$/1M H$_2$SO$_4$ for samples prepared by three different methods: (a) the sample as received, (c) reduced by polarization to -100 mV in 1M H$_2$SO$_4$ and then transferred to the ambient and immersed in the plating solution; or (e) polarization of the as-received sample in 1mM KI/1M H$_2$SO$_4$ to -100 mV, followed by emersion to ambient and immersion in the plating solution. For each CV, the scan was started at the OCP; ~ +420 mV, swept negative until the onset of hydrogen evolution, then swept anodically to remove copper from the surface at a scan rate of 25mV/s.

Fig 4.2 (Left) CV of Cu deposition and anodic stripping in 0.05 M CuSO$_4$/1M H$_2$SO$_4$ on (a) Ru pretreated by reduction at -100 mV for 30 s in 1M H$_2$SO$_4$ + 1mM KI, followed by emersion to ambient and subsequent immersion in plating bath; (c) Ru pretreated by reduction at -100 mV/30s in 1M H$_2$SO$_4$ followed by emersion to ambient and subsequent immersion in plating bath; (e) as-received RuScan rate = 25 mV/s (Ag/AgCl). (d,e,f) Expanded views of CVs, showing corresponding UPD regions in greater detail. The UPD region of the Ru electrode reduced in 1M H$_2$SO$_4$ + KI (d) exhibits a UPD-related feature.
On the as-received Ru sample and the sample reduced in H₂SO₄, the total current was higher and the Cu deposition peak broader than on the sample reduced in KI/H₂SO₄. This result indicates that the broad reduction peak in the CV of the as-received sample (Fig. 4.2e) includes contributions from the oxide reduction feature (Fig. 4.1) as well as from Cu deposition. A similar broad cathodic peak is also observed in the H₂SO₄-reduced sample (Fig. 4.2c). Although shifted cathodically relative to the corresponding feature in the as-received sample, the broad nature of the reduction peak is consistent with some reformation of the oxide upon emersion from the H₂SO₄ electrolyte into ambient prior to immersion in the plating solution. The sample reduced in H₂SO₄ + KI (Fig. 4.2a) exhibits a narrower Cu deposition feature than the sample reduced at H₂SO₄ only, and a shift in the Cu stripping peak to more anodic potentials relative to that observed for the sample reduced in H₂SO₄ only. Figures 4.2b,d,f are magnified portions of the corresponding CV’s (Fig 4.2a,c,e) in the region where under potential deposition (UPD) occurs. A small Cu UPD feature at ~80 mV was observed for the Ru sample reduced in the iodine solution (Fig. 4.2b). No Cu UPD peak was observed for the as-received Ru or the sample reduced in H₂SO₄ only (Fig. 4.2d, f).

Chronoamperometry was used to investigate the nucleation behavior of Cu on Ru in 0.05M CuSO₄/1M H₂SO₄. The sample was stepped from OCP (+420mV) to a cathodic potential sufficient to induce copper electrodeposition. A series of current-time transients are shown in Figs 4.3-5 for samples as received (Fig. 4.3), reduced in H₂SO₄ (Fig. 4.4) and reduced in H₂SO₄+KI (Fig. 4.5). Each figure includes a series of current vs. time curves (Figs, 4.3a, 4.4a and 4.5a), and the corresponding Scharifker-Hill plots (Figs. 4.3b, 4.4b and 4.5b) in which the data are plotted against dimensionless parameters: \((i/i_{max})^2\) vs. \(t/t_{max}\). In each transient there is an initial
increase in current due to the increase in surface area wherever nucleation takes place. Nuclei will begin to overlap as nucleation progresses. A Cu diffusion zone will be formed around each nucleus and, as the nuclei grow, the diffusion zones will overlap and eventually cover the entire surface. When this occurs the current will reach its maximum ($i_{\text{max}}$) and subsequently decay as $t^{-1/2}$ under diffusion control.

Scharifker et al. developed two models (instantaneous and progressive) to describe 3D copper nucleation behavior, with distinct plots in terms of dimensionless parameters for time and current; ($t/t_{\text{max}}$) and $(i/i_{\text{max}})^2$. Instantaneous nucleation occurs when all the active sites for nucleation are activated at once leading to smaller, more uniform nuclei. For instantaneous nucleation, the normalized current transient is given by:

$$\left(\frac{i}{i_{\text{max}}}\right)^2 = 1.9542 \left(\frac{t_{\text{max}}}{t}\right) \left[1 - \exp\left(-\frac{1.2564t}{t_{\text{max}}}\right)\right]^2$$

In the progressive nucleation mode, nucleation sites form at different times, with growth resulting in, generally, a broader distribution in nuclei size. The expression for progressive nucleation is

$$\left(\frac{i}{i_{\text{max}}}\right)^2 = 1.2254 \left(\frac{t_{\text{max}}}{t}\right) \left[1 - \exp\left(-\frac{2.3367t^2}{i_{\text{max}}^2}\right)\right]^2$$

By plotting the experimentally obtained $(i/i_{\text{max}})^2$ vs. $(t/t_{\text{max}})$ and overlaying the values for the theoretical curves, a direct comparison can be made between the data and the progressive and instantaneous models. As shown in Fig. 4.3b, the observed behavior for the as-received Ru lies between the progressive and instantaneous models. Further, the nucleation kinetics (Fig. 4.3b) appear to be independent of electrochemical potential, with behavior somewhere between
instantaneous and progressive modes at short times \( (t/t_{\text{max}} < 1) \) and departing from both models at longer times. These results differ from those obtained by Chyan et al. on electrochemically formed Ru oxide films, which demonstrated progressive nucleation at all reported potentials.

Corresponding data for Ru that has been reduced by polarization in 1 M H₂SO₄ immediately prior to the experiment are displayed in Figure 4.4. As with the as-received Ru sample, the Cu nucleation behavior does not correspond well at short times to either instantaneous or progressive nucleation models. At longer times and higher overpotentials \((-400 \text{ mV}, -500 \text{ mV})\) however, the results lie closer to the limit for instantaneous nucleation, but still vary with applied potential, indicating the deposition at this process is neither entirely diffusion- or kinetically-controlled. Guo, et al. observed similar results for Cu reduction on pre-reduced wafers in the absence of additives; no variation in \( t_{\text{max}} \) with applied potential, a
mixture of diffusion and kinetic control, and complex behavior that cannot be described by either the progressive or instantaneous nucleation model.

The Cu reduction kinetics on the as-received sample (Fig. 4.3) and sample pre-reduced in H₂SO₄ but exposed briefly to ambient prior to Cu deposition (Fig. 4.4) are similar to the data of Guo, et al. for Cu deposition on pre-reduced Ru - nucleation behavior which is a poor fit to either the instantaneous or progressive nucleation model, mixed kinetic and diffusion control at long times, and insensitivity of the nucleation process (e.g., t_max) to applied potential. Such behavior differs significantly from the progressive nucleation observed on Ru oxide. Guo and co-workers ascribed such behavior to reduction of a thin Ru oxide layer occurring more rapidly than the Cu deposition process, so that Cu nucleation occurred primarily on Ru, rather than on the oxide.

Fig. 4.4. (a) Current–time transient curves for Cu deposition on Ru in 0.05M CuSO₄/1M H₂SO₄ on Ru reduced by polarization (-100mV for 30s) in 1M H₂SO₄, followed by emersion to ambient and immersion in the plating bath. The potential was stepped from OCP (+420 mV) to various potentials (−500 mV, −400 mV, −300 mV); (b) Current–time transient data plotted in reduced-variable form for Cu deposition on Ru.
Data are displayed in Fig. 4.5 for the sample polarized in 1mM KI/1M H₂SO₄ for 30 s at -100 mV prior to deposition of copper. For samples reduced in the iodide solution the time \( t_{\text{max}} \) for reaching the current maximum \( i_{\text{max}} \) decreased with increasing negative overpotential, in contrast to either the as-received Ru electrode (Fig. 4.3a), or the Ru electrode reduced in H₂SO₄ (Fig. 4.4a). The observed current densities \( i_{\text{max}} \) for the sample reduced in KI+ H₂SO₄ were also higher than the corresponding values at similar applied potentials for the as-received Ru electrode.

![Fig. 4.5](image)

The Scharifker-Hill plot (Fig. 4.5b) shows that, contrary to the as-received Ru electrode, the Cu nucleation behavior for the I-modified Ru electrode changes with applied potential. At short times (Fig. 4.5b, \( t/t_{\text{max}} < 1 \)), the observed plot is close to the instantaneous model for an applied
potential of -300 mV. The behavior becomes more “progressive-like”, however, at more cathodic potentials, approaching the progressive limit at -500 mV. At longer times, however (Fig. 4.5, t/t_{max} >1), the behavior is insensitive to applied potential and exhibits diffusion control.

4.3.2 UHV-EC Studies: XPS/electrochemical Characterization of the I Adlayer

XPS core level spectra, acquired in the UHV-EC system, of the as received Ru film and the electrode surface after polarization for 30s at -100 mV in 1mM KI/1M H_{2}SO_{4} followed by rinsing in dilute electrolyte and transfer to UHV, are displayed in Fig. 4.6. Corresponding core level spectra are displayed in Fig. 4.7 for the I-modified electrode polarized in 1M H_{2}SO_{4} to -200 mV (Ag/AgCl)—the onset of H_{2} evolution on an as-received sample (Fig. 4.1). The Ru(3d_{5/2}) feature of the as-received sample prior to reduction (Fig. 4.6a), is dominated by a mixture of components for metallic Ru (280.1 eV) and RuO^{2−} (280.8 eV). Smaller components at higher binding energies may reflect small concentrations of higher Ru oxides (RuO_{3}, RuO_{4})

However, these features may also be an artifact of using Gaussian-Lorentzian components to fit a conductive RuO_{2} oxide spectrum asymmetrically broadened by core-hole/valence electron coupling. A comparison of the Ru(3d) spectrum before and after reduction (Fig. 4.6a,b) shows an increase in metallic Ru intensity as well as a shift towards lower binding energy indicating a reduction in the amount of RuO_{2}. The O(1s) spectrum for the as-received sample prior to polarization (Fig. 4.6c) was fit with four components each with a fwhm of 1.42 eV at binding energies of 530.6, 531.7, 532.8, and 533.9 eV. The components at 530.0, 531.7, 532.8, and 533.9 eV are assigned, respectively, to RuO_{2}, absorbed sulfate, hydroxide species, and
absorbed \( \text{H}_2\text{O} \). The presence of the sulfate feature (confirmed by a S(2p) peak (Fig. 4.6e,f), prior to sample emersion was due to a constant background of sulfate in the introduction/electrochemical chamber. The S(2p) spectrum (Fig. 4.6e, top) has a peak at 168.5 eV, that can be attributed to an absorbed sulfate species \(^{14, 25}\). The O/S atomic ratio derived from the intensity ratio of the \( \text{O}_{531.7} / \text{S}_{168.5} \) component intensities is \( \sim 4:1 \), consistent with the presence of a sulfate species. After polarizing the sample in the iodine-containing solution the O(1s) spectrum (Fig. 4.6d) shows a decrease in the peak at 530.0 eV, which further indicates a reduction in the amount of \( \text{RuO}_2 \). The thickness of the \( \text{RuO}_2 \) layer of the as-received sample was estimated (Eq. 4.1) to be 6 Å. The average thickness of the oxide layer after reduction in the KI/\( \text{H}_2\text{SO}_4 \) solution was estimated to be 0.9 Å. A comparison of the Ru(3d) and O(1s) spectrum before (Fig. 4.6a,c) and after reduction (Fig. 4.6b,d) indicates a sharp reduction in intensity of the \( \text{RuO}_2 \)-related features in both the Ru(3d) and O(1s) spectrum. O(1s) features attributable to chemisorbed oxygen and OH also exhibited reduced intensity. The I(3d) spectrum after reduction in the 1mM KI/1MH\( \text{H}_2\text{SO}_4 \) solution (Fig. 4.6g) was well fit with a single doublet, with the 3d\(_{5/2}\) peak at 619.9 eV. This binding energy is higher than that reported for I adsorbed on Au (618.5 eV) in a zero-valent state \(^{26}\), but similar to that reported \(^7\) for I adsorbed on Ru(0001) by exposure to I\(_2\) under UHV conditions. The 1 eV difference between the result reported here and that of Blasini, et al., may be due to their referencing the C(1s) binding energy for adsorbed hydrocarbon species (methylene carbon groups) at 284 eV \(^{26}\), compared to our reference energy of 285 eV for adventitious carbon \(^{27}\). The average thickness of the iodine adlayer was calculated to be 1.8 Å, and, using an I covalent diameter of 2.6 Å \(^7\), indicates a coverage of \( \sim 0.69 \) ML. This estimated coverage is significantly higher than the \( \sim 0.45 \) monolayer saturation...
In order to determine the electrochemical stability of the iodine adlayer in acidic conditions, the I-treated Ru sample was immersed in 1 M H₂SO₄ in the UHV-EC system and pulsed at -200 mV for 30s. Figure 4.7 shows the XPS Ru(3d), O(1s), S(2p) and I(3d) spectra of the I-modified Ru electrode prior to and after polarization in 1 M H₂SO₄. A comparison of the Ru(3d) spectrum before (Fig. 4.7a) and after polarization (Fig. 4.7b) shows a decrease in the
overall intensity, but no observable change in binding energy or peak shape. A similar decrease in absolute intensity is observed for the I(3d) spectrum (Fig. 4.7g,h). The O(1s) peak intensity after polarization increased mainly due to increase in sulfate (531.7eV) and hydroxide peaks (532.8eV) and to a lesser extent H₂O adsorption (533.4eV). A significant increase in intensity is also observed for the S(2p) region (Fig. 4.7f). These changes indicate that decreased Ru and I intensities are due to attenuation by the increase in hydroxide/H₂O and sulfate coverage. A detailed comparison of Ru and I intensities before and after polarization indicates that the iodine coverage stays constant (1.6Å average thickness or ~0.6ML) indicating that the I adlayer is not displaced by polarization of the Ru electrode under these conditions.

Fig. 4.7. Ru, O, I, and S core level XPS spectra for I-modified Ru (pulsed at -100 mV for 30 s in 1 mM KI/1 M H₂SO₄) (top trace), and after polarization at -200 mV vs. Ag/AgCl (bottom trace) for 30s in 1M H₂SO₄ solution. Note, data in top trace are the same as in Fig. 4.6, bottom trace.

4.4 Discussion
The data presented here demonstrate that cathodic polarization of an air-exposed Ru electrode in 1 mM KI/1 mM H₂SO₄ solution results in formation of ~2/3 monolayer of adsorbed I on the reduced Ru surface (Fig. 4.6h). The iodine adlayer inhibits Ru oxide formation upon exposure to ambient, as demonstrated by previous studies ¹⁴, and the fact that the I-modified Ru electrode (exposed to ambient prior to immersion in the plating solution) exhibits a Cu UPD feature, whereas the as-received Ru electrode surface and the reduced surface re-exposed to ambient do not (Fig. 4.2). Additionally, the CV of the I-modified electrode exhibits a narrow cathodic peak indicative of Cu reduction, whereas the broader features of the other electrodes indicate oxide reduction is occurring in addition to Cu deposition. These data indicate that the I ad-layer effectively inhibits Ru oxide reformation after cathodic reduction of the oxide and emersion to ambient.

The I-adlayer has a significant but complex effect on the kinetics of Cu deposition. Notable in Figs. 4.3-5 is that the Cu nucleation kinetics on the as-received Ru electrode and the electrode reduced in H₂SO₄ are independent of applied potential for t/tₘₐₓ < 1 (Figs. 3 and 4), while the nucleation behavior on the electrode reduced in KI/H₂SO₄ varies monotonically with electrochemical potential in the same time regime (Fig. 4.5). Additionally, the Cu nucleation behavior on the I-modified Ru surface at short times (t/tₘₐₓ) < 1 is not well-described by either the instantaneous or progressive nucleation models, while at longer times, behavior at all potentials is close to that of the instantaneous model (Fig. 4.5b), indicating diffusion control of the deposition process. The presence of I not only inhibits reformation of the Ru oxide during ambient exposure (Figs 4.2 and 4.6) but also enhances the maximum current density during Cu deposition (Figs 4.3-5). Although exposure of a pre-reduced sample in the absence of I to
ambient prior to Cu reduction undoubtedly results in partial regrowth of a thin oxide surface layer, the similarity of the data in Figs 4.3 and 4.4 to each other and the results of Guo, et al. (in the absence of additives) are consistent with the conclusion of that study, that reduction of the thin oxide overlayer occurred more rapidly than the Cu deposition process, leading to Cu nucleation primarily on Ru, rather than on RuO₂. Therefore, the effects of I cannot be ascribed entirely to inhibition of surface oxide reformation during exposure to ambient. A possible explanation for the significant variation in kinetic behavior with potential at short times on the I-modified surface (t/tₘₐₓ < 1, Fig. 4.5), compared to the relatively potential-independent behavior of this surface at longer times, is migration of I adatoms from the surface of the Ru electrode to the surface of growing Cu nuclei. At short times, this migration would leave part of the Ru surface uncovered by either I or Cu, yielding enhanced Cu deposition on uncovered portions of the Ru surface. At longer times, with a surface uniformly covered by I-modified Cu, diffusion controlled deposition behavior is observed.

While the complex nucleation behavior of the I-modified surface is of fundamental interest, the practical impact with respect to industrial application is the apparent fact that the I-adlayer is readily applied by polarization of the wafer in a KI-modified H₂SO₄ solution, inhibits RuO₂ formation during emersion and brief exposure to ambient, and remains stable in 1 M H₂SO₄ upon cathodic polarization to at least -200 mV. The complex nucleation kinetics, as discussed above, are attributable to the fact that the plating is occurring in a halide-free electrolyte. Plating in a typical plating solution, including Cl⁻, as well as other additives, would undoubtedly minimize the effects of I migration from Ru to Cu, as the entire surface would be (presumably) uniformly covered with halide species, leading to less potential-dependent
behavior than that observed here (Fig. 4.5). Some support for this comes from the fact that Guo, et al., determined that deposition on pre-reduced electrodes, using 0.1 M Cu sulfate solution containing Cl\textsuperscript{-} additives, exhibited nucleation kinetics (e.g., $t_{\text{max}}$) insensitive to applied potential.

4.5 Conclusion

The XPS and electrochemical data presented here show that cathodic polarization of Ru in a solution of 1 M H\textsubscript{2}SO\textsubscript{4}+ 1 mM KI results in ~2/3 ML of I adsorbed in a zero-valence state. This ad-layer protects Ru from re-oxidation during a brief exposure to ambient, as indicated by XPS and the presence of a UPD feature for this surface. The presence of an I adlayer also leads to a lower rate of Cu deposition, while altering the nucleation kinetics in a complex, potential-dependent manner that is not well described by either instantaneous or progressive nucleation. The I adlayer is also stable during cathodic polarization in H\textsubscript{2}SO\textsubscript{4} to -200 mV, the edge of the hydrogen evolution region on as-received Ru. These data therefore indicate that polarization of Ru electrodes in a KI-containing acidic solution has potential for practical application for inhibiting Ru electrode oxidation during exposure to ambient in the Cu electrodeposition process under industrial conditions.

4.6 References


CHAPTER 5

CHARACTERIZATION OF A GRAPHENE/HEXAGONAL HETEROSTRUCTURE GROWN ON Ru(0001)

5.1 Introduction

Graphene, a two-dimensional (2D) array of sp$^2$-bonded carbon atoms, has received great interest due to its exceptional electronic properties including high electron mobilities and polarizabilities$^{1,2}$ and applications in advanced electronics and spintronic applications$^{3-5}$. The primary focus of previous efforts have focused one of two avenues to graphene formation: (1) transfer – graphene sheets are cleaved from HOPG or grown on a metallic substrate$^{6-9}$ and then transferred to a pre-patterned substrate (e.g. Si, SiO$_2$) or (2) epitaxial growth on SiC(0001) – a SiC(0001) substrate is heated to temperatures above 1500K causing Si to evaporate leaving behind epitaxial graphene layers$^{1,2,10}$.

Both approaches present several obstacles to device fabrication and integration with CMOS/low-k on an industrial scale. While individual transfer can produce graphene sheets of up to millimeter size, the process is delicate and time consuming and therefore not practical on a large scale. While devices can be grown on SiC(0001)$^{1,2,10}$, SiC presents significant problems as a device material and is not readily integrateable with Si CMOS$^{11}$. In addition, a more complete understanding and control of graphene/dielectric interactions and their influence on graphene electronic behavior is critical to the development of real device applications$^{12,13}$. We report here the deposition of monolayer and multilayer h-BN(111) films on Ru(0001) via ALD and the subsequent growth of epitaxial graphene by CVD. This method of film growth is significant for several reasons. Direct growth of graphene growth on a dielectric substrate by means of CVD and ALD are easily adaptable to industrial conditions. The use of an ALD process allows for a
systematic approach to varying the dielectric film thickness in order to regulate the graphene/metal substrate interactions.

Previous work has shown that BN(111) monolayers can be grown on various substrates through the thermal decomposition of borazine $^{14-17}$. The main drawback to this approach is that the film is limited to a single monolayer due to the chemical inertness of the first layer towards additional borazine decomposition. The ALD method for formation of multilayer BN epitaxial films is adapted from a previously reported BN ALD growth method $^{18}$. The BN(111)/Ru(0001) interface reported here differs from the BN/Ru(0001) “nanomesh” structure derived from borazine thermal decomposition, which indicate the applicability of graphene/BN heterojuctions to a variety of substrates for spintronics and other advanced electronic applications. Data from the LEED, STM and Raman demonstrate graphene layers that are in registry with the BN substrate, differing from the azimuthally randomized graphene/borazine-derived BN double layer previously reported $^{19}$.

5.2 Experimental

Experiments were carried out in a combined growth/ultra-high vacuum (UHV) surface analysis system shown schematically in Fig. 5.1. The system consisted of two parts: the custom built growth chamber and the UHV surface analysis chamber. The sample transfer between the growth and analysis chambers occurred under controlled UHV conditions. The custom built growth chamber (base pressure, $10^{-7}$ Torr) was equipped for ALD and CVD at sample temperatures up 1100 K and precursor pressures up to 10 Torr. The UHV surface analysis chamber (base pressure, $3.2 \times 10^{-10}$ Torr) was equipped for ambient temperature STM/STS
Raman spectra were acquired ex-situ in the reflective mode. The substrate was a Ru(0001) single crystal 1 cm diameter, cut and polished strain free, and was obtained from Princeton Scientific. Cleaning of the Ru sample was carried out via Ar\(^+\) sputtering followed by annealing to 1000K in UHV. This process was repeated until no further change in the Auger spectra was observed and the Ru(0001) surface exhibited a sharp (1x1) LEED pattern. The ALD precursors, BCl\(_3\) (99.99%) and anhydrous NH\(_3\) (99.99%), were purchased from Praxair. The CVD precursor, C\(_2\)H\(_4\) (99.99%), was acquired from Scott Specialty Gas. Sample exposure was accomplished by backfilling the growth chamber using a manual leak valve to control the pressure. Gas pressure was measured either with a nude ion gauge (<10\(^{-4}\) Torr) or a baritron gauge (>10\(^{-3}\) Torr).

![Diagram](image)

Fig. 5.1. The growth/UHV system used in this study. The system is equipped with STM, LEED, and AES capabilities.

5.3 Results

BN films were grown by alternating doses of BCl\(_3\) and NH\(_3\) (A/B cycle) at pressures of 1.5 Torr at 550K for 12 min followed by annealing in UHV at 1000K. Auger spectra indicate a growth
in average film thickness of ~1.1 Å per A/B cycle, which was in agreement with previously reported studies on polycrystalline substrates \(^{18}\). For reasons not yet understood, thicker films became increasingly boron-rich. A multilayer film grown by 6 AB cycles at 550 K is shown in figure 5.2. The constant current STM image (Fig. 5.2a) indicates broad terraces with step heights of atomic dimensions. Individual steps measured 3.2 Å high, corresponding to the 3.3 Å hexagonal BN interlayer distance, and are indicated in the line scan (Fig. 5.2b). No LEED pattern was observed prior to annealing to 1000 K. After annealing to 1000 K the expected hexagonal diffraction pattern was observed in the LEED (Fig. 5.2c), demonstrating that the annealed BN film has long range order.

![Fig. 5.2. (a) Constant current STM image of ALD-grown (6 BCl\(_3\)/NH\(_3\) cycles) BN film on Ru(0001). (b) Line scan demonstrating characteristic 3.2 Å step height. (c) LEED image of BN(111) film indicating 6-fold pattern. Tunneling conditions: V\(_{\text{bias}}\) = -1.0 eV. Scan size is 220x220nm. LEED electron energy = 75 eV.](image)
Acquisition of high resolution STM data on multilayer films proved to be difficult and LEED images were not detailed, both possibly reflecting the insulating nature of the BN film. In order to overcome this difficulty, a single layer BN film (2 AB cycles) 2.2 Å thick was deposited via ALD. The BN film was characterized by LEED and STM/STS and used as a substrate for graphene growth. Figure 5.3 shows the data for both the LEED and scanning tunneling spectroscopy (STS) data. The STS curves consist of computer derivatives of I/V curves to yield dl/dV vs. V plots, proportional to the local density of states for the monolayer BN(111) film grown on Ru(0001) (Fig. 5.3a,b) and for graphene grown on the monolayer BN film by CVD of C₂H₄ at 1000 K (Fig. 5.3c,d). Despite the difficulty in obtaining atomic resolution STM on the monolayer BN and graphene/BN, consistent STS spectra were obtained over multiple areas of each film. The results in Fig. 5.3(b,d) are typical for the respective surfaces.

Fig 5.3. (a) LEED image for a single layer (2BCl3/NH3 cycles) BN film grown Ru(0001). (Insert) a principle LEED spot enhanced by background subtraction, showing the actual presence of two spots. (b) Corresponding STM-derived dl/dV (density of states) data for monolayer BN(111)/Ru(0001). (c) LEED image for a graphene overlayer on BN(111)/Ru(0001). The BN and graphene film average thicknesses, determined by attenuation of Ru substrate Auger features are 2.2 Å and 4.4 Å, respectively. LEED electron beam energy = 60 eV.
The LEED image for the BN(111) monolayer film on Ru(0001) (Fig. 5.3a) indicates the formation of a R30 (√3 x √3) LEED pattern. This type of reconstruction allows for the accommodation of a flat BN layer to the bulk-terminated Ru(0001)(1x1) surface as shown in Fig. 5.4. The inner spots on the LEED image corresponding to the expanded unit cell (orange trace, Fig. 5.4) appear split, indicating multiple domains.

Fig 5.4. Model of the BN(111)/Ru(0001) interface. The BN flat lattice mesh (red and blue spheres) can accommodate itself to the Ru(0001) surface (gray spheres) by a thirty degree rotation. The R30(√3x√3) unit cell is displayed as a dashed line. Bulk in plane lattice constants of 2.71 Å and 2.50 Å were used for Ru(0001) and BN(111), respectively. Model graphic courtesy of Prof. Jincheng Du, UNT.

The insert in Fig. 5.3a shows that the main LEED spots are actually double spots and indicative of the different in-plane Ru and BN lattice parameters. The LEED image with a rotated and expanded unit cell differs from the corresponding image for the borazine-derived “nano-mesh" reported 14 for monolayer BN on Ru(0001), but similar to the unit cell observed for a borazine-derived monolayer film on Pd(111) 15. The in-plane lattice constants are similar for Pd(111) and
Ru(0001), 2.75 Å and 2.71 Å respectively) rendering the similarity in the LEED structures reported here to that observed on Pd not that surprising. The difference in the LEED image for the ALD deposited BN film on Ru (Fig. 5.3a) vs. the borazine-derived nanomesh indicates that the film formation is determined not only by the film/substrate mismatch, but also the detailed and yet to be understood process of nucleation and growth.

In the absence of graphene, typical STM-derived density of states (dI/dV data) for the monolayer BN(111) film (Fig. 5.3b) on Ru(0001) has a ~ 2 eV band gap. Near edge X-ray absorption fine structure (NEXAFS) and photoemission studies of borazine-derived monolayer BN films on Ni(111) and Cu(111) indicate strong metal (3d)-BN(π/π*) hybridization, resulting in apparent band gaps that are much smaller than the bulk value of 5.97 eV. Similar interactions between the Ru(4d) and the BN(π/π*) system may also occur and afford a rationale for the observed 2 eV band gap for monolayer BN(111) (Fig. 5.3b). Angle-resolved spectroscopy (ARPES) data for the borazine-derived nanomesh/Ru(0001) data indicate a valence band maximum ~ 1.5 eV below the Fermi level, not inconsistent with the dI/dV data in Fig 5.3. (lower left). The available photoemission and STM/STS data for BN monolayers on Ru metal substrate indicate strong BN (π/π*)-substrate d orbital hybridization, regardless of the method of film formation or structure of the BN overlayer.

The formation of a graphene overlayer (Fig. 5.3, top) was achieved by exposure of the monolayer BN(111) film to C2H4 at 1000 K and a pressure of 0.1 Torr for 60 sec. Using the attenuation of Ru, B(KVV), and N(KVV) in the Auger spectra (Fig 5.5), an average graphene thickness of 4.4 Å was calculated. The LEED pattern (Fig. 5.2c) yielded a well-defined hexagonal pattern, but with a number of smaller spots attributable to multiple scattering. The well-
defined spots, including multiple scattering, indicate graphene overlayers in registry with each other and with the BN substrate, similar to LEED images for a few-graphene overlayers on SiC(0001) \(^3,12\). In contrast, BN and graphene layers with azimuthal orientation randomized with respect to each other would exhibit streaks in the diffraction pattern, as reported for multiple graphene sheets on SiC \(^2\).

Fig. 5.5 AES Spectra of ALD 2.2 Å BN film grown on Ru(0001) followed by subsequent dosing of C\(_2\)H\(_4\) (4.4 Å) at 1000K (0.01 Torr for 1 min).

The dI/dV data for CVD graphene on monolayer BN(111) (Fig. 5.3d) indicate a shallow valley near 0 eV bias. Similar dI/dV data have been reported for HOPG,\(^{23}\) as well as for ~ 2.5 ML graphene on SiC(0001) \(^3\). The dI/dV data in Fig. 5.3c are typical for a zero band gap.
semiconductor. The dI/dV data therefore indicate that the carbon overlayer has “graphene-like” electronic structure rather than a C-rich interfacial layer with non-graphene electronic characteristics.

After acquisition of STM/STS and LEED data, the sample was removed from the chamber, exposed to air, and placed in a second vacuum system with XPS and reverse-view LEED capability. XPS after air exposure (not shown) indicated small amounts of oxygen, as well as C(1s), Ru(3d), B(1s), and N(1s) signals. No Cl(2p) peak was observed, indicating that no Cl impurities were present in the ALD grown film. There was also no evidence of Ru or B oxidation. The sample was flash annealed to 1000K in UHV which resulted in the removal of O and observation of the same LEED pattern as in Fig. 5.3 (upper right). In contrast, when ALD-grown BN films on Ru or other substrates were exposed to the ambient; O was incorporated into the films via B oxidation and was not removed by flash annealing in UHV. Although the relative inertness of graphene layers is well documented, the ability of the graphene overlayer to effectively inhibit oxidation of either BN or the Ru substrate in ambient suggests a largely continuous graphene overlayer, as well as the practical stability of such assemblies for further ex-situ studies.

Raman spectra were acquired ex-situ, in the reflective mode, using a 514 nm excitation source, at UT-Dallas by Dr. Luigi Colombo and Adam Pirkle. The spectrum for the graphene/BN sample is shown in Figure 5.6. A spectrum was acquired on the same instrument from an HOPG sample for comparison. Raman of graphene and graphite samples has been the focus of numerous studies. Raman spectra from hexagonal BN have received less attention. The Raman spectrum from the graphene/BN sample (Fig. 5.6) exhibits intense broad features <
1000 cm$^{-1}$, a sharp “G” peak (graphene ring breathing mode) near 1560 cm$^{-1}$, and an intense “2D” (two phonon) feature, red-shifted more than 350 cm$^{-1}$ from the corresponding HOPG feature. The various broader features $<1000$ cm$^{-1}$ (labeled “BN”, Fig 5.6) are attributable to IR-active BN modes visible in Raman due to the broken symmetry of the ultrathin film and proximity to a metal substrate. The relative intensities of the G and 2D features (Fig. 5.6) are representative of those observed for single or few-layered graphene samples. The position of the G peak (ring breathing mode) is slightly red-shifted from that of HOPG and consistent with reported values for single or few-layered graphene. The magnitude of the red shift of the 2D feature is unusually large, however. Amorphous sp$^3$ carbon displays a Raman signal at the same approximate frequency as the 2D peak in Fig. 5.6. The Raman spectra of amorphous carbon, however, yields only a very broad feature centered near 1500 cm$^{-1}$, in contrast to the sharp feature observed in Fig. 5.5, and entirely inconsistent with the well-defined LEED pattern in Fig. 5.3 (upper right). Raman 2D red shifts of $\sim 100$ cm$^{-1}$ have been reported for graphene monolayers under tensile stress, with smaller red shifts for the G peak of these samples. The shift of the magnitude observed here (Fig. 5.6), however, suggests significant coupling with the substrate. Charge donation from the N(2p$_z$) orbitals into the nominally empty graphene π* band, would lead to a lower C-C bond strength and Raman shift. The observed positions of both the G and 2D peaks (Fig. 5.6) are in excellent agreement with the preliminary results of both ab initio and semi-empirical calculations, indicating strong electronic interactions with the BN substrate.
Fig 5.6. Ex-situ Raman spectra (514 nm excitation energy) for the graphene/BN/Ru(0001) sample (red) and an HOPG sample (blue). The graphene/BN sample is the same as in Figure 5.3.

The strong BN/graphene interactions indicated by both LEED (Fig. 5.3) and Raman data (Fig. 5.6) are not inconsistent with a previous report. In that study, formation of a graphene/BN bilayer by sequential thermal decomposition of borazine and benzene on Ni(111) resulted in a broad, indistinct LEED pattern, which the authors attributed to interlayer disorder. HREELS data, however, indicated strong BN/Ni(111) hybridization in the absence of graphene, but a more “bulk-like” BN character upon subsequent graphene overlayer formation. This strongly suggests, in that study, graphene/BN charge transfer also occurred, in spite of the apparent orientation between the two layers.

DFT calculations have predicted that h-BN/graphene interactions will, due to broken symmetry, induce a band gap \( \sim 0.05 \text{ eV} \) or more in the graphene density of states. The \( \text{dI/dV} \)
data reported here (Fig. 5.3d) are not consistent with this prediction, but instead strongly resemble that for HOPG. 23 A possible reason for this discrepancy between DFT predictions and experiment is Ru(4d)/BN(π/π*) interaction, as described above, and which yields the ~ 2 eV band gap for the BN(111) monolayer (Fig. 5.3b). Such BN/substrate interactions were not considered in the DFT study 31.

5.4 Conclusion

The data presented here demonstrate a novel route for the growth of graphene monolayers directly on insulating BN(111) substrates of variable thickness by ALD and CVD. In contrast to BN films derived from borazine decomposition on transition metal substrates, 14-17 both monolayer and multilayer BN(111) films can be produced on Ru(0001) by ALD using BCl₃/NH₃ cycles at 550K followed by annealing in UHV to 1000 K. The monolayer film displays a well-defined LEED pattern indicating a R30 (√3x√3) overlayer, qualitatively different from the borazine-derived nanomesh on this substrate 12, 14. STM dI/dV data indicate a band gap of ~ 2 eV. This substrate then serves as a template for the growth of a graphene overlayer via CVD of C₂H₄ at 1000 K. LEED data and Raman data indicate that the graphene film is in registry with the BN substrate and strongly coupled to it, in contrast to previously reported results for graphene films formed by benzene decomposition on a borazine-derived BN monolayer on Ni(111) 19. STM dI/dV data indicate that the graphene has an electronic density of states expected of a zero band-gap semiconductor. Thus, the STM and Raman data indicate that the graphene surface layer is truly “graphene-like”, rather than a C-rich ordered interface with non-graphene-like electronic properties. The presence of a distinct interfacial layer cannot, however, be ruled out by the existing data.
The difference between BN films and graphene/BN interfaces discussed here, and those formed by borazine and subsequent benzene decomposition is striking. Azimuthal randomization is reported \(^{19}\) for graphene films grown by benzene decomposition as well as for multiple graphene sheets grown by Si evaporation from SiC \(^2\). Such lack of azimuthal orientation between layers is not surprising for what are, essentially, 2-dimensional materials. The high degree of graphene/BN interaction and structural registry shown here, therefore suggests that the nanostructure of the BN film grown by ALD is substantially different from that of the borazine-derived film, and this notion is reinforced by the absence of a puckered nanomesh structure in the ALD BN film on Ru. The results presented here, however, conclusively demonstrate that ALD BN film can serve as a template for direct graphene growth on a dielectric substrate. This in turn presents a broad array of novel possibilities for growing novel graphene/BN/metal(111) structures in a manner that lends itself to industrial scale production and patterning. Finally, charge transfer to/from graphene molecularly absorbed donors/acceptors has been demonstrated \(^{32}\) to greatly enhance electron mobilities without significant change in carrier density. This has been explained as due to enhanced screening of charged impurities \(^{33}\). Since BN → graphene charge transfer is strongly suggested by the Raman data (Fig. 5.6), the electronic properties of BN supported graphene afford an exciting subject for further investigation.

5.5 References


