Preparation and Characterization of Epitaxial Thin Films with Applications in Catalysis and Microelectronics

Asim Khaniya
University of Central Florida

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PREPARATION AND CHARACTERIZATION OF EPITAXIAL THIN FILMS
WITH APPLICATIONS IN CATALYSIS AND MICROELECTRONICS

by

ASIM KHANIYA
B.Sc., Tribhuvan University, 2010
M.Sc., Tribhuvan University, 2013
M.S., University of Central Florida, 2016

A dissertation submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy
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Major Professor: William E. Kaden
ABSTRACT

Ubiquitous in the modern world, the epitaxial thin film offers a wide range of practical applications in the field of microelectronics, solar industries, optical devices, and catalysis. This thesis deals with studying the growth and characterization of molybdenum nitride (MoN) and various dielectric encapsulated Ru(0001) thin films on single-crystal substrates. The phase-specific and single-crystalline MoN film was grown epitaxially on pre-nitrogen-covered Ru(0001) via physical vapor deposition and characterized by UHV based surface science analytical techniques, including X-ray photoelectron spectroscopy, helium ion scattering spectroscopy, auger electron spectroscopy, and low energy electron diffraction (LEED). The annealing temperature of 700 K was found to result in well-ordered hexagonal films that appear to grow layer-by-layer initially and in registry with the Ru(0001) support. The MoN film starts to decompose via a presumptive N₂ recombinative desorption mechanism upon annealing above T = 700 K, which leaves the film in a purely metallic Mo-Ru configuration by T = 1100 K. The oxidation kinetics of hexagonal MoN at ambient conditions predict the complete oxidation of single layer of MoN in ~30 days.

Enhanced scattering of electrons at surfaces is a critical factor for the resistivity size-effect observed in single-crystalline nanoscale metals. In this work, we have investigated the surface-dependent effects on resistivity for oxide-capped Ru(0001) films with thickness in the nanometer regime utilizing XPS and LEED to monitor the change in the chemistry and structure of the Ru(0001) interface. The variation in resistivities resulting from presumptive changes in surface structure and chemistry were related to the changes in the Ru surface's specularity (p) for electron
scattering in the context of the Fuchs-Sondheimer semi-classical model. In this context, we have demonstrated a fully (reversibly) tunable specularity at the metal interface (from fully specular to fully diffuse), buried under the amorphous oxide dielectrics.
To my parents
ACKNOWLEDGMENTS

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<th>Abbreviation</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>AES</td>
<td>Auger Electron Spectroscopy</td>
</tr>
<tr>
<td>HDN</td>
<td>Hydrodenitrogenation</td>
</tr>
<tr>
<td>LEED</td>
<td>Low Energy Electron Diffraction</td>
</tr>
<tr>
<td>LEIS</td>
<td>Low Energy Ion Scattering Spectroscopy</td>
</tr>
<tr>
<td>PVD</td>
<td>Physical Vapor Deposition</td>
</tr>
<tr>
<td>SiO₂</td>
<td>Silicon Dioxide</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoemission Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>XRR</td>
<td>X-ray Reflectivity</td>
</tr>
<tr>
<td>µΩ</td>
<td>micro-ohm</td>
</tr>
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CHAPTER 1 : INTRODUCTION

1.1 Background

Thin-film refers to a layer of materials deposited onto the substrate with thickness ranging from a single atomic layer to few micrometers. Ubiquitous in the modern world, thin-film usage dates back over 5,000 years [1], where a chemo-mechanically prepared gold layer is the earliest documented thin film [2]. Although the film's usage in those ancient times was limited to decorative purposes [3], and the techniques used to prepare those material layers were different from the ordinary methods we use in today's world, it is interesting to note the eminence of thin-films in separate cultures throughout history. However, it was not until the development of various vacuum technologies and thin-film characterization methodologies starting in the 1960s [4], making thin-film science more popular. The improvement in thin-film properties compared to its bulk counterpart and the availability of highly advanced material deposition techniques to prepare new thin-film materials to meet the ever-increasing demand for multi-dynamic and versatile materials have widened the applications of thin-film at the industrial level [5].

Epitaxial thin film is often preferred over polycrystalline films because the physical properties can easily be controlled and enhanced [6, 7]. A considerably small amount of material is needed for the equivalent performance compared to a randomly oriented polycrystalline thin film, which becomes a critical consideration in precious metal usage. Sometimes through epitaxial growth, certain phases of materials can be achieved, otherwise inaccessible. Therefore, it has attracted a great deal of attention from scientific and industrial communities [8, 9, 10]. Epitaxial growth refers to a phenomenon of forming a single crystalline film on top of a single crystal
substrate and subsequent growth evolution of a specific crystallographic orientation relationship between the substrate and the film as the film growth commences. The lattice parameters and the crystal systems of both the film and substrate govern the nature of the crystallographic orientation relationship. The epitaxial growth mechanism can broadly be divided into two categories: homoepitaxy and heteroepitaxy. Homoepitaxy refers to the state when the film and the substrate are of the same material, and hence there is no lattice strain at the film-substrate interface. However, in heteroepitaxial growth, where the film and the substrate are of different materials, generally, a lattice mismatch between the substrate and the film exists. Thus, the interface is either relaxed or strained depending upon the magnitude of the difference in lattice parameters. Therefore, lattice matching is one of the critical aspects of the thin film epitaxy.

1.2 Thin-film growth modes

The discovery of electron diffraction in the 1930s and the evolution of surface characterization techniques like LEED, STM, and the improvement in the development of the vacuum systems since the late 1950s have contributed significantly to understanding the phenomena behind the epitaxial growth of different materials [4]. The crucial factors influencing film growth include lattice misfit, the bonding between adatoms, and the substrate. From a thermodynamical perspective, the relationship between the film's surface energy, $\gamma_F$, the substrate's surface energy, $\gamma_S$, and the energy between the film and substrate, $\gamma_I$, plays an integral role in determining the nature of the growth mode of the heteroepitaxial film [11]. All thermodynamic systems try to minimize their free energy by maximizing the lowest energy surface
area while minimizing the interface energy. Ideally, the initial stage of thin-film growth can be divided into three characteristic modes [12].

![Diagram of film growth modes](image)

Figure 1.1: Schematic of film growth modes: (a) Frank-Van der Merwe (layer by layer), (b) Volmer-Weber (Island growth), and (c) Stranski-Krastanov(layer + island).
1.2.1 Frank van der Merwe: layer by layer growth

Frank van der Merwe growth (FM), also referred to as monolayer growth, is essentially the formation of a continuous, complete layer of atoms, as presented in Figure 1.1(a). For this growth mode, unique compatibility is required between the substrate and growing film in terms of chemistry and lattice parameter matching. The adatoms have a strong affinity with substrate atoms rather than in between adatoms. As a result, in FM growth mode, a monolayer-thick island of atoms is formed initially, which later intergrows to form a continuous single layer before developing new layers above it. The criterion for the growth of films in monolayer mode (FM) is depicted in equation (1.1) from surface energy consideration.

\[ \gamma_F + \gamma_I \leq \gamma_S \]  

(1.1)

In homoepitaxial growth, the substrate and film are of the same material, \( \gamma_I = 0 \), and \( \gamma_S = \gamma_F \), and equation (1.1) is still satisfied. For smaller misfit between the substrate and film, the interfacial energy is more likely to be lower. Therefore, the deposition of films on a dissimilar substrate with low misfits tends to result in monolayer growth in the presence of strong interaction between the film and the substrate. After completing a monolayer, subsequent layers grow on top of each other until a critical thickness [13] is reached. At this point, the monolayer growth is no longer favored energetically, and hence thereby, the layers start to relax due to the commencement of strain relief, resulting in the formation of misfit dislocations. With an increase in the numbers of monolayers, it is also necessary to consider elastic strain energy present in the film, which is
typically done by replacing $\gamma_I$ with $\gamma_{IN}$ in equation (1.1), where $\gamma_{IN}$ includes the strain energy for N monolayers.

1.2.2 Volmer-Weber: Island growth

If the energy reduction criterion in equation (1.1) is not satisfied, the adatoms initially nucleate to form isolated 3D islands and grow directly on the substrate surface. This island growth of epitaxial film, which is also referred to as Volmer-Weber growth mode, is schematically presented in Figure 1.1(c). In VM mode, the adatoms in the film bind more strongly to each other than to the substrate. The surface energy condition for this type of growth is expressed as,

$$\gamma_F + \gamma_I > \gamma_S$$  \hspace{1cm} (1.2)

When the sum of $\gamma_F$ and $\gamma_I$ has a value larger than the free surface energy ($\gamma_F$) of a substrate, it is energetically favorable for the system if the film covers a minimum area of a substrate as possible. This implies the film does not thoroughly wet the surface but instead develops the crystallites of several monolayers (3D growth) to minimize the film's surface area of contact. The formation of isolated 3D nuclei depends on the adequately high diffusion coefficient for the deposited atoms' migration over the substrate surface or by direct impingement of atoms at the active sites such as defects or impurities or atomic steps. These active sites help to reduce the activation energy for the phenomena of nucleation of atoms on the substrate surface.

A well-established classical nucleation theory [14, 15] can be utilized to understand the nucleation behavior of deposited atoms. According to these theories, the radius of a stable nucleus should be greater than a "critical radius" to meet the free energy criterion. The critical radius value
can be obtained by minimizing the free energy of a system, \( \frac{dG}{dr} = 0 \), \( G = \) free energy. The formation of nuclei with the minimum critical size is followed by an increase in the number of isolated nuclei as the deposition process continues until new nuclei formation is not favored energetically. Then, the increase in the size of existing nuclei takes place by the addition of extra atoms.

1.2.3 Stransi-Krstanov: Mixed growth(Layer + Island)

Stransi-Krstanov(SK) process represents the intermediate case between VW and FM growth modes. Typically, the growth of film in this mode starts with the deposition of one or two continuous monolayers followed by the formation of isolated 3D islands on top of the wetting layer, as represented in Figure 1.1(b). The lattice mismatch between the substrate and the film plays a crucial role in this phenomenon. Usually, it tends to happen when the misfit is more than about 2\%, and the contribution of elastic strain energy is significantly high compared to other surface energies (in equation 1.1).

1.3 Motivation for present work

Over the last few decades, a tremendous amount of progress has been achieved in the epitaxial growth of thin films of various single-crystalline metals, metal nitrides, and complex oxides, which has become possible only due to the robust improvement in vacuum technologies and material characterization tools needed to understand the surface structure and film growth mechanism in greater detail. Due to its often superior properties compared to polycrystalline counterparts, epitaxial thin films have gained massive attention from both the scientific and industrial communities. This thesis mainly focuses on an epitaxial metal nitride, molybdenum
nitride (MoN), and a single-crystalline metal, Ru(0001). The first part of the thesis deals with the study of epitaxially grown, phase-specific molybdenum nitride (MoN) thin films with the use of ultra-high vacuum-based surface science techniques. The second part of this work encompasses the study of electron scattering phenomena on a single-crystalline Ru(0001) interface and the influence of annealing temperature, annealing environment, and dielectric encapsulation on resistivity change to the Ru(0001) film.

Molybdenum nitride provides the broader range of functionalities necessary for the application in microelectronics (as diffusion barrier), catalysis, and tribological coatings [16-19]. Furthermore, the superconducting property of molybdenum nitrides has attracted significant research attention. The higher catalytic activity of molybdenum nitride towards hydrodenitrogenation (HDN) [20,21], the process of removing nitrogen from energy feedstocks during oil refining, is one of the primary motivations for the present work. The group of Levi Thompson in the early 1990s has conducted a series of comparative studies for the catalytic performance of MoN towards the HDN of pyridine and found that molybdenum nitrides, especially the δ-MoN phase, outperform the industrial catalyst, sulfided Co-Mo, and Ni-Mo on Al₂O₃ [22, 23, 24]. Even though extensive research efforts have been given into the preparation of phase-specific molybdenum nitrides [25-28], to this date, the literature reporting the large-scale growth of single-crystalline films with atomically planar surface terminations suitable for the surface-science investigation, highly used in the catalysis field, is not available to our knowledge. The surface science approach in heterogeneous catalysis rests on the studies of the well-defined model systems, ideally single crystals, under the ultra-high vacuum conditions, where the high complexity of a technical catalyst is stepwise broken into simple problems and addressed in a very
controlled environment. Such surface science studies of model catalysts have gathered a tremendous amount of information for various catalytic processes; a prominent example is the ammonia synthesis through the Haber-Bosch process on an iron-based catalyst [29]. The ultimate goal for this project is to develop the phase-specific, lamellar, smooth, and atomically planar epitaxial molybdenum nitride thin film, which will be used as a model catalyst for future HDN studies of N containing compounds, including pyridine and carbazole.

Due to a transition metal's high oxygen affinity, metal nitride is highly likely to oxidize upon air exposure, affecting these materials' catalytic properties and tribological properties [30, 31]. Therefore, it is highly desirable to understand the air stability and surface oxidation of molybdenum nitride model systems at ambient air conditions and higher temperatures. Although sufficient literature is available for the high-temperature oxidation kinetics of transition metal nitrides, including MoN, minimal effort is given to the oxidation study of metal nitrides at ambient conditions. We are not aware of any previous literature for the oxidation study of MoN at ambient conditions. Therefore, it motivated us to study the kinetics of the molybdenum nitride's surface oxidation by exposing the samples to ambient conditions.

Non-linear increase in resistivity of copper interconnects at a dimension smaller than the electron mean free path (39nm for Cu), also known as resistivity size effect, is one of the significant challenges facing current CMOS technology for the continued downscaling of integrated circuits due to the associated power consumptions at the interconnect level. Scattering of electrons from grain boundaries and metal surfaces are two major contributing factors to the resistivity size effect [32, 33, 34, 35]. The resistivity increase in both scattering phenomena, as explained by two
classical models, Fuchs–Sondheimer (FS) for surface scattering and Mayadas–Shatzkes (MS) for grain boundary scattering, scales with the product $\rho \times \lambda$; where $\rho$ is bulk resistivity of metal and $\lambda$ is the electron mean free path. Thus, the significant research efforts made towards exploring interconnect metals beyond copper are focused on minimizing this product. The density functional theory (DFT) based study conducted by Gall [36, 37] has reported Ru as one of the very few transition metals that have a lower value of the product $\rho \times \lambda$ in comparison to Cu. It indicates that, despite its higher bulk resistivity, Ru is expected to form a more conductive nanowire than Cu, and hence, has emerged as a promising replacement to the existing Cu interconnects [38, 39, 40, 41].

The experimental study conducted by Sun et al. [42, 43] in polycrystalline Cu films reported that the grain boundary scattering mechanism heavily dominates the resistivity increase in copper with dimensions below 39 nm. Similar results are reported by Barmark et al. in reference [44]. These results point out the importance of eliminating the source of grain boundary scattering to develop the interconnects beyond copper by implementing epitaxial, single-crystalline metal interconnects instead of polycrystalline Cu. Because Ru is known to exhibit the weaker correlation between the thickness and resistivity at thickness smaller than $\lambda$, it motivates this work on studies of the resistivity behavior of epitaxial single crystalline Ru films grown on (0001) surface terminated c-axis sapphire. The stronger desire to obtain a highly specular surface of a single-crystalline metal can be seen from previous research efforts [45]. Therefore, this work explores the possibility of obtaining a more specular Ru(0001) interface by introducing a chemical and structural change at the Ru interface.
1.4 Organization of thesis

In chapter 2, we present a summary of the experimental techniques that have been used in the preparation and characterization of epitaxial thin films. Thin films in this work were prepared by the PVD technique. The basic working principles of the characterization techniques, including XPS, LEIS, LEED, AES, XRR, XRD, and the van der Pauw method for resistance measurement, are summarized in chapter 2. The apparatus used to carry out the experimental work is also presented in this chapter.

Chapter 3 presents a detailed study of the epitaxial growth of hexagonal molybdenum nitride on Ru(0001) under ultra-high vacuum conditions. The molybdenum nitride thin film is found to crystalize into a hexagonal structure at the annealing temperature of around 700K. The stability of MoN film at higher annealing temperature is also discussed in this chapter.

The study of lattice mismatch between the epitaxially grown MoN and the Ru(0001) substrate has been conducted via LEED, presented in chapter 4 of this thesis work. The kinetics of the oxidation behavior of hexagonal MoN at ambient conditions is also discussed in this chapter.

Chapter 5 is dedicated to studying the surface scattering of electrons at metal/dielectric and metal/vacuum interfaces of Ru(0001) thin-films. Demonstration of a technique to achieve a highly specular Ru(0001) interface with a lower resistivity value is provided and explained in detail in this chapter. Ex-situ annealing of the Ru(0001) film to 950 °C in an Ar/H₂ (3%) atmosphere is found to lower the resistivity of film, which has been attributed to the presence of a highly specular Ru(0001) upper surface even when buried under the amorphous dielectric. Additionally, a
comparative study of the effect of the dielectric encapsulation material on the resistivity change of a 20nm Ru(0001) thin film is also included in this chapter. The results presented in this chapter are a part of our collaborative research work under the project name “E2CDA: Interconnects beyond Copper”.

Finally, chapter 6 summarizes the dissertation and describes the possibility of future work based on or continuing research work presented in this dissertation.

1.5 References


2. Greene, J. E., Tracing the 5000-year recorded history of inorganic thin films from~ 3000 BC to the early 1900s AD. *Applied Physics Reviews* 2014, 1(4), 041302.


CHAPTER 2: EXPERIMENTAL DETAILS

2.1 Introduction

In this thesis work, we have mainly utilized e-beam evaporation and sputtering techniques to grow thin films on single crystalline substrates. Various surface analytical techniques were utilized to study the fundamental structural, electronic, and chemical properties on the surface and the interface of such grown thin films. The experimental techniques include X-ray Photoemission Spectroscopy (XPS), low energy electron diffraction (LEED), low energy ion scattering spectroscopy (LEIS), X-ray diffraction (XRD), X-ray reflectivity (XRR), and the van der Pauw method for four-point resistivity measurements. The experimental techniques used in the preparation and characterization of samples are described in this chapter.

2.2 Thin-film deposition

Deposition technique plays an integral role in creating thin-film new materials and determines virtually all thin-film properties, such as surface morphology, microstructure, tribological, electrical, optical, corrosion, and hardness [1-6]. A single material's properties can be tailored to meet the optimum requirements for different applications using different deposition techniques. So, significant consideration should be given in choosing the deposition method depending on the field of applications. The deposition techniques are broadly classified into physical vapor deposition (PVD) and chemical vapor deposition (CVD). In PVD, the vapor is made up of atoms or molecules which simply condensate onto the substrate. In contrast, in CVD, vapor undergoes a chemical reaction on the substrate, resulting in film growth on the substrate.
Physical vapor deposition (PVD) is one of the most widely used deposition techniques, which involves the physical movement of atoms or molecules from the target to be deposited onto the substrate. PVD techniques have a wide range of applications, from decorative films to high-temperature superconductors. The rate of deposition can vary from angstroms to millimeters of film per minute. Every PVD processes obey three necessary steps [7, 8]:

(i) Creation of vapor-phase species
(ii) Physical transportation of material from source to the substrate, and
(iii) Film growth on the substrate

First, the solid material to be deposited is converted into the vapor phase via different techniques, including sputtering, evaporation, or ion-bombardment. The vapor-phase material is then transported onto the substrate under a high vacuum or low pressure of gases or plasma atmosphere. The molecules or atoms transported on a substrate start to nucleate, and film growth occurs by different processes. E-beam evaporation and sputter deposition are two different PVD techniques employed to grow films in this thesis work.

2.2.1 E-beam Evaporation deposition

The electron beam evaporation [9, 10] process uses a beam of electrons to impact a target material to increase its temperature locally, resulting in the atoms from the target to transform into a gaseous phase. These vapor phase atoms then condense into solid form, coating the substrate inside the vacuum chamber within the line of sight. The capability of localizing the intense beam of energy to a tiny part of a target makes the e-beam evaporation technique viable to produce a
significantly high flux of evaporates from refractory materials having high melting point such as tungsten, tantalum, and molybdenum, which otherwise would be almost impossible to deposit by thermal evaporation. For the significant evaporation of the material using the e-beam PVD technique, it must have sufficiently high vapor pressure at a reasonable temperature [11]. The vapor pressure curve for some of the most evaporated metals shown in Figure (2.1) provides excellent guidance for the material deposition rate at a reasonable temperature.

Figure 2.1: Vapor pressure curves for commonly evaporated metals [12].
The schematic representation of the e-beam evaporation is shown in Figure 2.2. The source material to be deposited is placed in a crucible, usually made of materials with higher melting points. The highly intensive beam of electrons generated from a filament placed nearby to the crucible is accelerated using high voltage (in kV range) to hit the target. When the heated electron strikes the target material, it loses its kinetic energy, converts into thermal energy, and heats the target surface.

Figure 2.2: Schematic representation of the e-beam evaporation process.

When the target surface temperature is high enough, the vapor is produced and deposited onto the substrate within the line of sight. Since the evaporation occurs near the electron beam bombardment site, the crucible contamination is almost none. As deposition of thin films via e-
beam evaporation is done under high vacuum conditions, the less interaction of vapor atoms/molecules of a target with possible surrounding contaminants results in highly pure and good quality thin-films. In this work, the e-beam evaporation technique is used to grow the epitaxial molybdenum nitride thin films on Ru(0001) substrate.

2.2.2 Sputtering Deposition

Sputtering is a high-rate vacuum coating process that falls under the category of physical vapor deposition and is mainly used for depositing metals, alloys, and compounds onto a wide range of materials with thickness up to a millimeter [13, 14]. It involves the process of dislodging atoms or molecules from the target, the source material, to deposit on the substrate through the bombardment of high energetic gaseous ions. The main advantages of this technique in comparison to other PVD processes include the simplicity in controlling composition and purity of film, uniformity in thickness of deposited films, better reproducibility, ability in maintaining the stoichiometry of film same as the target composition, and good adhesion to the substrate.

Depending upon the type of power source used, the sputtering process is generally classified into two categories as DC or RF sputtering [15,16]. Metals are mainly deposited by DC sputtering technique. However, in insulators, the localization of ions on the target surface builds up the positive ions over time and makes it unfeasible for the bombardment of the target surface by the energetic ions. The use of an RF power source can avoid this problem. Typically for RF sputtering, power sources with RF frequencies in the range from 5 to 30 MHz are employed. However, the standard frequency used for RF sputtering is 13.56 MHz [17]. Sputtering sources
often utilize magnetrons that use the strong magnetic field (B) to localize the charged gaseous ions close to the surface of the target, which causes more ionization collisions with target atoms and hence increases the sputter yield. It is also called the magnetron sputtering process.

The schematics of the sputtering deposition process is represented in Figure 2.3. In a typical sputtering process, the target material to be deposited is placed on the cathode, and the substrate is positioned at the anode. The external voltage is applied with a target in high negative potential (1-5 kV). The sputtering inert gas, usually Ar [1-10 mTorr], is introduced into the deposition chamber in-between target and substrate and the deposition chamber wall. The immense potential difference between cathode and anode causes the ionization of sputtering gas that forms a plasma.

![Figure 2.3: Schematics of the sputter deposition process.](image-url)
Whereas the plasma itself maintains the neutral charge, the ionization of inert gas results in a negatively charged electron and positively charged ion. The negative high voltage on the target attracts the positively charged ions and collides with the target material. A series of collision impact the target with sufficient energy to cause the ejection of neutral target atoms by momentum transfer. This process of releasing the target atom is also known as sputtering. During this process in together with neutral target atoms, electrons are also released. The flux of sputtered atoms, leaving the target surface with relatively higher energy, is then transported towards the substrate, where it condenses and forms a uniform thin film. The electrons further undergo collisions with the inert gas atoms, forming the plasma and maintaining the continuous supply of ions to perpetuate target atoms [18, 19]. In this thesis work, the DC magnetron sputtering deposition technique is employed to grow single-crystalline Ru(0001) metal on the sapphire substrate, and RF sputtering is used for the dielectric encapsulation(SiO₂, Cr₂O₃, Al₂O₃, MgO) material growth on Ru(0001).

2.3 Sample characterization techniques

The basic working principles of various surface analytic methods used in our experimental works are discussed here.

2.3.1 X-ray Photoemission Spectroscopy

X-ray photoemission spectroscopy (XPS) is one of the most widely used analytical techniques in surface science, which can be utilized to obtain information about the chemical composition, chemical state, and electronic state of elements present on the surface of the materials. The governing principle of XPS is the photoelectric effect [20]. In XPS, when X-ray
photons of energy $h\gamma$ strike upon the surface of a specimen, it knocks out the core level electrons from atoms to vacuum, represented graphically in Figure 2.4. The electrons emitted in this manner are referred to as photoelectrons. The following equation can express the kinetic energy, $E_{\text{Kin}}$, of the ejected photoelectrons:

$$E_{\text{Kin}} = h\gamma - (E_{\text{BE}} + \phi_S),$$  \hspace{1cm} (2.1)

Where $E_{\text{BE}}$ is the binding energy of an electron, and $\phi_S$ is the sample's work function.

If the sample and analyzer are electrically contacted, the fermi levels must be in equilibrium. If $\phi_A$ is the work function of an analyzer, the potential experienced by the
photoelectrons is given by the difference in the work function of the sample and analyzer. This difference, \( \Delta \phi = \phi_S - \phi_A \), is often referred to as a contact potential between sample and analyzer. By accounting for the contact potential, the kinetic energy of the photoelectrons measured by the analyzer is given by,

\[
E_{\text{Kin}} = h\gamma - (E_{\text{BE}} + \phi_S) - (\phi_S - \phi_A) = h\gamma - E_{\text{BE}} - \phi_S
\]  

(2.2)

Thus, the binding energy of the photoelectrons measured by the analyzer is given by,

\[
E_{\text{BE}} = h\gamma - E_{\text{Kin}} - \phi_A
\]  

(2.3)

Equation (2.3) shows that the binding energy of an electron measured by an analyzer is independent of the sample work function. The energy of the X-ray photon source is known. If the analyzer work-function is calibrated, the kinetic energy of photoelectrons determines the binding energy and vice-versa.

The detected kinetic energies of emitted photoelectrons provide information about the binding energies of core electrons, which are element specific. Because of the difference in binding energies for electrons at different atomic orbitals, for each element, there is a unique XPS energy spectrum, which is usually plotted in the form of the number of photoelectrons versus the kinetic or binding energy of the as-detected photoelectrons. Besides the sharp peaks representing those characteristic photoelectrons, a continuous background of electrons is also present in the spectrum. These background signals are originated from the energy loss electrons due to an inelastic scattering effect when they escape from the sample.

The positions of BE peaks in the XPS spectrum indicate both the presence of specific elements and their respective oxidation states. Furthermore, the binding energy of core electrons is very sensitive to the corresponding element's chemical environment. The interaction of the same
atom with different chemical entities results in a change in its core electrons' binding energy. This effect is termed as a chemical shift, which provides information about the chemical status of all elements present on the surface of the specimen and its local environment [21]. In addition to core-level peaks, the XPS spectra also consist of Auger electron peaks.

Although the penetration depth of X-rays in samples can be up to a few micrometers, the detected photoelectrons originate from the top ~ 100 Å of a material, which is the direct consequence of a small mean free path (5-20) Å, as shown in Figure 2.5 of low energy electrons through the solid resulted from inelastic scattering and absorption of electrons [22, 23]. The surface sensitivity of XPS derives from the short mean free path of electrons in solids, which implies the inability of electrons from a deeper layer to pass through the material surface to vacuum, and only electrons emitted from atoms close to the surface will avoid inelastic scattering and escape the solid. The intensity of a signal which has traveled through the material of thickness, d is then given by,

\[ I_d = I_0 e^{-\frac{d}{\lambda \cos \theta}} \]  

(2.4)

Where \( I_0 \) is the initial intensity of excited electrons, \( \theta \) is the detection angle with respect to the sample normal, and \( \lambda \) is the inelastic mean free path of an electron.
The qualitative analysis of the XPS spectra collected from the sample is usually done by comparing the measured core level photoelectron line with the reference, for example, Handbook of X-ray photoemission spectroscopy [22]. The number of photoelectrons of any element collected at the detector mainly depends on the atomic density of that particular element. So, XPS can also be used to quantify the chemical composition of a homogeneous sample by using empirically derived sensitivity factors. The atomic concentration of an element Y in a homogeneous sample, $C_Y$, can be expressed as follows,

$$C_Y = \frac{I_Y/S_Y}{\Sigma I/S}$$  \hspace{1cm} (2.5)
Where $I_Y$ is the XPS intensity of an element Y, $S_Y$ is the sensitivity factor for the measured photoelectron line of element Y, and $\Sigma I/S$ is the sum of normalized intensities of all the detected elements.

Figure 2.6: Schematic representation of XPS Setup.
The schematic of an XPS instrumentation is presented in Figure 2.6. The experimental setup for XPS consists of an X-ray photon source, the sample under investigation, and an electron analyzer to record the energy of photo-emitted electrons from the sample surface.

![XPS spectrum](image)

Figure 2.7: XPS Survey spectra of single-crystal Ru(0001) sample using Alkα X-ray source.

In most of the XPS laboratory, the X-rays are created by bombarding Al or Mg target with high energy electrons generated by accelerating electrons from the heated filament. The main characteristic emission spectrum used in XPS are Mg Kα at 1253.6 eV (linewidth 0.70 eV) and Al Kα at 1486.6 eV (linewidth 0.85 eV). A thin Al foil window is used at the X-ray exit to avoid the
sample from stray electrons, contaminations, and heat from an anode. The X-ray source is generally operated at (200W-1KW) power with 5-15 Kev, and therefore, water cooling of the x-ray source is required to prevent interdiffusion of Al and Mg, in the case of dual anode XPS system. Various types of analyzers have been used in analyzing the photo emitted electrons in XPS. The beam of photoelectrons ejected from the sample is channeled to the input segment of a hemisphere by the acceptance angle of the entrance aperture and lensing system. Then, the electrons with definite energy (called pass energy) are directed towards the detector by applying a desired voltage to the electrodes of the analyzer.

The XPS measurements presented in this thesis are carried out using a SPECS Electron spectrometer with a PHOIBOS 100 Hemispherical Energy Analyzer and XR 50 Al Kα X-ray source (1486.67 eV). The representative XPS spectra collected from clean Ru(0001) single crystal is shown in Figure 2.7, where each characteristic XPS peak at specific binding energy corresponds to the different orbitals of Ru from which the electron was emitted. In addition to core-level XPS peaks, spectra associated with auger transitions are also visible.

2.3.2 Low energy Ion Scattering Spectroscopy

Low-energy ion scattering, which is often also referred to as ion scattering spectroscopy (ISS) [24], is a surface analytical technique that can be employed in determining the elemental composition of the sample surface. In a typical LEIS experiment, a surface of a specimen is bombarded by a beam of low energy noble gas ions (He+, Ne+, Ar+, Kr+), and the kinetic energy of the elastically scattered ions from surface atoms is measured, which contains the information about the scattering atom present on the surface. LEIS is extremely surface-sensitive; the strong
scattering signals are limited to a few topmost layers. So, it is necessary to have a sample clean, and even a small quantity of contamination can significantly influence the LEIS spectrum.

The schematic representation of LEIS is shown in Figure 2.8, where ions with a fixed energy $E_0$ are directed onto the target, and the elastically scattered ions from the surface atoms are collected at the detector. Using the principle of conservation of linear momentum and energy, the relevant quantity while dealing with ISS, the ratio of scattered and incident ion energies ($E_0/E_s$) can be calculated as:

$$\frac{E_s}{E_0} = \frac{\cos\theta \pm \left(\frac{M_2}{M_1}\right)^2 - \sin^2\theta} {\left[1 + \frac{M_2}{M_1}\right]}^{1/2} \left(\frac{M_2}{M_1}\right)^2$$

(2.6)

Where,

$\theta = \text{Scattering angle}$
E_s = Kinetic energy of scattered ions
M_2 = relative mass of a scattered ion
M_1 = relative mass of the primary ion

For a typical LEIS experiment, the scattering angle, \( \theta \), is usually kept constant. Also, the mass (M_1) and the energy of the incident ion (E_1) are known. So, from equation (2.6), we can see that the energy of a scattered ion, measured at the detector, depends only on the mass of the scattering atoms on the material surface. Therefore, the energy distribution of scattered particles yields the elemental composition of the sample surface. The high surface sensitivity of this technique is attributed to the high differential scattering cross-section in this energy range (0.1-10) KeV and

![ISS spectra figure](image)

Figure 2.9: He^+ (500 eV) ISS spectra collected from hexagonal MoN growth epitaxially grown on Ru(0001).
high probability of neutralization of noble ions beneath the outer atomic layer of material. This capability of separating the information from the outer atomic layer to its bulk makes this technique unique for the in-situ study of the early stages in thin-film growth.

An ion scattering spectrum generally includes a separate peak for each element present on the sample surface, with the energy separation depending on the elements' atomic masses. The representative LEIS spectrum is shown in Figure 2.9. Figure 2.9 shows that the scattered ion beam intensity of a primary 500 eV He$^+$ ion beam scattered through an angle of 54° from a Molybdenum nitride (MoN) thin film is plotted against the relative final energy ($E_f/E_0$). The peaks resulting from the scattering of He$^+$ ions from Mo and N atoms can be seen. A differentially pumped ion gun (Specs, IQE-12/38) and a hemispherical energy analyzer (Specs, PHOIBOS 100) is used for this LEIS measurement.

2.3.3 Low Energy Electron Diffraction

Low energy electron diffraction (LEED) is one of the first and most successful surface science techniques used for solid materials' structural information. Davisson and Germer made the first LEED experimental on Ni single crystal at Bell Laboratory [25, 26]. In the LEED experiment, an electron beam with well-defined low energy (20 – 200 eV) is directed to the sample, and the diffraction pattern of the elastically backscattered electrons is recorded using a position-sensitive detector. Bragg's diffraction law is used to describe the angular distribution of such backscattered electrons from a periodic array of atoms on the surface. The electron mean free path of low energy electron (20-200 eV) in solid is only in the order of a few atomic layers [22, 23]; that is why LEED provides information about the surface structure in contrast to X-ray Diffraction.
The experimental setup of LEED, shown in Figure 2.10, mainly consists of three components: an electron gun to emit low energy electrons, a sample holder with a sample, and a display unit to observe the diffraction pattern formed by the elastically backscattered electrons. The electron gun unit consists of a cathode filament, a grid cylinder (Wehnelt), and a lens with...
apertures \( L_1, L_2, L_3, \) and \( L_4 \). The display unit consists of four concentric grids and a fluorescent screen. The electron passes to the sample through the central hole present in each grid and a screen. The Wehnelt cap has the same or a somewhat negative bias with respect to the cathode filament, and it provides initial collimation to the electron beam produced from the filament. The increase in Wehnelt voltage decreases the electron beam's width, and the sharpness of a diffraction spot can be improved. The sharp focus over a broad range of energies can be obtained by optimizing the lens voltages as a function of electron energy. While the cathode is at a negative potential \((-V)\), the last apertures of the lens \((L_1 \text{ and } L_4)\), sample, and the first and last grids are grounded. The second and third grids are negatively biased with a magnitude slightly smaller than cathode potential to remove the inelastically scattered electrons from the sample. The fluorescent screen is biased with a positive high voltage \((\sim 5 \text{ kV})\) to reaccelerate the elastically scattered electron from the sample. Thus, the elastically backscattered electrons get reaccelerated towards the fluorescent screen and produce the diffraction pattern. This pattern can be directly observed or recorded with a charge-coupled device (CCD), a camera interfaced with a computer to acquire frames of diffraction patterns. A well-ordered crystalline surface produces a pattern with bright, sharp spots on the screen. The presence of defects and imperfections cause broadening and weakening of the spots. The polycrystalline samples and amorphous or disordered surfaces do not produce diffraction patterns in LEED. When the surfaces have superstructures formed on top, additional LEED spots are developed due to reconstructions of the surface layers or new structures formed after depositing a new material. To acquire a nice diffraction pattern sample should be well ordered and free from any surface contamination. So, the experiments are performed in the ultra-high
vacuum system, and the sample surface is prepared in-situ by Ar\(^+\) sputtering and annealing or any other suitable methods such as cleaving.

Figure 2.11: LEED structure of (a) hexagonal Ru(0001) single crystal, (b) oxygen covered Ru(0001) forming 2x2 overlayer of Oxygen on Ru(0001).

The diffraction pattern observed in LEED due to the interference of backscattered electrons from a well-ordered surface is a two-dimensional reciprocal representation of the surface unit cell periodicity in real space. The fluorescent screen is considered an Ewald sphere, and the backscattered electron beams produce diffraction spots where reciprocal lattice rods intersect the Ewald sphere. The number of spots observed in the fluorescent screen depends on the size of the Ewald-sphere. When electron beam energy is increased, de Broglie wavelength is increased. It results in to increase in the radius of the Ewald sphere, brings diffraction spots closer to each other,
and more spots can be seen on screen. If the superstructure has doubled the periodicity in real space compared to the bulk unit cell, then the diffraction pattern in the reciprocal space would exhibit half-order spots. The representative LEED images collected from UHV cleaned Ru(0001) single crystal at 68 eV of the electron energy beam are shown in Figure 2.11(a), where (1x1) hexagonal lattice corresponding to Ru(0001) is evident. The diffraction pattern corresponding to the (2x2) superstructure of the oxygen overlayer formed on Ru(0001) is presented in Figure 2.11(b). It is clear from the figure that the diffraction spots corresponding to the (2x2) superstructure are closer than the 1x1 hexagonal lattice of Ru(0001)(K-space).

Although the typical LEED experiment gives information about the symmetry and the surface unit cell's periodicity, it does not provide information about the structure and atomic positions. The structural properties can be obtained by analyzing the intensities of diffraction spots. It is experimentally simple to change the incident electron energy in LEED by changing the electron accelerating voltage V, and so to obtain a record of the intensity of a spot as a function of voltage V. This experimental obtained LEED I-V curve is then compared with simulated I-V curves to predict the structure of a well-ordered sample surface [27, 28].
2.3.4 Auger electron Spectroscopy

Auger electron spectroscopy (AES) is one of the most commonly used surface-sensitive techniques to identify elemental compositions at the material’s surface. The Auger effect was first discovered by Pierre Auger in 1925 while working with X-rays and using a Wilson cloud chamber [29], and the AES technique was developed in the late 1960s when the UHV system became available [30]. AES is a suitable technique for surface analysis. It is sensitive to almost all elements except hydrogen, and helium, being most sensitive to the low atomic number elements. The surface sensitivity of AES is due to the low survivability of low energy electrons backscattered from the crystal surface.

![Diagram of KLL transition in auger process](image)

Figure 2.12: Schematic diagram illustrating KLL transition in auger process.

The working principle of AES is graphically presented in Figure 2.12. When an energetic beam of electrons (1-5 KeV) strikes the atom of a material, core level electrons with binding energy less than the incident beam energy of electrons may be ejected from the inner atomic orbital. This
process creates a hole and electrons (incident and ejected) and leaves an ionized atom in an excited state. As an example, the ionization of an atom by removing a K-shell electron is shown in Figure 2.12(b). Thus, the electron vacancy created in K-shell is filled by electrons excitation from the outer energy level, as L₁ in Figure 2.12(c) The energy released in this process is simultaneously transferred to a second electron. A part of this energy is utilized to overcome the binding energy of a second electron, while the rest is transferred into the kinetic energy of an ejected auger electron. In the Auger process, the final state is doubly ionized with two core holes in L₁ and L₂,₃, as shown in Figure 2.12(c). In general, an auger transition is written in XYZ format, where X indicates the initial level of ionization, Y is the level where the second electron involved in transition comes from, and Z is the level from which the auger electron is emitted. The auger transition depicted in Figure 2.12 is called KL₁L₂,₃.

The kinetic energy of an Auger electron, \( E_{\text{Auger}} \), resulted from ABC transition is given by

\[
E_{\text{Auger}} = E_X - E_Y - E^*_Z - \Phi
\]  

(2.7)

where \( E_X \) and \( E_Y \) are binding energies in atomic levels, X and Y. \( E^*_Z \) is the binding energy of an electron in level Z in the presence of a hole, and \( \Phi \) is a work function of the sample. From equation (2.7), it is seen that the kinetic energy of an Auger electron is independent of the primary energy of an electron.

The schematic of the AES experimental setup is shown in Figure 2.13. The electron gun emits the primary beam of electrons with a typical energy of 1 to 5 KeV. The electron sources are based either on thermionic emission or field emission. Hemispherical or cylindrical mirror
analyzers are used to detect auger electrons. Usually, the intensity of an auger peak is small compared to the background signal due to secondary electrons; that is why AES is often recorded in derivative mode. The typical AES spectra collected from UHV cleaned Ru(0001) surface is presented in Figure 2.14, where MNN transition can be seen. The utilization of the AES technique to study the initial growth mode of ultra-thin Molybdenum nitride films will be discussed in chapter 4.

Figure 2.13: Schematic diagram showing AES instrumentation.
Figure 2.14: Auger electron spectra for a clean Ru(0001) surface after repetitive cycles of argon ion sputtering and annealing under UHV.

2.3.5 X-Ray Diffraction

X-ray diffraction (XRD) is a non-destructive analytical technique that can identify the phase and crystalline nature of the materials [31, 32]. The wavelength of X-rays is in the range of atomic size, making the XRD technique viable for probing the atomic structures in a wide range of materials. This technique is based on the constructive interference of monochromatic X-rays diffracted from a crystalline sample. A crystal is a periodic array of atoms or molecules and acts as a scattering center for X-rays. The X-rays scattered from lattice planes separated by interplanar
distance, \( d_{hkl} \), interfere constructively if the path difference between the scattered waves is equal to an integral multiple of the wavelength of X-ray [33, 34]. This condition is also known as Bragg's law, which can be expressed as;

\[
2d_{hkl}\sin\theta = n\lambda
\]  

(2.8)

Figure 2.15: Constructive interference of the X-rays (red lines) reflected from a crystal lattice plane with interplanar spacing \( d_{hkl} \).

Where \( \lambda \) is the wavelength of an incident X-ray, \( \theta \) is the angle of X-ray incidence on the crystal surface, \( d_{hkl} \) is the interplanar spacing where \( h,k,l \) are miller indices. Figure 2.15 depicts the basic principle of constructive interference of the reflected X-rays from the parallel plane of atoms formed by the material's crystal lattice. If \( \lambda \) is known and a scan obtains the intensity of the
diffracted beam over a range of $\theta$ (known), then the interplanar spacing between two miller planes can be determined as defined in equation 2.8.

The XRD studies reported in this thesis work were performed using a Panalytical X-pert3 MRD system with a copper $K_\alpha$ radiation source ($\lambda=1.54056$ Å). The XRD technique with specular ($\theta - 2\theta$) scans and non-specular phi-scans ($\phi$) is used in this work to identify the crystalline phase and purity of epitaxial single crystalline Ru(0001) films grown on c-axis sapphire along (0001) direction.

2.3.6 X-Ray Reflectivity

X-ray reflectivity (XRR) is an effective non-destructive technique to study the surfaces and buried interfaces in thin-film systems [35,36]. In this technique, a narrow beam of X-rays is incident upon a flat or smooth surface, and the intensity of the reflected beam at an angle equal to an incident angle, specular direction, is measured. The variation in the intensity of such a specular reflected beam of X-rays as a function of the common incidence and reflection angle can be analyzed to extract the information regarding sample density, sample thickness, and root mean square roughness of surfaces. In this work, the thickness and roughness of samples were characterized via XRR measurements with the same X-ray optical configurations used for the XRD measurements.

The XRR data were interpreted using the PANalytical X'Pert Reflectivity software. The bare ruthenium samples were modeled as a RuO$_2$/Ru/sapphire structure, whereas the samples with dielectric overlayers (SiO$_2$, Al$_2$O$_3$, MgO, Cr$_2$O$_3$) were modeled as dielectric/RuO$_2$/Ru/sapphire.
Figure 2.16: Representative XRR result from 4.8 nm thick MgO on Ru(0001) following the 500°C annealing process in Ar/H₂ 3% atmosphere. Blackline(a) represents the fitted curve, and the red line(b) is the measured intensity.
2.4 Thin-Film Resistivity Measurement

The van der Pauw technique is one of the most used experimental methods in determining the resistivities of uniform thin metallic films of arbitrary shapes. The error in the van der Pauw resistivity measurement is generally within 3% [37]. The configuration of this technique consists of four electrical terminals, as shown in Figure 2.17, where two of them are used to apply electric current and the rest two terminals to measure the resulting potential drop across the defined portion of the sample. The system used consisted of a coupled Keithley 2400 Source meter and 2182 nano voltmeter with a reversing polarity square wave current signal to determine the sample resistance independent of any thermally induced DC voltage that may be present.

![Diagram of van der Pauw method](image)

*Figure 2.17: Resistance measurement in the Van der Pauw method.*
The resistance measurement was performed in a sample contacted in a van der Pauw geometry, as shown in Figure 2.17. The resistances according to the above Figure 2.17 are calculated using ohmic law as,

\[ R_A = R_{1234} = \frac{V_{34}}{I_{12}} \quad (2.8) \]
\[ R_B = R_{1432} = \frac{V_{32}}{I_{14}} \quad (2.9) \]

Where R = Resistance, V = voltage, and I = current

In equation (8), \( R_{1234} \) represents the measured resistance of a thin-film, where the current is sourced from 1 to 2, and voltage was measured across 3 to 4. To calculate the average sheet resistance, \( R_s \), the van der Pauw method performs two measurements. First, it sources current along the horizontal edge of the film \((1 \rightarrow 4)\) and measures the voltage drop across the opposite edge \((3 \rightarrow 2)\). Then, it sources the current along the vertical edge \((1 \rightarrow 2)\) of the film and measures the voltage drop across the opposite edge \((3 \rightarrow 4)\). The average vertical and horizontal resistances are calculated as,

\[ R_{\text{horizontal}} = \frac{R_{1432} + R_{3214}}{2} \quad (2.10) \]
\[ R_{\text{vertical}} = \frac{R_{1234} + R_{3412}}{2} \quad (2.11) \]

Then, the sheet resistance, \( R_s \), is calculated by solving the following van der Pauw equation[38],

\[ \exp \left( -\pi \frac{R_{\text{horizontal}}}{R_s} \right) + \exp \left( -\pi \frac{R_{\text{vertical}}}{R_s} \right) = 1 \quad (2.12) \]
Finally, the average resistivity of a sample is determined as a product of sheet resistance, Rs, and the thickness of the film, h.

\[ \rho = R_s \times h \]  \hspace{1cm} (2.13)

In this work, we have also performed the in-situ measurement of resistivity on Ru(0001) films. Patterned Ru films with four touchpads at the corner of a square sample for four electrical connections, as depicted in Figure 2.18, were used as van der Pauw resistance measurements.

Figure 2.18: Diagram of the Van der Pauw geometry for the in-situ resistance measurements.
2.5 Experimental Apparatus

The experiments for the epitaxial growth and characterization of molybdenum nitride were conducted in a multichambered ultra-high vacuum system [Figure 2.19] at Thin film, Catalysis, and Surface Science laboratory, University of Central Florida. The base pressure of the UHV system was $2 \times 10^{-10}$ Torr.

Figure 2.19: Ultra-high Vacuum system used for the in-situ growth and characterization of thin-films.
The UHV system is equipped with low energy electron diffraction optics (OCI Vacuum Microengineering Inc., BDL600-LMX) for LEED measurements, an X-ray photoelectron spectroscopy system using dual anode Mg/Al Kα source (SPECS, XR-50), and a hemispherical energy analyzer (SPECS, Phoibos 150 MCD), four-pocket evaporator (SPECS, EBE-4) for thin-film growth via e-beam PVD, ion sputtering (SPECS, IQE-12/38) gun for sputtering, and mass spectrometer. The growth and characterization of ultra-thin molybdenum nitride films were conducted in this UHV system.

The single crystalline Ru(0001) on sapphire and dielectric coated Ru(0001) films, used for the study of electron scattering phenomena on Ru interfaces, were prepared in a different vacuum chamber in-housed in a cleanroom of the engineering building at UCF. The material characterization facility (MCF) at UCF was used for the XRD and XRR measurements.

2.6 References


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CHAPTER 3 : EPITAXIAL GROWTH OF ULTRATHIN δ-LIKE MON FILMS ON Ru(0001)

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3.1 Introduction

Despite being among the least studied classes of transition-metal-nitrides, molybdenum-nitrides are known to present attractive mechanical, electronic, and catalytic properties of interest to a wide gamut of scientific fields and practical applications. For example, (i) hexagonal δ-MoN exhibits mechanical elasticity and hardness values comparable to cubic BN and diamond [1-3], (ii) both hexagonal and cubic phases of molybdenum-nitride are known to be superconducting [4-7], with the ideal metastable cubic phase predicted to exhibit $T_c$ values as high as 30 K [8], and (iii) various combinations of $\text{Mo}_x\text{N}_y$ materials are known to provide highly active surfaces for hydrotreatment reactions [9-12], particularly hydrodenitrogenation (HDN), where molybdenum-nitrides have been shown to outperform commercial Ni-Mo, and Co-Mo derived catalysts [13-18]. In the latter application, results from a rigorous set of applied-catalysis studies conducted by the group of Levi Thompson have suggested a preference for δ-MoN vs. γ- or β-phases of Mo$_2$N when activating pyridine towards HDN [15-23].
Due to their many exciting properties, several groups have developed recipes to produce phase-specific molybdenum-nitrides under varying conditions, and a comprehensive review of recent advances in the growth and application of both supported and unsupported forms of these materials has been published by Jauberteau et al. in the journal Coatings [24]. To summarize the main conclusions of the review in the context of this paper, many groups have succeeded in creating molybdenum-nitride materials of various crystallographic phases and stoichiometries using a wide array of highly disparate materials synthesis approaches [4-7, 25-52], but, to-date, publications reporting the creation of large-scale, single-crystalline analogues with atomically planar surface terminations, akin to those typically employed in ultrahigh vacuum (UHV) surface-science investigations common to the field of catalysis, remain absent from the literature. Instead, previous works have focused on phase-isolation and have generally produced samples comprised of large ensembles of small grains, often present in heterogeneously distributed orientations, with rough surface terminations.

Notably, of the few groups who have attempted to leverage epitaxy to improve long-range order, Luo et al. have succeeded in producing near-perfect δ-MoN and γ-Mo₂N crystalline films using a solution-based, polymer-assisted deposition approach [7], and, as a result, have observed corresponding superconducting properties in rare agreement with those expected for the two phases of the material. Despite capturing near-perfect agreement with the bulk properties of the crystallographic phases, the surface terminations of these films remain quite rough (by model-catalysis standards), with rms roughness values ranging from 3-5 nm. Using the same Mo precursor, Xie et al. have published results from another solution-based chemical process, which they claim produces a novel, lamellar form of hexagonal MoN [53]. The reported structure of the
new phase consists of weakly interacting sheets of (fully saturated) δ-like MoN structures, which the group claims to have isolated via liquid exfoliation.

![Structural models of (a) Ru(0001) and (b), (c) top and side views of δ-MoN.](image)

Figure 3.1: Structural models of (a) Ru(0001) and (b), (c) top and side views of δ-MoN.

Leveraging the many advances made by the community in the development of phase-pure molybdenum-nitrides, our ambition with this paper is to take the first step towards the development of surface-science compatible, Mo$_x$N$_y$ analogues suitable for UHV model-catalysis studies (i.e., studies amenable to elucidations of the most fundamental physicochemical interactions governing reactions at interfaces). Given its reportedly enhanced activity towards HDN, we have chosen to
begin our work with the development of δ-MoN analogues. To do this, we have coupled nitrogen ion-assisted film growth techniques with well-established physical vapor deposition (PVD) approaches to ultrathin epitaxial film growth [20-23, 54-56]. Due to its favorable lattice agreement and intermediate nitrogen-affinity, we have opted to support our films on Ru(0001), for which a = 2.71 Å (vs. 2.86 Å for δ-MoN) [6, 56]. Models of both the Ru(0001) interface and the targeted δ-MoN crystal structure are provided in Figure 3.1. Other metals under consideration as possible supports for future investigations include Mo (112) and Pt (111), which provide comparable epitaxial agreement with δ-MoN, but higher and lower N-affinities, respectively. As both epitaxy and surface flatness is critical motivations to our work, we have chosen to operate in an exclusively low ion energy regime to leverage only the additional reactivity afforded by cationic nitrogen without introducing possible complications caused by high-energy impacts.

It is important to note that N-Ru(0001) interactions have been investigated by a number of groups and that those findings indicate upper-limit coverages of ~0.45 monolayers (1 ML=1.57 atom/cm²) via decomposition of ammonia or hydrazine [57, 58], and that ordered 2×2 and √3×√3 R30° superstructures have been observed to form at coverages of 0.25 and 0.33 ML, respectively [59, 60].

3.2 Experimental Section

Experiments were performed within an ultra-high vacuum chamber (base pressure of 3x10⁻¹⁰ Torr) equipped with a four-pocket, electron bombardment PVD source (Specs, EBE-4), a rear-view, low energy electron diffraction assembly (LEED, OCI Microengineering), an Al Kα X-ray source (Specs, XR-50), a differentially pumped ion gun (Specs, IQE-12/38), and a hemispherical
energy analyzer (Specs, Phoibos 150) allowing for X-ray photoelectron (XPS) and He+ ion scattering spectroscopy (ISS) measurements when used in tandem with either the X-ray source or ion gun, respectively. LEED images were collected using collimated beams of 60 eV electrons reflectively diffracted from a ~1 mm diameter area of the sample surface. XPS spectra were collected using a pass energy of 20 eV to filter electrons emerging along the surface-normal from a 5 mm diameter collection area using a 55° source-sample-analyzer geometry. He+ ISS spectra were also collected from a 5 mm diameter sampling area using a pass energy of 100 eV to filter 500 eV incident ions, leaving the sample along the surface normal after traversing through a fixed 135° scattering angle.

Based on good epitaxial overlap with our targeted nitride termination, an 8 mm-diameter x 1 mm-thick Ru single-crystal cut to within ± 0.1° of the (0001) crystallographic plane (Princeton Scientific, 99.999%) was mounted to a sapphire backing plate by way of tantalum resistive heating wires, which were spot-welded to the back of the crystal, and, in turn, held in place by tantalum spring clips. Temperature measurements were made using a K-type thermocouple, also spot-welded directly onto the back of the crystal. Heating was typically controlled by electron bombardment using a throriated tungsten filament positioned near the backside of the crystal, and cooling was provided by flowing liquid nitrogen through a cryostat in contact with the sample. Using this arrangement, sample temperatures are readily attained and controlled from 100 - 1500 K.

For the film growth studies, clean Ru(0001) surfaces were first established using several 2.0 keV Ar+ sputtering/1500 K UHV annealing cycles, with surface cleanliness verified by XPS
and LEED. Once sufficiently clean, as evidenced by the presence of only Ru(0001) features in both XPS and LEED, the Ru(0001) surface was exposed to a ~20 nA flux (~ 40 nA/cm² current density measured at the sample) of nitrogen cations within an 8×10⁻⁷ Torr back-pressure of N₂ at room temperature for about 25–30 min. Cations were created by 100 eV electron impact interactions, and the chosen exposure corresponds to the amount of time needed to achieve a self-saturated concentration of Ru-bound N under our conditions. Postmortem XPS characterization of such "prenitrided surfaces" exhibits an N 1s: Ru 3d integrated peak ratio of ~0.0076:1 (~0.40 ML, see below). Assuming fragmentation similar to that reported in the NIST Webbook (Eₗionization=70 eV) [61], we might expect an N₂⁺: N⁺ ratio of ~0.85:0.15, and on that basis, we estimate an effective dose of ~6.9×10¹⁴ to 8.3×10¹⁴ N/cm²/cycle (~0.44 to 0.53 ML), which is in good agreement with our XPS and ISS estimates for this coverage (provided below), and further indicates high sticking probability for the ionized nitrogen species on Ru below this threshold coverage. Using the same general approach, the total equivalent exposure provided throughout the cumulative, sequential process used to create the thickest molybdenum-nitride film studied in this work (tₓMo=950 s, described below) is estimated to be ~6×10¹⁵ N/ cm² (i.e., enough N to account for~4 fully wetted layers of δ-MoN should it form). After depositing the nitrogen precursor layer, molybdenum atoms were deposited via PVD onto the prenitrided surface. During PVD, Mo fluxes were indirectly controlled by maintaining fixed 10 nA ion flux values (measured at coaxially configured~50 mm² cylindrical collection plates located within the exit aperture of the evaporator), which typically required e⁻ beam currents of ~30 mA when biasing the Mo rod at 800 V (measured at the Mo rod). Finally, the surface was again exposed to the nitrogen ion flux for another 25 min, before flash annealing to 700 K within the ion-containing environment to simultaneously complete
nitridation and promote film crystallization. Each successive step in the sequential film growth described below has included both pre- and post-nitridation following the above procedures before and after each successive addition of Mo. The sample was biased to match the kinetic energies of incoming ions in each of the steps to avoid possible sputtering or implantation effects, which might be expected to create defects within the crystalline lattice of both the support and the resultant film (i.e., the impact energy of the nitrogen and any PVD-generated Mo ions was nominally 0 eV in both cases).

3.3 Results and Discussion

Figure 3.2 provides XPS data taken from a series of molybdenum-nitride films sequentially grown on Ru(0001) via iterative repetition of the nitrogen and molybdenum deposition and annealing steps described in the experimental section. From these plots, we note linear increases in the intensity of both the N 1s and Mo 3d peaks, coupled with a concomitant linear attenuation of the Ru 3d peak, all as a function of increasing total Mo exposure. This behavior suggests that our films remain relatively thin over this range of conditions, such that curvature in the trends due to self-attenuation of inelastically scattered wetted δ-MoN layers placed on an "infinitely thick" slab of Ru [57], convergence between simulated and observed Mo 3d: Ru 3d peak integral ratios are established when modeling the most covered sample (t_{Mo} = 950 s) as a 7.1 Å thick film (Mo 3d: Ru 3d = 0.38).

In our model, the production of photoelectrons of given energy at a given depth is presumed to depend only on the concentration and relative photoemission cross-section associated with a corresponding atom in a given layer, with the latter presumed to be in direct proportion to a given transition's atomic sensitivity factor (ASF) [58]. The number of electrons escaping to the interface of an
Figure 3.2: (a) Mo 3d, (b) Mo 3p/N 1s, and (c) Ru 3d XPS spectra are plotted for sequentially prepared molybdenum-nitride thin-films following 0 seconds (black), 200 seconds (brown), 450 seconds (orange), 700 seconds (dark grey), and 950 seconds (light grey) cumulative exposure to the Mo PVD flux. Quantitative analysis of the Mo 3d, N 1s, and Ru 3d XPS peaks shown in (a), (b), and (c) are plotted as a function of cumulative Mo deposition time for the same set of sequential film growths in frames (d), (e), and (f), respectively. Peak integrals in (d) and (e) are normalized to the value obtained from the most covered sample ($t_{Mo} = 950$ Secs) and to the value obtained from the clean Ru(0001) sample ($t_{Mo} = 0$ Sec) for f.
"infinitely thick" Ru slab is then obtained by finding the asymptotic limit achieved when plotting the cumulative number of photo emitted electrons surviving to reach the surface as a function of sampling depth after accounting for depth-dependent attenuation effects established using the EAL database. Further attenuation of both these and the film-generated electrons is then calculated using a separate set of EAL values for electrons of those types traveling through the overlayer material, and the surviving quantities of each electron are then compared to produce the modeled intensity ratios.

Interestingly, when benchmarking our model, we found good agreement between modeled and observed Si 2p: Ru 3d peak ratios for well-established monolayer and bilayer SiO$_2$/Ru(0001) thin-films (~20% discrepancy between model and measurement), despite significantly larger errors in the Ru 3d peak attenuation caused by these films in the same models (~200% discrepancy between model and measurement) [56]. To rationalize this result, we have hypothesized that errors in the EAL estimations are likely to be systematic and similar for different electrons with similar kinetic energies traveling through the same material. If true, then much of the systematic errors related to overlayer-derived signal attenuation likely factor out when comparing the EAL-corrected escape probabilities for electrons originating in both the support and the film, thereby providing a possible explanation for the improved accuracy of the comparative values.

Fits used to determine Mo 3d and N 1s peak positions and relative intensities for the most covered film presented in Figure 3.2 ($t_{\text{Mo}} = 950$ s) are provided in Figure 3.3. Mo 3d spectra are fitted by a single line shape using mixed Gaussian-Lorentzian function (19% GL) after subtraction of Shirley background. To deconvolute the Mo 3p (black) and N 1s (blue) contributions in Figure 3.3b), we have: (i) fit the Mo 3p peak using a single line shape (51 % GL) sufficient to fully account
for the higher binding energy (BE) spin-orbit-splitting component \( (J = \frac{1}{2}) \), and (ii) fit the residual intensity in the Mo 3p\(_{3/2}\) region to a single peak attributed to N 1s electrons. The fit positions for both peaks are located at BEs consistent with the formation of a nitride in an MoN chemical-state (BE = 228.75 and 397.65 ± 0.05 eV for Mo 3d\(_{5/2}\) and N 1s, respectively) [58, 59]. Consistent with this interpretation, the ASF-corrected stoichiometry of the film, estimated from a comparison of the Mo 3d and N 1s peak intensities (Mo 3d: N 1s ≈ 7.82:1), is Mo\(_1\)N\(_{0.95}\). Near-identical peak positions and relative intensities were obtained when fitting data from all films characterized in Figure 3.2. Therefore, we conclude that the formation of MoN superstructures occurs independently of coverage (within our range of conditions) when following our ion-assisted PVD recipe.

Figure 3.3: Fits used to establish core level XPS peak intensities and positions for (a) Mo 3d and (b) Mo 3p/N 1s collected from the film produced by 950 s total Mo exposure in Figure 3.2.
500 eV He\(^+\) ISS spectra associated with the samples investigated in Figure 3.2 are shown in Figure 3.4(a). In this case, however, the sample exposed to no Mo (black plot) is present in its prenitrided form, which consists of a self-saturated layer of nitrogen at the Ru(0001) interface. With increasing Mo exposure, we initially note the growth of the peak attributed to N (blue fits), reduction of the peak attributed to Ru (green fits), and the appearance and growth of a new peak attributed to Mo at He\(^+\) fractional scattering energies (E/E\(_0\)) overlapped with, but slightly lower than, those for Ru (red fits).

Thanks predominantly to the exceptionally low ion survival probability for He\(^+\) scattering events, peak intensities in Figure 3.4(a) are almost entirely attributable to exclusively top layer atoms, with atoms residing in lower layers being undetectable due to a combination of nearly 100% efficient beam shadowing and detection blocking effects caused by the presence of the top layer atoms above them [60]. Therefore, monitoring changes in peak intensities with increasing overlayer coverage can provide some insight into how the surface-projected, two-dimensional footprint is occupied by each of the various elements’ changes at the solid-vacuum interface during film growth. Accordingly, Figure 3.4(b) plots the N and Mo ISS peak intensities normalized to an average of the values obtained from the two most covered samples (t\(_{Mo} = 700\) and 950 s).
Figure 3.4: (A) ISS spectra associated with the films described in Figure 3.2 as a function of cumulative Mo exposure. (B) Quantitative analysis of the Mo (red) and N (blue) peak intensities shown in (A) as a function of cumulative Mo deposition time for each film. Values for the first two points of the N plot have been corrected to remove estimated contributions from Ru-bound nitrogen atoms. The uncorrected data are plotted as stars rather than circles.
Since N signal can potentially arise from atoms both in the film and at the Ru interface, we have used the signal from the prenitrided Ru sample to help account for the Ru-bound species, which contribute to a peak that is ~40% the size of that observed from the most covered MoN/Ru samples. When progressing to the least covered MoN sample ($t_{Mo} = 200$ s), we note increasing intensity for both peaks (Mo and N), but accurate quantification sufficient to account for contributions resulting exclusively from atoms present in the film is hampered by convoluting factors in each case since the emergence of both spectral features comes at the expense of unrelated features that happen to be present at, or very near, the same fractional energies. For N, the competing contributions come from N in the film, which is presumed to initially grow with increasing film coverage due to the increasing number of top-layer scattering sites, and N at the Ru interface, which is presumed to initially attenuate due to the blocking and shadowing effects caused by the film. Because of the close $E/E_0$ proximity of the Mo and Ru peaks, a similar effect is observed for the same reasons when comparing ISS intensities associated with Mo in the film and Ru beneath it. To help deconvolute this latter pair of contributions, we have used characteristics of the Ru peak collected from the prenitrided sample to fit the high $E/E_0$ peak in the $t_{Mo} = 200$ s plot in Figure 3.4(a). Using two components, we first fit the higher fractional energy portion of the feature to a peak constrained by the prenitrided Ru peak’s position, shape, and width (green). The residual fit needed to account for the remainder of the intensity in the feature is then attributed to Mo (red). At higher coverages, the Ru peak was no longer necessary to fit the feature when fixing the characteristics of the Mo peak and was, therefore, no longer included. By assuming that coverage-dependent attenuation of the Ru-bound N peak scales in exact proportion to the attenuation of the Ru peak, we have adjusted the raw intensity of the N peaks (denoted by stars) to
reflect our estimate of the intensity attributable to N from the film (denoted by circles), which was again only necessary when plotting the intensity for the $t_{Mo} = 200$ s point in Figure 3.4(b).

When further increasing the film coverage, the average normalized intensity of Mo and N peaks (taken together as an aggregate value to partially mitigate against random anomalies caused by low signal-to-noise and sputtering-induced intensity fluctuations) continues to increase in a near-linear fashion until $t_{Mo} \approx 490$ s. Beyond this coverage, the aggregate average value appears to saturate, which we take to denote the Mo exposure needed to create an MoN film that fully covers the Ru support since any MoN added onto a completely covered sample will simply prevent detection of an equivalent number of first-layer MoN atoms to result in no change to the detected Mo or N intensity. Interestingly, the XPS peak ratio simulated for 1 ML (≈2.8 Å) [6] of a fully wetted δ-MoN superstructure (Mo 3d: Ru 3d = 0.128:1) agrees quite well with the peak ratio interpolated for this coverage ($t_{Mo} = 490$ s) from peak integrals trends established by data associated with the plots in Figure 3.3 (Mo 3d: Ru 3d ≈ 0.123:1). We interpret this agreement, and the approximately linear dependence between Mo exposure and film-attributed ISS intensity at low coverages, as strong indications in favor of either Frank-van der Merwe or Stranski-Krastanov growth modes (i.e., the first layer appears to wet the surface before the addition of second layer structures).

To characterize changes in surface crystallinity, we have collected LEED images upon reflective diffraction of normally incident, 60 eV electrons from samples associated with various stages of the film growth (and decomposition) process (see Figure 3.5). Figure 3.5(a) represents the Ru(0001) surface during the later stages of cleaning. The clear pattern of hexagonal reflexes is
indicative of the Ru(0001) surface lattice, while the very faint satellites located near those reflexes are presumed to indicate the presence of undetectably small (by XPS) quantities of carbon remaining on the sample. Samples like this are further cleaned by sputtering and annealing until only the 1x1 Ru(0001) reflexes remain.

Figure 3.5: LEED images of (a) Ru(0001), (b) after depositing Mo onto the prenitrided surface at room temperature \( t_{\text{Mo}} = 950 \text{ s} \), (c) after annealing sample (b) to 700 K in a nitrogen cation-rich environment, and (d) after annealing sample (c) to 1100 K in UHV. Electron energy = 60 eV in all cases.
Figure 3.5(b) shows a LEED image taken from the $t_{Mo} = 700$ s sample described in Figures 3.2 and 3.3 after a 25-minute exposure to the cationic nitrogen flux, followed by subsequent exposure to Mo for 250 s, all at room temperature. As shown, the combined effects from exposure to both nitrogen and molybdenum result in a completely disordered superstructure, as evidenced by the completely diffuse LEED pattern. Similarly, diffuse patterns are obtained after equivalent exposures to Mo and ionic nitrogen fluxes independent of previous MoN coverage.

Figure 3.5(c) shows a LEED image captured from the same sample used in Figure 3.5(b), but after an additional 25-minute exposure to the ion beam at room temperature, followed by subsequent heating to 700 K in the continued presence of the cationic nitrogen flux (i.e., this image corresponds to the $t_{Mo} = 950$ s sample discussed in Figures 3.2, 3.3, and 3.4). Following this treatment, we note a clear reemergence of the hexagonal pattern observed from Ru(0001), albeit with slightly more diffuse reflexes than those noted from the sample characterized in Figure 3.5(a), which indicates a slight decrease in the overall long-range crystalline quality of the superstructure relative to the support. It is important to note that the 700 K annealing temperature used to grow the series of films described in this paper was chosen on a trial-and-error basis using the quality of LEED images as the primary feedback source. Since we have established with He$^+$ ISS that the Ru surface should be entirely covered by MoN under this condition, we take Figure 3.5(c) to imply the presence of a 1x1 MoN/Ru(0001) superstructure. From the LEED images of clean Ru(0001) [$a=2.71$ Å] and δ-MoN film, which are the representations of the reciprocal lattice, unit cell parameter of an overgrown film MoN can be obtained from direct comparison of the inverse of the distance between two bright diffraction spots. The average lateral lattice parameter of δ-MoN is observed to be contracted by ~5% relative to that observed in bulk δ-MoN ($a=2.86$ Å). LEED
images recorded from all other post-annealed films exhibit similar patterns, indicating that film crystallinity does not significantly vary with coverage within our range of conditions.

Summarizing the conclusions drawn from XPS, ISS, and LEED to this point, we find that our ion-assisted PVD recipe results in superstructures exhibiting: (i) a ~1:1 Mo:N stoichiometry, (ii) a nitride chemical-state consistent with MoN, (iii) a growth mode that wets the first layer before occupying subsequent layers, (iv) an apparent monolayer thickness close to ~2.8 Å, and (v) a hexagonal surface termination with a lateral lattice parameter well-matched to that from Ru(0001). By combining these insights, we conclude that the recipe described in this paper results in the growth of an atomically-planar (or at least very nearly planar), the single-crystalline sheet of δ-phase MoN (or at least a reasonable analogue thereof) on Ru(0001) up to a coverage of 1 monolayer (ML) and continues to grow with the same stoichiometry and in the same chemical-state at greater coverages.

To test both our conclusions and the logical foundations upon which they are derived, we can calculate the concentration of terminal N atoms presumed to be present in an atomically planar sheet of δ-MoN and compare that to the concentration of N predicted to be present on the "prenitrided" Ru surface by both XPS and ISS. Assuming 100% detection efficiency for atoms contained within the two-dimensional unit-cells at the sample surface, we can expect an ISS-visible concentration of ~0.158 N/Å² from a (5% contracted) δ-MoN-terminated sample at coverages exceeding one monolayer equivalent (i.e., \( t_{\text{Mo}} \geq 490 \)s) [6]. By comparing N ISS intensities recorded from the prenitrided Ru and the fully covered MoN/Ru samples, we can estimate that the prenitrided interface should contain ~0.063 N/Å² (provided that the saturated
MoN film is compatible with a δ-phase termination. Using the EAL-established effective XPS sampling concentration for uncovered Ru, we can apply simple ASF corrections to predict an N 1s: Ru 3d XPS peak ratio of 0.0075:1 for a prenitried sample containing the ISS-predicted concentration of Ru-bound N, which is in excellent agreement with our measured value for the prenitried Ru (~0.0076:1); thereby validating our original δ-MoN-consistent film growth presumption and the models that were used to imply its possible existence.

To investigate thermal stability, we have conducted a series of LEED and XPS measurements after heating the most covered sample (t_{Mo} = 950 s) to various temperatures in UHV. Figure 3.5(d) provides a LEED image captured after heating to 1100 K, while Figure 3.6 presents changes to Mo 3d, Mo 3p, and N 1s XPS spectra when increasing sample temperature from 700 - 1100 K. From XPS, we note a gradual loss of nitrogen from the surface, coupled with concomitantly decreasing Mo 3p and 3d peak BEs, until nearly all N is lost, and remaining Mo is left in a metallic state (BE = 228.0 ± 0.05 eV), after heating to 1100 K. LEED images taken from samples exposed to these conditions (i.e., Figure 3.5(d)), have been found to exhibit Moire patterns and primary reflexes in new positions indicative of lattice contraction relative to the 1x1 Ru(0001) reflexes. Interestingly, this pattern is extremely sensitive to conditions and varies significantly from sample-to-sample and even across the face of individual samples heated to the same nominal temperature. From this, we conclude only that various well-ordered Mo/Ru surface structures may form and coexist at this temperature following removal of N through a presumed recombinative desorption mechanism, something that has been noted by others at similar temperatures during δ-MoN TPD studies [17, 66].
To investigate air stability, a film was removed from and then reintroduced into the vacuum system to characterize any air-induced changes to the sample. After reintroducing the sample, LEED images (not shown) initially show no pattern, but Mo 3d, N 1s, and Mo 3p XPS spectra (also not shown) show no changes other than a slight attenuation to all peaks, which is presumed to reflect a layer of air-derived adsorbates present at the interface. After heating to 700 K in UHV, we note complete recovery of all MoN/Ru LEED and XPS properties and, therefore, conclude that the films produced by the methods outlined in this paper are air-stable and suitable for ex-situ experiments/characterization.
3.4 Conclusion

Epitaxial growth of anatomically planar, single-crystalline, δ-MoN-like film has been established on a Ru(0001) substrate using an ion-assisted, PVD approach. The film appears to develop via either a Frank-van der Merwe or Stranski-Krastanov growth mode and exhibits a lateral crystalline structure approximately equivalent to, and in registry with, the Ru(0001) termination of the substrate. Film decomposition occurs at temperatures above 700 K via a presumptive N$_2$ recombinative desorption mechanism, which eventually leaves only metallic Mo/Ru remnants at the interface after heating to 1100 K. As such, this film is expected to provide an ideal model for surface-science experiments dedicated to developing better understandings of interactions specific to δ-MoN interfaces at temperatures below 700 K. Future work intended for later publication includes characterization of local atomic-scale characteristics via scan-probe microscopy, ex-situ investigations of the vibrational structure via infrared reflection absorption and/or Raman spectroscopy, and inputs from density functional theory to collectively develop a more detailed description of the film structure resulting from the procedures described in this paper.

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4.1 Introduction

The combination of exciting chemical, electrical, and mechanical properties of molybdenum nitrides has led to its numerous technological applications. The different forms of crystalline molybdenum nitrides, including γ-Mo$_2$N (cubic), β-Mo$_2$N (tetragonal), and δ-MoN (hexagonal), have gained a great deal of research attention due to their superconducting properties [1-5]. The superconducting transition temperature as high as 29 K is predicted theoretically for B1-MoN with NaCl type structure [6], which is the highest among all refractory nitrides. Concerning the catalytic activities, various phases of molybdenum nitrides are known to be active for the hydrotreatment processes, particularly for hydrodenitrogenation (HDN) [7-10]. Besides, the higher activity of molybdenum nitrides for oxygen reduction reaction (ORR) [11, 12, 13] and the hydrogen evolution reaction (HER) [14, 15, 16] are also reported.

In our previous effort to study the epitaxial growth of MoN on Ru(0001) substrate, from the quantitative analysis of XPS and ISS data, we have concluded that the growth of MoN overlayer adapts either Frank–van der Merwe (FM) mode or Stranski–Krastanov (SK) mode. The extremely surface sensitive property of ISS makes this technique suitable for the study of the initial growth of ultra-thin films. However, the familiarity of ISS in the scientific community is inadequate compared to AES. To support our previous conclusion about the nature of the growth model of MoN film, drawn based on ISS and XPS study, we have conducted a series of AES studies on step-wise grown MoN films of varying thickness and compared with the previous result. The
detailed evolution of MoN film on the hexagonal Ru(0001) substrate, as studied through LEED, is also described in this chapter.

Although the transition metal nitrides are thermodynamically stable, given its large oxygen affinity, they are readily oxidized even at room temperature [17, 18]. The contamination of oxygen or oxidation can be a significant problem because it drastically modifies the properties of these materials. The surface oxidation can be intentional sometimes to improves the properties [19]. The incorporation of oxygen in MoN films is expected to alter the superconducting, catalytic, and mechanical properties of the films. A recent study by M. E. Kreider et al. [20] has reported that the maximum ORR activity is achieved by minimizing the content of bulk oxygen in a mixed hexagonal-cubic molybdenum nitride thin-film. Similarly, the study conducted by J. Barbosa [21] reports that the hardness, young's modulus, and residual stress of molybdenum nitride thin films decrease with an increase of oxygen content within films.

Most of the previous research efforts on investigating the oxygen interaction with transition metal nitrides have been carried out in determining the kinetics of air oxidation of nitrides at above room temperature [22-27], and significantly less attention has been given to the room temperature oxidation of transition metal nitrides. P. Prieto et al. [28] have conducted a spectroscopic study to characterize oxygen interaction with ZrN at room temperature, which reports the formation of an oxynitride and oxide species on the surface of ZrN. However, no literature till this date is available for the room temperature oxidation of molybdenum nitride in ambient air condition, which motivates this work.
The study of oxidation of molybdenum nitrides is essential since their electrical, catalytic, and mechanical properties can drastically be changed by the oxidation of the surface layer of these materials. In this study, X-ray photoemission spectroscopy is used to investigate the chemical state change of Molybdenum (Mo) when hexagonal molybdenum nitride \((\delta\text{-}MoN)\) is exposed to ambient conditions. The quantitative analysis of the XPS data collected from the MoN film after exposure to air for varying amounts of time allows us to deduce the information about the various species formed due to the interaction of oxygen with a nitride film, and also the rate of oxygen incorporation within a film.

4.2 Experimental Methods

The experiments were conducted within a multichambered ultra-high vacuum chamber with a base pressure of \(2\times10^{-10}\) Torr. The UHV system includes the facilities for X-ray photoemission spectroscopy (XPS), Ion-scattering spectroscopy (ISS), and low energy electron diffraction (LEED) measurements. The hardware of LEED is also compatible with making auger electron spectroscopy (AES) measurements as well. The system is also equipped with a four-pocket, electron bombardment PVD source (Specs, EBE-4), which we have used for the epitaxial growth of ultra-thin molybdenum nitride film. All the experimental work presented in this chapter was conducted on the same 7 mm diameter Ru(0001) single crystal, spot welded to a pair of thin Ta wires and mounted in a sample plate in a way that is compatible with e-beam heating by the use of tungsten filament positioned near to the backside of crystal. E-beam heating with a cooling system, flowing of liquid nitrogen through a cryostat connected to a sample holder, was used.
during the rigorous annealing of Ru(0001) substrate to a higher temperature (around 1500K) before deposition of the film, and resistive heating was used for low-temperature annealing post-deposition of the film for crystallization. The temperature measurement of the samples was recorded by using a K-type thermocouple spot welded directly on the back of the crystal.

Near stochiometric hexagonal molybdenum nitride (δ-MoN) thin-film on Ru(0001) is prepared by using an N+ ion-assisted physical vapor deposition (PVD) technique. The detailed procedure of film-growth is explained in chapter 3 and also in the literature [29]. The stepwise deposited films were characterized by AES, LEED, and XPS at every step of the film growth procedure. For the XPS characterization of samples, we use a hemispherical energy analyzer (SPECS, PHOIBOS 100) to collect the photoelectrons emitted from within the upper ~10nm of the sample surface while irradiating it with Al Kα x-rays (1486.6 eV, XR-50), directed to the surface at 54.7° angles of incidence. The pass energy of an analyzer was set at 100 eV and 20 eV for the survey and high-resolution scans, respectively. Samples were electrically grounded during XPS acquisition to avoid the possible surface charging effects. The thickness of the MoN overlayer was estimated from the quantitative analysis of the attenuation of the core-level XPS peak of Ru substrate. LEED images were collected using collimated beams of 60 eV electrons reflectively diffracted from a ~1 mm diameter area of the sample surface. AES spectra were collected using a 3KeV electron beam backscattered from the sample surface [OCI Microengineering AES/LEED system].

The oxygen atom interaction with the molybdenum nitride thin film at room temperature is studied using XPS from ambient air-exposed ~3ML thick molybdenum nitride thin film. The film
was routinely exposed to lab air for a varying amount of time and then transferred back into the UHV chamber via a fast entry load-lock. The effect of ambient air on such air-exposed films' surface chemistry is studied by XPS, without further sample processing.

Density Functional Theory (DFT) based first-principles calculations are used to calculate the surface energies of Ru substrate, MoN overlayer, and MoN-Ru interface. DFT calculations are carried out using PAW (Projector Augmented Wave Method) implemented in VASP (Vienna ab initio Simulation Package) [30,31] with the inclusion of van der Waals effects (vdW) using optB88 exchange-correlation functional [32]. The calculation for determination of lattice constant for bulk Ru and hexagonal MoN is carried out using 18x18x18 Monkhorst k-point mesh [33] with an energy cut-off of 800 eV. The calculations were optimized until forces on ions are less than 0.01 eV/Å. Calculated lattice constants of Ru (a=2.733 Å and c=4.303 Å) and MoN were comparable to experimental values [34, 35].

Surface energy (E_{sur}) was calculated by the relation:

$$E_{sur} = \frac{[E_{slab} - n E_{bulk}]}{2A}$$

(4.1)

Here, $E_{slab}$ is the energy of the slab in a vacuum, $E_{bulk}$ is the energy of the corresponding bulk system, n is the total number of formula units of bulk material used to make the slab, and A is the area of the slab. The factor of 2 is employed to account for both surfaces of the slab.

Adsorption Energies (ΔE) per unit area for the interaction of film on a substrate are calculated by the relation:

$$\Delta E = \frac{[E_{sub} + E_{ads.} - E_{ads.-sub}]}{A}$$

(4.2)

While $E_{sub}$ is the adsorption energy of the substrate, i.e., Ru(0001), $E_{ads}$ is the energy of the standalone adsorbate, i.e., a single layer of MoN, and $E_{ads.-sub}$ is the energy of the whole system.
4.3 Results and Discussion

The molybdenum nitride thin films are prepared in a multi-step process via PVD technique, the recipe of which is explained with greater detail in ref. [29]. In our previous study, the amount of Mo deposited in each step of a multi-step film growth process was relatively higher to monitor the evolution of LEED patterns of MoN film on Ru(0001) substrate. Therefore, in this work, we have minimized the amount of Mo deposition in each step and utilized LEED to report any structural change during the evolution of MoN film on Ru(0001).

4.3.1 LEED and AES characterization

Figure 4.1 represents the series of LEED images recorded from a clean Ru(0001) substrate, as well as 0.75 ML, 1.3 ML, 1.9 ML, and 3 ML MoN thin-film, grown on Ru(0001) substrate. The hexagonal LEED pattern typical for the (0001) orientation is obtained in the case of a clean ruthenium substrate, the diffraction point marked by a red circle in Figure 4.1. While no diffraction pattern was observed immediately after the deposition of molybdenum vapor at room temperature, the subsequent anneal of a film at 700 K leads to a new hexagonal diffraction pattern corresponding to the crystalline molybdenum nitride formed on Ru(0001) substrate, marked by blue circles in Figure 4.1. It is evident that the diffraction spots corresponding to Ru and MoN are not overlapped to each other but displaced by a fixed distance, independent of the thickness of the MoN overlayer.
Figure 4.1: Evolution of LEED pattern during the growth of MoN on Ru(0001) substrate. LEED images of (a) Clean Ru(0001), (b) 0.75 ML MoN on Ru(0001), (c) 1.3 ML MoN on Ru(0001), (d) 1.9 ML MoN on Ru(0001), and (e) 3 ML MoN on Ru(0001) collected with 60 eV electron beam energy. The bright spots circled by red dots in (a), (b), and (c) corresponds to the diffraction from Ru(0001), and blue circles in (b), (c), (d), and (e) highlights the diffraction from crystalline MoN.
The ratio of the distance between the central spot (00) and any red marked spot, i.e., diffraction from Ru(0001) and the distance between the central (00) spot and any marked blue spots, i.e., diffraction from MoN is about 0.95, which indicates that the MoN lattice in real space is slightly relaxed compared to the Ru(0001) substrate (a$_{\text{Ru}}$ = 2.71 Å). From the qualitative analysis of diffraction spots corresponding to both MoN and Ru(0001), the lattice constant of our MoN film is estimated to be ~ 2.85 Å, and the misfit between the film and substrate lattices is ~5%. The estimated lattice parameter of our film (2.85 Å) compares well to the previously reported numbers, 2.868 Å in ref. [36], and 2.86 Å in ref. [37] for δ-MoN films.

At the lower coverages of MoN on Ru(0001), both the diffraction patterns of ruthenium and MoN are visible, both of which are hexagonal and are very close to each other, as shown in Figure 4.1 (b) and (c). It is also evident from the figure that with an increase in the thickness of the MoN overlayer, the intensity of diffraction spots corresponding to Ru is diminishing, whereas the spots associated with MoN is getting sharper. For thicker MoN films, the survivability of low energy electrons, backscattered from Ru(0001) interface and after passing through the molybdenum nitride overlayer, is significantly low. Hence, only the diffraction spots representing hexagonal MoN are visible in Figure 4.1(d) and (e). So, the LEED study shows that the MoN overlayer adapts the crystallographic orientation of the substrate with a ~ 5% lattice mismatch.

The low-energy helium ion scattering spectroscopy (ISS) study of stepwise grown molybdenum nitride films on Ru(0001) [38], detailed explanation presented in chapter 3, predicted the growth of MoN to be either in layer-by-layer mode or layer-plus-island mode. It means the hexagonal molybdenum nitride thin films, prepared by the recipe used in this work, thoroughly
wet the Ru(0001) surface before the addition of overlayer structures. There is no doubt that ISS is a powerful surface-sensitive technique suitable for studying ultrathin films within a monolayer range. Nevertheless, it is not widely popular in the scientific research community. So, to support the results from our previous ISS study and provide more insights into the initial growth mode of the MoN film, we performed a series of experiments, where molybdenum nitride thin films of varying thickness were prepared in a stepwise growth manner, and the auger electron spectroscopy (AES) technique was employed to characterize the films at every preparation step. The MoN thin film was prepared on pre-nitrogen-covered Ru substrate by the deposition of Mo vapor and subsequent annealing to 700 K. The flux of Mo vapor during each deposition step was maintained constant. The XPS measurements were also made together with AES, which was analyzed quantitatively to estimate the thickness of films.

Figure 4.2(a) (red curve) shows an auger electron spectrum collected from a clean Ru(0001) substrate, prepared by repetitive cycles of Ar\(^+\) sputtering and annealing at a higher temperature, ~1400 K. The spectrum displays the characteristic auger peaks of Ru at 150 eV, 184 eV, 231 eV, and 273 eV, corresponding to Ru MNN auger transitions [38]. Auger peaks corresponding to carbon and oxygen are absent, indicating the cleanliness of the Ru(0001) substrate, which was also satisfactorily characterized by XPS and LEED. The auger electron spectrum collected from ~1.8 ML MoN on Ru(0001) is shown in Figure 4.2(a) (blue), which shows diminished Ru\(_{\text{MNN}}\) transition peaks and the appearance of new peaks at 162 eV, 187 eV, and 222 eV corresponding to the Mo\(_{\text{MNN}}\) auger transition.
Figure 4.2: (a) Auger electron spectroscopy recorded from a clean Ru(0001) substrate (red), and ~1.5ML MoN grown on Ru(0001) (blue), and (b) Auger electron intensity ratio of Mo to Ru as a function of Mo evaporation time on a pre-nitrogen covered Ru(0001) substrate.
AES was also utilized to calibrate the deposition rate and the thickness of MoN on Ru(0001). The Mo/Ru AES ratio as a function of Mo evaporation time on nitrogen pre-covered Ru(0001) is presented in Figure 4.2(b). The linear increase in the AES Mo/Ru ratio with the gradual increase in Mo evaporation time is broken around 830 secs of Mo. This breakpoint in the intensity plot corresponds to the amount of Mo needed for the completion of the first monolayer of molybdenum nitride (MoN) on Ru(0001). The evaporation rate of molybdenum nitride in our experimental setup is then estimated to be 0.07 ML/min, where the flux of Mo vapor leaving the source, kept at ~20 cm apart from the substrate, was maintained at 10 nA. The films at every step were also characterized by XPS. The extrapolation of the data collected from XPS suggests the Mo/Ru intensity ratio at ~830 secs of Mo deposition time is about ~0.17, which lies in the range (with ~20 % error) for a Ru substrate thoroughly wetted by a single layer of molybdenum nitride as predicted from the EAL based slab model described in chapter 3. From the AES intensity plot (Figure 4.2(b)), we observed that a fully wetted layer of MoN film forms on Ru(0001) substrate before the addition of overlayers materials, which suggests the growth of MoN to be either Frank–van der Merwe (FM: layer-by-layer) mode or Stranski–Krastanov (SK: layer-plus-island) mode. This result is consistent with the ISS derived conclusion in our previous study [29].

From DFT calculations, the surface energies of Ru substrate, MoN overlayer, and MoN-Ru interface are calculated. Five layers of Ru(0001) and two layers of MoN(0001) terminated by Mo on both sides are considered for the calculations. Both surfaces are modeled by an orthorhombic supercell. The energy cut-off for surface optimization used is 400 eV with the Monkhorst-Pack grid of 2x2x1. From DFT calculations, the surface energies of Ru and MoN are estimated to be 0.87 eV/Å² and 0.34 eV/Å², respectively. For the calculation of the interaction
between MoN and Ru, adsorption energies per unit area are considered. A monolayer of MoN is adsorbed on five layers of Ru(0001) slab. The different possible structures of MoN overlayer on Ru surface are explored, and the adsorption energies of these structures are found to be in the range of (0.2-0.3) eV/Å². The surface energy of the Ru substrate (0.87 eV/Å²) is greater than the sum of surface energies of the MoN overlayer and interface (<0.64 eV/Å²), suggesting that the MoN film growth mode is either FM or SK, which satisfy with the results deducted from ISS and AES study of MoN films.

4.3.2 Surface oxidation of Molybdenum nitride at room temperature

The interaction of oxygen with hexagonal δ-MoN at room temperature is studied by subjecting molybdenum nitride thin films in ambient air for varying amounts of time. For this experiment, ~3 ML (8.85Å) thick δ-MoN on Ru(0001) is prepared under UHV condition. The freshly prepared film is exposed to ambient lab air and inserted inside the UHV system again after a specific exposure time. The film is then characterized by x-ray photoemission spectroscopy technique without any cleaning procedure to study the change in the chemical state of molybdenum because of oxygen incorporation in the film.
Figure 4.3: Mo\(3p\), N\(1s\) (a), and Mo\(3d\) (b) XPS spectra of clean $\delta$-MoN and $\delta$-MoN after different ambient air exposure (in terms of time). The XPS peaks of Mo\(3p\) and N\(1s\) are overlapped, as shown in (a). BE positions of these peaks are estimated by the deconvolution of the entire Mo\(3p\)-N\(1s\) region.

The XPS spectra for Mo\(3p\), N\(1s\), and Mo\(3d\) core levels for air-exposed MoN samples for a different amount of time (as labeled in the Figure) are presented in Figure 4.3. Spectra corresponding to freshly prepared MoN film (zero air exposure time) under the UHV condition is
also included for the comparison. The overall effect of the increasing air exposure on the film can be seen in Figure 4.3. At exposure times less than 20 mins (not shown here), the shape of the XPS spectra remains almost unchanged except for a minimal change in the overall intensity of the entire BE region compared to that of the freshly prepared MoN surface (zero air exposure). However, a noticeable change in the XPS spectra is observed after as small as 2 hours of air exposure. The formation of a new feature can be seen in the higher binding energy side of Mo3d and Mo3p BE spectra. To determine the formation of new species during air exposure and its intensity, the Mo 3d spectra collected from air-exposed samples were analyzed in terms of two different components; the line shape analysis of those peaks is summarized in Figure 4.4.

Figure 4.4 shows that there is more than one phase in all cases except for clean MoN film ($t_{air} = 0$). The mixed Gaussian-Lorentzian function [12] is used for fitting the Mo 3d XPS peaks. To deconvolute the contributions of different components of the Mo 3d peak as a function of air exposure time, we have first fit the Mo 3d peak of the clean MoN film using a single line shape (12% Gaussian) while constraining the spin-orbit splitting to be 3.13 eV [39] between the Mo 3d_5/2 and Mo 3d_3/2 peak positions. Once we established the empirical line shape for the nitride phase of molybdenum (MoN) from our freshly prepared MoN sample under UHV, we constrained the position, width, and line shape of a nitride peak, and the second peak associated with MoO_3 was added to each spectrum, for air-exposed samples, as needed for the proper fitting of experimental data.
Figure 4.4: Mo 3d XPS spectra collected from the MoN sample as a function of ambient air exposure time. The deconvolution of the entire Mo3d BE region shows two species of molybdenum associated with MoN and MoO$_3$. An increase in the intensity of oxide peak in higher binding energy region at BE= 232.6 eV is observed with more air exposure time.
The XPS intensity of binding energy peak at 229.1 eV, associated with the molybdenum nitride (MoN) [39], decreases upon the air exposure. On the contrary, the higher binding energy peak at 232.6 eV, consistent with MoO$_3$, grows with the air exposure time. The quantitative analysis of oxide and nitride component of molybdenum in air-exposed films shows that the intensity changes in a logarithmic trend for both cases.

From the observed trend of decrease in nitride component and increased oxidized peak intensity of molybdenum, we can expect that the exposure of molybdenum nitride in ambient air leads to the replacement of nitrogen atoms on film by oxygen and eventually develops the oxide layer of Molybdenum on MoN. The BE position of an oxidized molybdenum component at 232.6 eV is consistent with MoO$_3$ [40], which implies that three oxygen atoms replace a single nitrogen atom present in the MoN layer when the film is exposed to air. The growth in the XPS intensity of the MoO$_3$ component and attenuation in the MoN component is also evident from Figure 4.4.

The quantitative analysis of the change in XPS intensity of MoN and MoO$_3$ components resulting from the exposure of the film to ambient conditions for varying amounts of time can be used to estimate the concentration of oxygen atoms incorporated into the films.

**Calculation of oxygen concentration in air-exposed MoN film from the change in peak intensity of nitride and oxide component of molybdenum:**

The unit cell parameters of δ-MoN are a = 2.86 Å, c=2.81 Å.

Number of Mo atoms in 2.81 Å thick film = 1.373E$^{+15}$ per cm$^2$

No. of Mo atoms = 4.886E$^{+14}$ per cm$^2$ per Å thickness
The thickness of a film used in this experiment is ~8.85 Å, estimated from the quantitative analysis of XPS data.

So, no. of Mo atoms in our MoN film = \(4.324 \times 10^{15}\) per cm\(^2\) (for 8.85 Å thick film)

Now, from the attenuation of an XPS intensity of the MoN component in the film, we can estimate the number of converted Mo sites from MoN to MoO\(_3\). For example, 2 hours of air exposure resulted in the XPS intensity of the MoN component attenuated from 1 to 0.939. Now, the number of Mo sites converted from MoN to MoO\(_3\) is;

\[
= (1 - 0.939) \times 4.324 \times 10^{15}
\]

\[
= 2.621 \times 10^{14}\text{ per cm}^2
\]

As we know, the single N atom in MoN film is replaced by three oxygen atoms during oxidation, and hence the number of oxygen atoms incorporated in the film from 2hrs (7200 secs) of air exposure should be equal to three times the number of MoN lost, which is estimated to be \(7.863 \times 10^{14}\) per cm\(^2\).

Similarly, the number of oxygen atoms incorporated in a film can also be estimated from the growth in the intensity of the oxide component of molybdenum. For example, the intensity of the oxide component of molybdenum in a film exposed to lab ambient air for 20 hours is 0.075, 1 being the intensity for a freshly prepared MoN film under UHV condition (no air exposure). Now, the number of oxidized Mo sites are

\[
= 0.075 \times 4.324 \times 10^{15}\text{ per cm}^2
\]
Therefore, the number of oxygens incorporated in the film during 20 hours of air exposure = \(3 \times 3.243 \times 10^{14} = 9.729 \times 10^{14}\) per cm\(^2\).

Figure 4.5: Concentration of oxygen atoms incorporated in MoN films calculated from attenuation of MoN peak intensity (blue) and growth in molybdenum oxide peak as a function of air exposure time.
Adopting the approach explained above, the number of oxygen atoms incorporated in a film resulting from the exposure of an MoN film to lab air at room temperature for a varying amount of time is calculated from both the MoO$_3$ peak growth and MoN peak attenuation. The growth in oxygen concentration within the film is plotted against the ambient air exposure time and is presented in Figure 4.5. Both sets of data points (red and blue) follow the logarithmic trend of an increase in the oxygen content in the film; the equation is shown in Figure 4.5. The number of oxygen atoms present in a single uniform layer of MoO$_3$ is expected to be 4.1E+15 per cm$^2$. From the extrapolation of data points presented in Figure 4.4, it is estimated that it will take about 30 days to convert a single layer of MoN to MoO$_3$. This result shows that the oxidation of molybdenum nitride in the air at room temperature is relatively slow compared to the oxidation of titanium oxide [39].

The rate of change in the concentration of incorporated oxygen in the film resulting from air exposure at room temperature, as estimated from the graph presented in Figure 4.5, is given by,

$$\frac{\Delta[O]}{\Delta[t]} = [(6.0 \pm 0.2) \times 10^{14}] \times [(\Delta t)]^{-1} \text{atoms/Sec} \quad (4.3)$$

The results from this study give a tentative idea about the surface chemistry of molybdenum upon air exposure at room temperature. However, the approach we have used to quantify the oxidation of molybdenum nitride in the ambient condition is simple and straightforward and is based on the experiments performed on a single thickness of the MoN sample. Future work in this area includes studying the oxidation process in MoN films of varying
thickness and using better slab models to quantify the various components of Mo present within the film.

4.4 Conclusion

The epitaxial growth of hexagonal molybdenum nitride on (0001) terminated Ru substrate is studied via XPS, AES, and LEED. The AES study of the stepwise grown films indicates the completion of a thoroughly wetted single layer of MoN on Ru(0001) before starting to form the overlayer structures indicating the nature of MoN film growth to be either Frank-van der Merwe or Stranski-Krastanov, which supports our previous claim about the film growth based on XPS/ISS results [29]. The room temperature oxidation molybdenum nitride thin film in ambient air condition is studied by X-ray photoemission spectroscopy. The exposure of MoN film to ambient air for as low as 2 hours leads to the formation of the oxidized molybdenum layer (MoO$_3$) due to the N atom's substitution by three oxygen atoms. The oxidation kinetics of MoN in the air at room temperature air is logarithmic, and the quantitative analysis of the XPS peak intensities of various components of Mo (MoN and MoO$_3$), collected from air-exposed samples, predict that the single layer of MoN converts ultimately into MoO$_3$ layer in about 30.6 days.

4.5 References


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CHAPTER 5: ELECTRON SCATTERING PHENOMENA ON Ru(0001)

5.1 Introduction

The electrical resistivity of conductors increases drastically as their physical dimensions approach or become smaller than the bulk electron mean free path (EMFP), also known as the resistivity size effect [1,2,3]. Increases in resistivity at smaller dimensions are mainly attributed to the scattering of electrons at metal surfaces [4, 5, 6] and grain boundaries [7, 8], and it exacerbates upon increased surface roughness [9] and defects [10]. This well-known resistivity size effect has become one of the major limiting factors in the performance of current (Cu), and future interconnects on account of the associated power consumption [9, 10] as the trend of downscaling of integrated circuits continues. Therefore, it has gained enormous interest from both the scientific community and the microelectronics industry. As a result, research efforts in a significant amount have been focusing on improving the Cu line conductivity and seeking a potential replacement material for current Cu interconnects [11, 12, 13].

The electron scattering phenomenon on metal surfaces is explained by a Fuchs and Sondheimer model [15, 16] of surface scattering, which quantifies the impact of electron-surface interactions using a specular scattering coefficient (p), whose value ranges from 0 to 1. Specular scattering of electrons (p=1) corresponds to electron reflection from the metal surface with the conservation of parallel components of momentum [17], and hence thereby, no effect on resistivity increases. Conversely, zero specularity (p=0) represents the case of complete diffuse scattering, resulting in the maximum increase in resistivity. Similarly, the Mayadas–Shatzkes (MS) model is commonly employed to quantify the contribution of electron scattering from grain boundaries on
resistivity increase. MS Model treats each grain boundary as an internal surface [18]. When an electron collides with a grain boundary, the probability of transmission or reflection is quantified by a reflection coefficient, \( R < 0 \leq 1 \). Both models, FS and MS, in approximated form, predict that resistivity increase scales with the product of bulk resistivity (\( \rho_o \)) and the mean free path (\( \lambda \)), \( \rho_o \lambda \). Therefore, the metals with the lower value of \( \rho_o \lambda \) products are expected to exhibit the smaller resistivity size effect [6] and should, therefore, be most conducive to the limit of thin films and narrow lines. Based on theoretically calculated electron mean free path, Ru is one of the transition metals with a lower \( \rho_o \lambda \) product value than copper [6]. Despite its larger bulk resistivity, Ru yields more conductive lines than copper at smaller dimensions, and hence it has emerged as a promising candidate to replace Cu as a future interconnect [6, 12-14].

Furthermore, from previous studies performed on polycrystalline Cu films by Sun et al. [19, 20, 21] and Barmark et al. [22], it is found that grain boundary scattering is the more dominant mechanism in comparison to the surface scattering of electrons. Therefore, it points out the importance of implementing epitaxial single-crystal metal interconnects instead of polycrystalline metal to eliminate the grain boundary effect on resistivity increase.

Several previous studies performed to quantify the impact of grain boundaries [7,8], surface roughness [9], and scattering of electrons [10-13] from the metal surface on resistivity increase point out the significant interest in obtaining the most specular surface to decrease the resistivity size effect. Surfaces with partially specular electron scattering have been reported for Cu [23], Ag [24], Au [25, 26], and Co [27]. Most of these prior studies mainly explored the variations in surface chemistry and structure at an exposed metal/vacuum or metal/vapor
interfaces. In integrated microelectronic circuits, metallic interconnects are necessarily in contact with dielectrics. From an applied point of view, it is crucial to understand the metal/dielectric interface in detail and its effect on electron scattering phenomena.

In this work, we have studied the variations in electron scattering from the surface of single-crystal metal films with the variation of structure and chemistry of the surface. We observe significantly higher specular metal interfaces that are air-stable, even when overcoated with dielectric materials. For the metal/dielectric interface study, we focus on 20 nm thick Ru single crystal on sapphire as our conductor and 5 nm thick amorphous Cr$_2$O$_3$, Al$_2$O$_3$, MgO, and SiO$_2$ as our dielectrics. The change in resistivity and electron surface scattering from a dielectric/metal interface as a function of annealing temperature and annealing environments (oxidizing and reducing) are studied. We have used X-ray photoelectron spectroscopy (XPS) to determine the chemical bonding at the embedded Ru interface, while X-ray reflectivity (XRR) is used to determine the Ru thickness and interfacial roughness of the upper metal surface.

5.2 Experimental Details

The Ru thin films were deposited on (0001) Al$_2$O$_3$ sapphire substrates, obtained from MTI Corporation, in a high vacuum DC magnetic sputtering system (ATC2200 UHV, AJA International Inc.) with a base pressure of ~10$^{-8}$ Torr. One side polished two-inch diameter sapphire substrate was cleaned by heating in a tube furnace in the air at 1000 ºC for 30 minutes to remove adsorbed contaminants and loaded immediately to the deposition chamber to minimize the possibility of recontamination. The ruthenium deposition rate of 1.3 nm/Sec was obtained using constant magnetron power of 200W. The ruthenium substrates were maintained at 700 ºC during
the deposition process. In this study, four series of samples were prepared, as described in Table 5.1.

Table 5.1: Listing of sample series studied

<table>
<thead>
<tr>
<th>Sample series</th>
<th>Ru layer Thickness(nm)</th>
<th>Dielectric Overlayer</th>
<th>Deposition Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>~18</td>
<td>None</td>
<td>700 °C</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>SiO₂ Sputtering</td>
<td>700 °C</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>SiO₂ Sputtering</td>
<td>700 °C</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>Cr₂O₃, Al₂O₃, MgO, SiO₂ Sputtering</td>
<td>700 °C</td>
</tr>
</tbody>
</table>

Sample series 1, bare Ruthenium without dielectric encapsulation, was prepared in the thickness range of ~18 nm via magnetron sputtering of 99.95% pure ruthenium target. Ruthenium thin films deposited on sapphire were cut into small square pieces of 7 mm by 7 mm by a CO₂ laser incident upon the backside of the wafer for further processing. After laser cutting, all small coupons of samples were step annealed to 950 °C in Ar/H₂ 3%. For sample series 2 and 3, 20nm thick Ru film was overcoated with a single 5 nm thickness of sputter-deposited SiO₂ via radio frequency (RF) sputtering in 4 mTorr of argon at room temperature using 99.95 % pure 2-inch diameter SiO₂ target. Similarly, sample series four was prepared by the deposition of dielectric oxides (Cr₂O₃, Al₂O₃, MgO, SiO₂) on 20 nm Ru film via RF sputtering technique. The thickness of the dielectric overlayer in sample series 2, 3, and 4 is 5 nm, which is chosen to be sufficiently thin to allow subsequent XPS characterization of the buried Ru/dielectric interfaces.
Uncovered Ru and dielectric overcoated \([\text{dielectrics} = \text{SiO}_2, \text{Al}_2\text{O}_3, \text{MgO}, \text{Cr}_2\text{O}_3]\) Ru thin film samples were characterized utilizing X-ray diffraction (XRD), XRR, XPS, LEED, and four-point sheet resistance measurements. XRD measurements were taken using a PANalytical X’pert3 MRD system with copper K\(\alpha\) radiation source \((\lambda = 1.54056 \text{ Å})\), equipped with a graded multilayer mirror for the incident beam and the 1D PIXcel detector for the diffracted. The single crystalline nature of selected bare ruthenium films, without any encapsulation, is confirmed by the XRD measurements with 0-20 scans exhibiting the Ru (0002) and (0004) peaks and the sapphire (0006) and (00012) peaks as shown in Figure 5.1(a), which is collected from a 20 nm thick Ru(0001)/Al\(_2\)O\(_3\) film deposited at 700\(^\circ\)C. The non-specular \(\phi\) scans at \(\chi = 57.71^\circ\) and \(2\theta = 84.68^\circ\) exhibits the six-fold symmetry of the Ru \{11\overline{2}2\} peaks, and at \(\chi = 42.3^\circ\) and \(2\theta = 57.499^\circ\) shows the six-fold symmetry of the sapphire \{11\overline{2}6\} peaks, as shown in Figure 5.1(b). A 30\(^\circ\) offset in the phi positions of these two peaks were observed for 30\(^\circ\) rotational honeycomb epitaxial relationship of (0001) Ru \(/\parallel (0001)\) sapphire and \(<11\overline{2}0>\text{Ru} \|<10\overline{1}0>\) sapphire, which is consistent with the results that have been previously reported [28, 29]. The same X-ray optical configuration in XRD measurements was used for XRR acquisition, which was further analyzed to estimate the film thickness and roughness. The samples without a dielectric overlayer were modeled as a sapphire/Ru/RuO\(_2\) structure, and the samples with the dielectric overlayer as sapphire/Ru/RuO\(_2\)/dielectric. Bulk density values of 3.989 g/cm\(^3\), 12.4 g/cm\(^3\), 6.97 g/cm\(^3\), 2.196 g/cm\(^3\), 3.58 g/cm\(^3\), and 4.35 g/cm\(^3\) were used for the sapphire, Ru, RuO\(_2\), SiO\(_2\), MgO, and Cr\(_2\)O\(_3\) respectively.
Figure 5.1: Representative (a) XRD for a Ru film on sapphire (0001) deposited at 700°C with thickness $d = 20.8$ nm, (b) an XRD $\phi$ scan of the Ru $\{11\bar{2}2\}$ peaks overlaid with a scan of the sapphire $\{11\bar{2}6\}$ peaks.
Figure 5.2: Representative XRR result from 4.8 nm thick MgO layer on Ru(0001) following the 500 ºC annealing process in Ar/H$_2$ 3% atmosphere. Redline represents the measured intensity, and the black line is from the fitted curve.

Figure 5.2 is the representative XRR analysis for a 4.8 nm thick MgO layer on Ru(0001) after annealing in Ar/H$_2$ 3% environment for 2 hours at 500 ºC. The measured XRR intensity is plotted in the red line on a logarithmic scale as a function of scattering angle, and the black line indicates the results from curve fitting. The thickness of ruthenium estimated from XRR analysis and sheet
resistance measured via the Vander pau method is used to measure the film's resistivity measurement. The chemistry of the Ru film surface and Ru/dielectric interfacial region was studied by XPS. The high-resolution XPS spectra were collected under ultra-high vacuum (base pressure $\sim 5 \times 10^{-10}$ Torr) conditions using XR 50 Al K$_{\alpha}$ X-ray source (1486.67 eV) and a SPECS Electron Spectrometer with a PHOIBOS 100 Hemispherical Energy Analyzer. The surface structure of the Ru films in UHV conditions was assessed by back-view LEED (OCI, Microengineering). The LEED measurements were performed with a primary electron beam energy of 68 eV.

5.3 Results and Discussion

5.3.1 Surface chemistry of Ru(0001) and SiO$_2$/Ru(0001)

For this study, two series of samples (sample series 1 and 2 as described in Table 5.1), uncovered Ru(0001), and silica capped Ru(0001) films are annealed sequentially under two different environments (Ar/H$_2$ and air). The Ru interface's chemistry change as a function of annealing conditions is monitored with X-ray photoemission spectroscopy (XPS). The series of Ru 3d XPS spectra collected from bare and silica capped ruthenium at different annealing conditions is presented in Figure 5.3. In all cases, the black dotted spectra denote the contributions resulting from metallic Ruthenium (Ru$^0$), and solid black fits are for the oxidized Ru species (Ru$^{\delta^+}$). The misfits in the higher binding energy, 3/2 spin-orbit splitting component of Ru 3d, is resulted from the varying amounts of adventitious carbon (C 1s, blue dotted curve) present on the surface of the sample, which also shows a peak in this binding energy region.
Figure 5.3: Series of XPS Spectra of Ru 3d peaks collected from (a) Ru(0001) and (b) SiO$_2$/Ru(0001) samples annealing in two different environments, Ar/H$_2$ (3%) and air alternatively at 300 °C.

To generate the XPS fits of Ru 3d BE region, we first established an empirical line shape for the metallic Ru (Ru$^0$), using a rigorously cleaned Ru(0001) single-crystal kept within the vacuum system. With the shape, width, and position of this peak constrained to fixed values equivalent to those from the control sample, a second peak associated with RuO$_2$ (Ru$^{5+}$) was added.
to the experimental spectra of each sample as needed to ensure proper fitting of the $5/2$ spin-orbit splitting components, where the C 1s signal is not expected to contribute to the XPS intensity. With the $5/2$ part fitted by the two features associated with oxidized and unoxidized Ru, residual differences between the data and the fitting in the Ru 3d$_{3/2}$ component region of the spectra, the higher binding energy (BE) feature present in each spectrum, were fit to a single unconstrained C 1s peak. The variation in the C 1s peak intensity correlates with the ambient air exposure time rather than the annealing temperature and environments.

Table 5.2: Process sequence with primary characterization results for the first series of samples consisting of 20nm Ru(0001) deposited at 700 °C

<table>
<thead>
<tr>
<th>Process step</th>
<th>Resistivity (μΩ-cm)</th>
<th>Ru Thickness (nm)</th>
<th>Ru Oxide Thickness (nm)</th>
<th>Ru Roughness (nm)</th>
<th>XPS Ru$^{δ+}$/Ru$^0$ Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposit Ru</td>
<td>9.40</td>
<td>18.61</td>
<td>0.32</td>
<td>0.29</td>
<td>0.18</td>
</tr>
<tr>
<td>300 °C Ar/H$_2$</td>
<td>9.04</td>
<td>18.56</td>
<td>0.22</td>
<td>0.13</td>
<td>0.14</td>
</tr>
<tr>
<td>300 °C Air</td>
<td>9.25</td>
<td>18.44</td>
<td>0.64</td>
<td>0.17</td>
<td>0.47</td>
</tr>
<tr>
<td>300 °C Ar/H$_2$</td>
<td>9.12</td>
<td>18.35</td>
<td>0.27</td>
<td>0.12</td>
<td>0.22</td>
</tr>
<tr>
<td>300 °C Air</td>
<td>9.23</td>
<td>18.68</td>
<td>0.71</td>
<td>0.15</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Figure 5.3 shows that Ru samples mostly in the metallic state are observed following annealing within the reducing Ar/H$_2$ environment, and the highly oxidized samples are noted following annealing steps conducted in the air. The ratio of an oxidized component of ruthenium to metallic Ruthenium (Ru$^{δ+}$/Ru$^0$) obtained from the quantitative analysis of the XPS spectra of uncovered Ru is shown in Table 5.2, which agrees qualitatively with the thickness of ruthenium.
oxide as predicted from XRR. Besides, the roughness of the upper Ru surface, as predicted from XRR, seems to increase by a small amount after oxidizing anneal and reduces in Ar/H₂ anneal. Similarly, Ru film's resistivity increases after annealing in the oxidizing environment (air) and decreases subsequent reducing (Ar/H₂) anneal. This trend of reversible increase/decrease in resistivity of uncovered ruthenium film upon oxidizing/reducing anneal, as shown in Table 5.2, appears to track with the degree of Ru surface oxidation.

Table 5.3: Process sequence with primary characterization results for the second series of samples consisting of 5nm amorphous SiO₂ on 20nm Ru(0001)

<table>
<thead>
<tr>
<th>Process step</th>
<th>Resistivity (μΩ-cm)</th>
<th>Ru Thickness (nm)</th>
<th>XPS Ru&lt;sup&gt;δ⁺&lt;/sup&gt;/Ru&lt;sup&gt;⁰&lt;/sup&gt; Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 °C Ar/H₂</td>
<td>8.98</td>
<td>20.48</td>
<td>0.08</td>
</tr>
<tr>
<td>300 °C Air</td>
<td>9.03</td>
<td>20.39</td>
<td>0.38</td>
</tr>
<tr>
<td>300 °C Ar/H₂</td>
<td>9.02</td>
<td>20.51</td>
<td>0.11</td>
</tr>
<tr>
<td>300 °C Air</td>
<td>9.12</td>
<td>20.31</td>
<td>0.35</td>
</tr>
</tbody>
</table>

The oxidation behavior of SiO₂ capped (Figure 3.2(b)) Ru films is also similar to that of uncapped Ru films, where the increased intensity of the oxidized component of ruthenium obtained from air oxidation is found to be decreased upon subsequent annealing in Ar/H₂. Although the trend in both cases (capped vs. uncapped) is the same, the intensity ratio of oxidized to metallic ruthenium in the case of bare ruthenium is found to be higher compare to that of silica capped
ruthenium film, which indicates the formation of a thinner oxide layer in the case of SiO$_2$ covered Ru. The resistivity data and XPS intensity ratio (Ru$^{5+}$/Ru$^{0}$) of silica capped Ruthenium samples are presented in Table 5.3. The correlation between Ru oxidation and resistivity is significantly small compared to that of bare Ru.

The increase in resistivity at a lower dimension of metal is mainly due to the enhanced scattering of electrons at the metal surface. The RuO$_2$ layer formation on Ru is expected to distort the ordered nature of the single-crystalline Ru surface, increasing the diffuse scattering of electrons, thereby increasing the resistivity. The results from these series of samples suggest the critical role of chemical and structural change in metal/vacuum and metal/dielectric interfaces on resistivity increase of 20 nm Ru(0001) film. The reversible nature of resistivity change upon oxidizing/reducing anneal of bare and SiO$_2$ capped ruthenium demonstrates the possibility of minimizing Ru film's resistivity via annealing. However, the annealing temperature for this work was limited to 300 °C. So, in the next section, we will discuss the structural and chemical change of the Ru/SiO$_2$ interface at different annealing environments and temperatures (>300 °C) and its effect upon resistivity of the film.

5.3.2 Electron surface scattering on Ru films interface [metal/vacuum and metal/dielectric]

The influence of film thickness and its surface characteristics upon the resistivity of the metal film is described by the Fuchs-Sondheimer (FS) model [16] of surface scattering, given in a simplified version, by the equation below:
\[ \rho_{FS} = \rho_0 \left[ 1 + \left( \frac{3\lambda(1-p)}{8h} \right) \right] \]

where \( \rho_{FS} \) is the film resistivity, \( \rho_0 \) is the bulk resistivity of the, \( \lambda \) is the electron mean free path (EMFP), \( p \) is the average of the specular scattering coefficients (probabilities) of the upper \( (p_u) \) and lower \( (p_l) \) surfaces of the film, and \( h \) is the thickness of the film. In this model, changes in the resistivity for metal with constant thickness are associated with changes in the surface scattering specularity, \( p \). Conversely, the specularity \( (p) \) of the metal film surface of a certain thickness can be estimated using equation (5.1) from an independently calculated experimental value of resistivity \((\rho)\).

5.3.2.1 SiO\textsubscript{2}/Ru interface

In our recent collaborative research work [30], we have thoroughly investigated the effect of temperature and annealing environment on the surface scattering of electrons at Ru/vacuum and Ru/SiO\textsubscript{2} interface. In that work, a ~20 nm-thick Ru(0001) film was first deposited via DC magnetron sputtering onto a 2-inch diameter c axis sapphire, (0001) Al\textsubscript{2}O\textsubscript{3} wafer maintained at 700 °C temperature within a 4 mTorr Ar environment. After deposition, the wafer was removed from the sputter deposition vacuum chamber and laser-cut into several ~7 × 7 mm\textsuperscript{2} coupons for further processing and characterization. The sequential processing steps of this series of samples [sample series 3, described in an experimental section] are listed below.

(1) Ru film deposition,

(2) ex-situ step-annealing to 950 °C in Ar/H\textsubscript{2} 3% environment,
(3) room temperature deposition of amorphous SiO\textsubscript{x} via RF sputtering,

(4) *ex-situ* annealing to 500 °C in Ar/H\textsubscript{2} (reducing anneal),

(5) annealing to 500 °C in 1 atm air (oxidizing anneal),

(6) annealing to 500 °C in Ar/H\textsubscript{2} environment,

(7) annealing to 950 °C in Ar/H\textsubscript{2} environment (repetition of step 2),

(8) annealing to 400 °C within 1atm Ar/O\textsubscript{2} 20%,

(9) annealing to 500 °C in Ar/H\textsubscript{2} (repetition of steps 4 and 6),

(10) annealing to 350°C within 1 atm Ar/O\textsubscript{2} 20% and

(11) annealing to 950 °C in Ar/H\textsubscript{2} 3% environment (repetition of step 7).

It should be noted that five samples were simultaneously subjected to all the sequential processing steps. The resistivity values were calculated from each sample’s sheet resistance and thickness, measured at each step to avoid the source of variability. X-ray photoelectron spectroscopy (XPS) was used to monitor variations in the relative abundance of interfacial Ru in oxidized and reduced chemical states. Low energy electron diffraction (LEED) was also employed to examine the long-range crystalline order of Ru films before SiO\textsubscript{x} deposition.

In this study [30], the resistivity change trend as a function of Ru film thickness, ex-situ annealed in Ar/H\textsubscript{2}, was well fitted with the well-accepted Fuchs-Sondheimer (FS) resistivity size effect model. As we can see in equation (3.1), the electron mean free path and specularity are not independent parameters and cannot be uniquely estimated; only the product $\lambda(1-p)$ is constant. Among few possible set of FS model parameters which is constrained by the condition: $\lambda(1-p)=constant$, we choose to use the set of parameters; $\rho_0 = 8.0 \, \mu\Omega\text{-cm}, \lambda = 11\, \text{nm}, p_u = 78\%$, and $p_l$
= 0% as these values provide for variations of resistivity associated with changes to the upper Ru surfaces. It is essential to note that Ru samples' resistivity values were calculated at room temperature in ambient air after ex-situ annealing to 950 °C in Ar/H₂ 3%. The high upper surface specularity, 78% of the air-exposed Ru samples, is surprisingly high compared to previous UHV experiments where ambient air or sub-monolayer exposure of gas is expected to induce fully diffuse scattering [23]. However, this high specularity result is consistent with the air exposure stability of the highly ordered surface structure of ex-situ annealed Ru films, as evidenced in LEED images. Figure 5.4(a) is a LEED image collected from a 20 nm thick Ru(0001) film, deposited at 700 °C and ex-situ step annealed to 950 °C in Ar/H₂ 3% environment, lab air-exposed and imaged without any surface cleaning or annealing procedure applied. Figure 5.4(b) is a LEED image collected from the same sample after being cleaned by Ar sputtering and annealing to 1000 °C in Ar/H₂ environment under UHV.

![LEED images](image)

Figure 5.4: LEED images collected at 68 eV of beam energy from (a) 20 Ru nm thick Ru(0001) film deposited at 700C and ex-situ annealed to 950 C in Ar/H₂ 3%, and (b) same sample after Ar⁺ ion beam sputtered and annealed to 1,000°C in UHV conditions with an H₂ background.
The presence of a clear diffraction pattern in Figure 5.4(a), which is qualitatively almost the same as Figure 5.4(b), supports the fact that Ru thin films deposited at 700 °C, after step annealed to 950 °C in Ar/H₂ 3% are of high surface ordered Ru single crystals whose atomic surface order persists even after the lab air exposure. From the measured resistivity values of Ru films undergoing various processing steps (step1 to step 11 as explained above), a readily apparent trend is observed for resistivity to decrease as a result of annealing in reducing environment (Ar/H₂) and to increase as a result of oxidizing anneal (air, Ar/O₂) and SiO₂ deposition. This resistivity change of Ru films is attributed to the changes in the upper ruthenium surface, which alters the electron scattering phenomena at the Ru surface. The use of the FS model estimates the upper surface specularity of Ru films as a function of the processing step, and in this case, the lower surface of Ru is considered to be diffused entirely, \( p_l = 0\% \), and remains unchanged throughout the processing steps.

Figure 5.5 depicts the trend of several measured sample characteristics as a function of sample processing and compare these changes with the upper surface specularity \( (p_u) \) of Ru films. The change in Ru metal thickness, RuO₂ layer thickness (XRR), XPS derived Ru⁶⁺/Ru⁰ ratio, upper Ru surface roughness, and calculated upper Ru specularity is presented in Figure 5.5. It is evident from Figure 5.5 that in-between steps (4) and (11), the upper surface specularity of the Ru surface is inversely correlated with the extent of ruthenium oxidation measured by X-ray photoemission spectroscopy (XPS). Both of these properties appear to be reversible by subsequent annealing within an oxidizing/annealing environment. The samples with increased Ru oxidation, as evidenced via XPS, simultaneously exhibit increased upper Ru surface roughness and RuO_x thickness with decreased Ru thickness estimated by XRR.
Figure 5.5: a) Ru metal thickness change, (b) Ruthenium oxide thickness, (c) XPS estimated ratio, Ru oxide to Ru metal, (d) Ru surface Roughness, and (e) upper surface specularity of Ru films as a function of sample processing. [Figure reproduced from Ref. 30].
The thickness of the RuO$_x$ layer estimated from XRR is compared with the XPS ratio of oxidized ruthenium to metallic Ruthenium (Ru$^{6+}$: Ru$^{0}$) in Figure 5.5 (b) and (c). The data from XPS is more sensitive to the oxide bond formation, which is mainly due to the surface-sensitive nature of the XPS technique compared to XRR. It is also important to note here that the extent of fluctuation in the roughness observed for the upper ruthenium surface is small and would account for only a fraction of resistivity change observed during oxidizing/reducing anneal [28, 31].

The case of increased specularity and a decrease in the upper Ru surface's roughness is also observed during the transition from steps 1 to 2. The addition of amorphous SiO$_2$ on annealed Ru (000) film (step 3) resulted in a decrease in upper surface specularity equivalent to the largest fluctuations observed throughout the sample processing. Interestingly, other surface characteristics, i.e., Ru thickness, roughness, and oxidation, did not appear to change within the measured values' uncertainty when depositing silicon dioxide. It implies that in transitioning from step 2 to 3, the deposition of amorphous SiO$_2$ induces the structural change in the Ru interface and hence, thereby increases the diffuse scattering of electrons from the surface, resulting in resistivity increase and decrease in specularity of upper Ru surface. Moreover, annealing the SiO$_2$-capped sample within Ar/H$_2$, at temperatures as low as 500 °C, fully restored Ru surface specularity to its uncovered value despite again causing no significant changes to any other tracked physical properties associated with the film.

In summary, the highly specular ruthenium metal surface, which was correlated with the relatively low resistivity, is obtained by annealing to 950 °C in Ar/H$_2$ 3% environment. The room temperature deposition of SiO$_2$ is found to decrease the specularity of the Ru upper surface. A
subsequent anneal to 950 °C in Ar/H₂ 3% restores the high surface specularity, whereas the oxidizing anneal (air, O₂) is again found to decrease the specularity. The lower and higher specular probability of the upper Ru surface is found to differ in magnitude by ~60% and are reversible upon oxidizing/reducing anneals. This work demonstrates that specular scattering at metal/dielectric can be improved, thereby motivating us to explore similar processing with different single-crystal metals or various dielectric encapsulation for possible future interconnects with lower resistivity, which we will discuss in the next section.

5.3.2.2 Comparative study of various dielectric coated Ru films

The previous results from the rigorous and thorough study of SiO₂ capped Ru(0001) films at different annealing conditions and the temperature seems to constitute a clear demonstration of an approach for controllably tuning scattering behavior of metal/dielectric interfaces. These results then triggered our interest in exploring the effect of similar processing conditions on Ru films' conductivity capped with different dielectrics. For this study, analogous experiments to reference [30] are performed to compare the changes in upper surface specularity following deposition and subsequent annealing of Cr₂O₃, Al₂O₃, MgO, and SiO₂ capped Ru films at higher temperatures in Ar/H₂ environment. The resistivity and upper surface specularity values of dielectric capped Ru films at different processing steps are summarized in Table (5.4).
Table 5.4: Resistivity and upper surface specularity of dielectric encapsulated Ru(0001) films at different sample processing steps.

<table>
<thead>
<tr>
<th>Process Step</th>
<th>Resistivity(μΩ-cm)</th>
<th>Specularity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cr$_2$O$_3$</td>
<td>Al$_2$O$_3$</td>
</tr>
<tr>
<td>950°C annealed Ru</td>
<td>8.33</td>
<td>8.37</td>
</tr>
<tr>
<td>Deposit Dielectric on Ru</td>
<td>8.74</td>
<td>8.71</td>
</tr>
<tr>
<td>500°C anneal Ar/H$_2$</td>
<td>8.41</td>
<td>8.44</td>
</tr>
<tr>
<td>950°C anneal in Ar/H$_2$</td>
<td>8.38</td>
<td>8.26</td>
</tr>
</tbody>
</table>

Figure 5.6 shows the plot of resistivity and specularity of four dielectrics encapsulated Ru(0001) films as a function of sample processing steps, summarized in table (5.4). The reported resistivity values were calculated from the sheet resistance and the Ru metal layer thickness; both parameters were measured for each sample at every process step to eliminate this variability source. The resistivity and specularity values shown in Figure 5.6 are the average values collected from five different samples at each processing step, and an error bar showing the range of maximum to minimum range of those values.
Figure 5.6: Film resistivity (a) and FS model upper surface specularity, $p_u$ (b) of SiO$_2$ (blue), MgO (red), Al$_2$O$_3$ (green), and Cr$_2$O$_3$ (purple) encapsulated Ru films as a function of sample processing. The numbers shown in the graph are the average of five samples with error bars to reflect the extreme values amongst them [Reproduced from Ref. 37].
The first data point in Figure 5.6 corresponds to a clean Ru(0001) film, ex-situ step annealed in Ar/H$_2$ 3% environment at 950 ºC. At this point, with no dielectric encapsulation, similar resistivity values are measured for all sets of samples, as expected for equivalent sample processing. The next step is the room temperature deposition of dielectric oxides via sputter deposition, resulting in a significant increase in Ru films' resistivity. The increase in resistivity is attributed to increased diffuse surface scattering of electrons upon oxide deposition. As we can see in Figure 5.6(a), the resistivity increase for MgO coated films is significantly higher than other oxides. Next, the samples are annealed in Ar/H$_2$ environment at 500 ºC, which resulted in a decrease in Ru film resistivity to the values comparable to that of the samples before oxide deposition, 950 ºC ex-situ annealed Ru films. The resistivity values even further decrease upon annealing the samples at elevated temperature, 950 ºC.

Change in the resistivities seen in Figure 5.6(a) is assumed due to the upper ruthenium surface (Ru/dielectric). The lower Ru interface (Ru/Al$_2$O$_3$) and the bulk of Ru are presumed not to be changed upon room temperature deposition of dielectrics and annealing to 500 ºC and 950 ºC, as it has already been annealed in 950 ºC Ar/H$_2$ before dielectric deposition. The effect of electron scattering resulting from the upper ruthenium surface changes is quantified in terms of a parameter called specularity ($p_u$), which is estimated using the FS model. The upper surface specularity values ($p_u$) of Ru films shown in Figure 5.6(b) are calculated using equation (5.1). From inspection, for a certain thickness (fixed) of metal, only the product $\lambda(1-p)$ is constant, which implies that we cannot uniquely determine $\lambda$ and $p$ only from the experimentally measured resistivity value. However, the average specularity, $p$, of Ru films are constrained by the FS model to be in the range of $p = 0$ (fully diffuse scattering) to $p = 1$ (fully specular scattering). To satisfy these boundary
conditions, the broader range of resistivities observed for the samples with MgO/Ru interfaces requires adopting a new set of FS parameters relative to those used in a previous study (28). The FS parameter used in the previous study were $\lambda = 11.0$ nm $p_l = 0$. In this study, those values are changed to $\lambda = 12.5$ nm $p_l = 0.30$ to produce physically meaningful results, shown in Figure 5.6(b), reflecting full-scale (0–1) fluctuation in upper Ru surface specularity, $p_u$, as a function of MgO coverage and annealing conditions. Figure 5.6(b) shows that the high specularity of the upper surface of ex-situ annealed Ru films is degraded upon deposition of oxide dielectrics, with a minimum value of $p_u = 0.1$ for MgO overcoated Ru films. The high specularity of the upper surface of ex-situ annealed Ru film is regained upon annealing in Ar/H$_2$ at 500 ºC, which even further increases at elevated temperature (950 ºC). A similar trend for specularity change is observed for all-dielectric overcoated Ru(0001) films with the highest fluctuations in MgO coated Ru films. The highest specular coefficient of 0.94 is observed for 950 ºC Ar/H$_2$ annealed MgO overcoated Ru film. Out of four oxide encapsulations, MgO and SiO$_2$ showed the highest and lowest fluctuation in resistivity/specularity change, respectively.

From an analysis of XRR data, the increase in roughness to ~0.1 nm is observed on upper Ru surfaces after the deposition of oxides overlayer without any significant variation amongst four different oxides coated Ru(0001) films. This extent of increase in roughness that we observed during the transition from step 1 to step 2 is very small and could contribute only a fraction of a resistivity increase [31] we observed for Ru films. Upon annealing to a higher temperature (500 ºC and 950 ºC) in Ar/H$_2$ environment, the roughness of the Ru upper surface did not change significantly. However, from Figure 5.6, it is clear that reducing anneal (Ar/H$_2$) of films at higher temperatures reduces the film resistivity and make the upper Ru surface more specular. Therefore,
these results suggest that electron scattering phenomena at the surface of single-crystalline conductors significantly contribute to resistivity increase at nanoscale conductors compared to surface roughness.

The Ru/dielectric interface chemistry is studied by using an X-ray photoemission spectroscopy (XPS) technique. Figure 5.7 shows the representative XPS spectra collected from 20 nm single-crystal Ru films overcoated with 5 nm thick amorphous MgO, following the annealing process of Ar/H$_2$ 3% at 500 °C. Figure 5.7(a) is an XPS spectrum of Ru 3d, where the overlaps between C1s and Ru 3d are evident, and the deconvolution of those peaks was performed using XPSPEAK software to identify the peak position. Ru 3d spectrum is perfectly fitted with a single peak associated with metallic ruthenium (Ru$^0$), as seen in Figure 5.7(a). While no oxidized component of ruthenium peak (Ru$^{\delta+}$) is needed to fit the entire Ru 3d spectra in MgO overcoated ruthenium film, a small fraction of oxidized ruthenium component, Ru$^{\delta+}$: Ru$^0 < 0.1$ was observed for some of the other oxides overcoated Ru(0001) samples (not shown here). The XPS peak position for C 1s in Figure 5.7(a) is about ~1.1 eV higher in the BE region than the C 1s XPS position for adventitious carbon present in any air-exposed sample. Interestingly, similar shifts in O 1s, Mg 4s, and Mg 2p peaks are observed for MgO/Ru(0001) films, as shown in Figures 5.7(b), 5.7 (c), and 5.7(d), respectively. These shifts in BE towards higher BE is expected due to the change in the work function upon annealing in the Ar/H$_2$ environment, which then results in equivalent band bending shifts in the core-level peaks (O1s, C 1s, and metal peaks; Mg, Si, Cr, Al) of an element present on or within the oxide overlayer.
Figure 5.7: XPS spectra for Ru 3d(a), O1s(b), Mg 2p–Ru 4p (c), and Mg 2s(d) collected from the 5 nm MgO overcoated 20nm-Ru(0001) sample following Ar/H$_2$ 500 °C annealing process.
The minimum shift in core-level peaks is seen in Cr$_2$O$_3$ encapsulate Ru(0001) comparing to other oxides, which might be due to the reason that Cr$_2$O$_3$ is more metallic corresponding to other dielectric oxides. However, there is no change in binding energy peak position for Ru 3d is observed for every dielectric overcoated sample, which lies in the range (280.25±0.05) eV.

The modeling of XRR data collected from Ar/H$_2$ annealed MgO/Ru(0001) samples shows the average thickness of the RuO$_2$ layer of ~ (0.07 ± 0.04) nm, which is minimum amongst the four different oxides overcoated Ru(0001) films. For other oxides, the average thickness of RuO$_2$ resulted from XRR simulation is 0.18 nm or more. This result also agrees with XPS analysis, where we observed no component of oxidized Ru (Ru$^{δ+}$: Ru$^0$ < 0.01) for MgO/Ru(0001). Also, it should be noted that the very thin (~ 0.2 nm or less) RuO$_2$ layers resulting from this modeling of XRR data may represent a physisorbed gas layer and/or a short wavelength roughness of the Ru metal surface, rather than a distinct oxide layer.

5.3.3 In-situ growth of crystalline SiO$_2$ on Ru(0001)

Till now, we have studied the effect of structural and chemical changes in the Ru interface, created via annealing in oxidizing/reducing atmosphere and amorphous dielectric deposition, upon the resistivity change of 20 nm Ru(0001) films. From this study, we have concluded that a higher specular Ru(0001) surface can be obtained by high-temperature annealing in the presence of Ar/H$_2$ atmosphere even when the Ru film is buried under amorphous dielectrics (SiO$_2$, Cr$_2$O$_3$, MgO, Al$_2$O$_3$), but we have yet to fully understand how changes in the specific nature of those oxides might impact this effect. The higher the upper Ru surface's specularity, the lower is the resistivity.
of Ru films, which motivates us to explore the possibility of making a Ru surface interface highly specular. So, moving forward, we want to study the possible structural change in dielectric encapsulation and its impact on the resistivity of Ru(0001) film. As ultra-thin SiO$_2$ is known to exist in various crystalline forms, as evidenced in several previous research efforts [32, 33], we have chosen SiO$_2$ as a dielectric encapsulation for this study to provide sufficient structural variation in terms of its crystallinity. It has been shown from previous research efforts that SiO$_2$ on Ru(0001) can grow as a chemisorbed monolayer or physisorbed bilayer. Also, the atomic structure of the SiO$_2$ film depends on the variations in the thickness and film growth conditions. So, in this work, we intend to study the growth of the growth varying crystalline form of SiO$_2$ on Ru(0001) and its impact on resistivity and surface scattering properties of the buried interface of Ru(0001)/SiO$_2$.

For this study, we started with the deposition of SiO$_2$ on a commercial Ru single crystal (8mm diameter, Princeton Scientific Corp.), shown in Figure 5.8(b), to calibrate the deposition rate of Si for monolayer and bilayer silica growth. The well-established method reported in previous research works [31-34] is employed to develop the films on Ru(0001) substrate. Before film growth, the Ru substrate was first cleaned by the repetitive cycles of Ar$^+$ sputtering and annealing to ~1400 K. LEED and XPS were utilized to check the substrate's cleanliness. The sputtering and annealing process was performed until a sharp (1x1) hexagonal LEED pattern corresponding to Ru(0001), as depicted in Figure 5.8(c), and the absence of non-Ru peaks in XPS is observed.
The preparation of SiO\(_2\) includes several steps. First, the clean Ru(0001) substrate was exposed to 3x10\(^{-6}\) torr of O\(_2\) at 1200 K for 5 minutes to form 3O-(2x2) overlayer on Ru(0001), shown in Figure 5.8(d). Then, Si was evaporated on oxygen pre-covered Ru(0001) surface at room temperature in the presence of 2x10\(^{-7}\) Torr of O\(_2\) via e-beam assisted evaporation (EBE, Specs). No LEED pattern was observed immediately after the deposition of Si on 3O(2x2)-Ru(0001). The final oxidation was performed by annealing the substrate to 1200 K in 3x10\(^{-6}\) Torr of O\(_2\) for 10 minutes, resulting in a crystalline SiO\(_2\) film. XPS was used to estimate the amount of Si in the film in terms of monolayer equivalent by adapting the well-established empirical formula in reference [32]. Figure 5.8 (d) represents the LEED image of the bilayer silica film on Ru(0001). The presence of sharp (2x2) diffraction spots and a ring-like feature in such silica bilayer film indicates well-ordered structures coexisting with the domains of disordered structures, which can be considered as 2-D vitreous silica [35]. The crystallinity of bilayer SiO\(_2\) can be controlled by varying annealing temperature, time, oxygen pressure, and the cooling rate of the sample following the high-temperature oxidation of the film. Out of these parameters, the post-annealing cooling rate plays a significant role in determining the film's crystallinity [35,36]. We have successfully grown the various forms of bilayer silica films ranging from perfect crystalline to vitreous form (not shown here).

After the successful growth of crystalline SiO\(_2\) films on an infinitely thick single-crystal Ru(0001) substrate, we moved our interest into 20 nm Ru(0001) films on a sapphire substrate. To correlate the resistivity change unequivocally with the structural change of SiO\(_2\), we should maintain a constant thickness of Ru(0001) film throughout cleaning Ru films and deposition of SiO\(_2\). So, instead of the Ar\(^+\) sputtering step in the cleaning procedure of Ru(0001) films, we
annealed the sample alternatively in H\textsubscript{2} and O\textsubscript{2} atmosphere at ~ 1250 K until we observed sharp hexagonal patterns in LEED and the absence of carbon and oxygen peaks in XPS. This process took a long time to clean the sample, but eventually, we cleaned the Ru sample with no Ar\textsuperscript{+} sputtering need. Figure 5.8 (a) is the picture of a Ru film during annealing under UHV conditions.

Figure 5.8: Ru Samples during annealing under UHV condition as a standard process of cleaning; (a) 20nm Ru(0001)/Sapphire, and (b) single crystal Ru(0001) and change in LEED pattern during SiO\textsubscript{2} growth; (c) clean Ru(0001) after repetitive cycles of annealing, (b) 3-O(2x2) layer formed from oxidation of Ru(0001) surface at 1200K, and (c) crystalline SiO\textsubscript{2} growth on Ru(0001).
After cleaning under UHV, we performed an ex-situ XRR measurement to estimate Ru film's thickness and found out that it remained unchanged compared to the thickness before the cleaning process. We have also grown monolayer and bilayer silica on Ru(0001) film on sapphire [sample shown in Figure 5.8(a)], where the change in LEED structure during the film growth was similar to Figure 5.8 (c), (d), and (e).

Until now, we have demonstrated the capability of developing silica film of various crystallinity on Ru substrate (both film and a thick crystal). Our main objective here is to study the resistivity/specularity change of Ru(0001) films/surface due to the structural change of SiO$_2$ encapsulation. So, it is essential to perform the in-situ measurement of Ru films' sheet resistance before and after the deposition of the silica layer. The Ru sheet sample, shown in Figure 5.8(a), is not compatible with our electrical connection arrangement inside the UHV system to probe for resistivity measurement in the van der Pauw geometry. So, we have designed a new set of samples with four touchpads at the corner of the 7x7 mm$^2$ coupon for this purpose, as shown in figure 5.9 (a), which is compatible with our UHV system to perform the in-situ resistivity measurement immediately after sample processing with no need of air exposure. For the patterned sample preparation, the 2-inch sapphire substrate was first deposited with 20 nm Ru(0001) film, then step annealed to 950 °C in Ar/H$_2$, and finally patterned using e-beam lithography before laser-cut into 7x7 mm$^2$ coupons. The four pins 1, 2, 3, and 4 in a Ru film mounted on a sample plate [Figure 5.9 (a)] are used, two for current measurement and two for voltage measurement in a van der Pauw configuration mode. Even though these samples are compatible with in-situ resistivity measurement, Ru films' surface quality has diminished significantly due to the photolithography and etching processes involved in preparing the patterned samples.
Figure 5.9: (a) patterned Ru(0001) sample, compatible for four-point probe resistivity measurement, after mounting in a sample plate and ready to insert into UHV, (b) Sample during annealing procedure under UHV, (c) LEED image of Ru(0001) sample immediately after inserting inside UHV, (d) LEED image of the sample shown in (a), and (b) after few cycles of annealing procedure under alternative environments H₂ and O₂.

Figure 5.9 (c) is a LEED image collected from an air-exposed Ru sample (patterned) without any cleaning procedure performed under UHV. The absence of LEED reflexes in the
patterned Ru sample indicates the decrease in Ru films' surface quality compared to the blanket Ru sample (samples described in section 5.3.2), where diffraction spots associated with hexagonal Ru(0001) were visible even for an air-exposed sample. It took significantly more time to clean these samples by repetitive cycles of annealing, alternatively in H₂ and O₂ atmospheres. Figure 5.9 (d) is the LEED image from the clean Ru sample after a rigorous cleaning process under UHV. Also, the XPS spectra corresponding to this sample indicated the absence of non-Ru peaks.

The in-situ sheet resistance measurement of the film was also made at room temperature after each annealing cycle. The resistivity of the 20.2 nm clean sample after annealing in H₂, associated with LEED image Figure 5.9(d), was measured to be 8.30 μΩ-cm, whereas resistivity was increased to 8.38 μΩ-cm after oxidizing anneal. Ru film's resistivity is observed to increase due to oxidizing anneal (O₂) and decreased upon reducing anneal (H₂). This trend of resistivity change is consistent with the data for ex-situ annealing of samples presented in subsection 5.3.1 of this chapter, but the weaker effect is observed for the in-situ annealing process, which could be due to the lower pressure of oxygen and hydrogen during UHV anneal.

We have already established the standard process for growing silica film (Figure 5.8) on Ru(0001). The Ru samples compatible with the in-situ measurement of sheet resistance in the van der Pauw geometry are also made. However, the surface quality of the patterned Ru sample, prepared via photolithography, has decreased. Hence, currently, we are in the process of developing sufficiently clean patterned Ru samples, which will require minimal effort for in-situ cleaning before silica growth. The near-future plan for this project involves the in-situ
development of SiO\textsubscript{2} on patterned Ru(0001) film and study the correlation between the resistivity change of Ru film and variation in crystallinity of SiO\textsubscript{2}.

5.4 Conclusion

The highly ordered atomic surface structure of 20 nm thick single-crystal Ru(0001) films stable to subsequent air exposure, as evidenced by LEED, is obtained by annealing to 950 °C in Ar/H\textsubscript{2} 3% environment. Films with this structure for the upper Ru surface have a lower resistivity, which was correlated with the relatively high specular scattering probability. The deposition of oxide dielectric layers on epitaxial films and annealing treatments in oxidizing gases (O\textsubscript{2}, air) at elevated temperatures in Ru shows the degradation of the upper surface specularity of metal layers. The higher specularity surface is regained upon high-temperature annealing in Ar/H\textsubscript{2}. All four dielectric oxides (Cr\textsubscript{2}O\textsubscript{3}, Al\textsubscript{2}O\textsubscript{3}, MgO, and SiO\textsubscript{2}) studied in this study follow a similar trend of decrease and increase in resistivity following the deposition of dielectric overlayer and annealing in Ar/H\textsubscript{2} at elevated temperature. The restoration of higher specularity of Ru metal surface even when embedded on dielectric overlayer upon subsequent annealing in reducing environment (Ar/H\textsubscript{2}) at higher temperature verifies that the specularity of the single-crystalline metal surface can be varied controllably. These results motivate in finding the most specular metal surfaces with potential applications as future interconnects beyond copper.

Moreover, we have initiated the experimental plan to grow the silicon dioxide of various crystallinity on the Ru(0001) surface to study the effect of structural change in the encapsulated dielectric material (SiO\textsubscript{2}) to the electron scattering phenomena at the Ru/SiO\textsubscript{2} interface. We have successfully grown crystalline silicon dioxide in 20 nm thick Ru(0001) films under UHV
condition, which is compatible with the in-situ measurement of resistivity. The future work in this research includes studying the change in surface specularity of the upper Ru(0001) surface with the variation in the crystallinity of the SiO₂ overlayer.

5.5 References


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CHAPTER 6: CONCLUSIONS AND FUTURE WORKS

There has been tremendous progress in the field of epitaxial thin-film technology in the last few decades, because of which significant attention is given to it from both the scientific and industrial communities. It is mainly because the physical properties can be tuned by choosing proper deposition techniques resulting in new material thin films with superior quality. This thesis has successfully investigated the growth and characterization of phase-specific epitaxial thin films by using ultra-high vacuum-based surface science methodologies. The epitaxial growth of molybdenum nitride thin films on hexagonal Ru(0001) substrate via physical vapor deposition is studied using XPS, ISS, LEED, and AES. The crystallization temperature of 700K was found to result in well-ordered hexagonal films that appear to grow layer-by-layer initially and in registry with the Ru(0001) support. While the film is stable in the temperature range of (600-700)K range, it starts to decompose via a presumptive N₂ recombinative desorption mechanism upon annealing above T = 700K in UHV, which leaves the film in a purely metallic Mo-Ru configuration by T = 1100 K. The oxidation behavior of molybdenum nitride at ambient condition is also studied with XPS, which predicts that a single layer of MoN completely oxidized to MoO₃ in about 30 days. So far, we have successfully grown single-crystalline hexagonal δ-MoN on Ru(0001) compatible with a model system for surface science-based catalysis. The future work for this research project includes studying the catalytic properties of MoN towards the HDN process, starting with the pyridine.

The resistivity-size effect observed in single-crystalline nanoscale metals with the thickness equal to or less than the electron mean free path (λ) is mainly contributed by the enhanced
scattering of electrons at metal interfaces. This thesis covers the comparative study of the surface-dependent effects on resistivity for dielectric encapsulated Ru(0001) films. The oxide dielectrics used in this work include SiO$_2$, MgO, Cr$_2$O$_3$, and Al$_2$O$_3$. The structural and chemical changes in the Ru(0001) interface, created by dielectric deposition at room temperature and high-temperature annealing in oxidizing (air, Ar/O$_2$) or reducing environments (Ar/H$_2$), were characterized by XPS and LEED. The (0001) surfaces of single-crystal Ru thin films ex-situ annealed at 950°C in Ar + H$_2$ 3% were found to form a highly ordered atomic surface structure that was stable to ambient air exposure, as evidenced by LEED and films prepared in this way were found to have a relatively low resistivity. Room temperature deposition of dielectric oxides on the Ru sample surface and annealing of these overcoated films in an oxidizing environment (air, Ar/O$_2$) were observed to increase the resistivity of the films. The film's resistivity was lowered upon a subsequent reducing anneal (Ar/H$_2$) at a higher temperature even when the film was buried under an oxide dielectric. The variation in resistivities resulting from presumptive changes in surface structure and chemistry were related to the changes in the Ru surface's specularity ($p$) for electron scattering. In this context, we have demonstrated a fully (reversibly) tunable specularity at the metal/dielectric interface (from fully specular to fully diffuse). However, we are still searching for direct physical evidence of the presumed accompanying structural/chemical changes at such interfaces. The tunability of the upper surface specularity of Ru(0001) film, obtained by high-temperature annealing in Ar/ H$_2$ atmosphere, motivates to look for the alternative material for interconnects beyond Cu.

So far, we have studied the effect of structural and chemical change of Ru interface on resistivity/specularity change. To explore the impact of structural change in encapsulated oxide
dielectrics to resistivity change of Ru film, we have chosen SiO$_2$ as a dielectric. SiO$_2$ is a choice of our dielectric because various crystalline forms of SiO$_2$ can be grown on Ru(0001) by controlling the growth parameters. Hence, it provides a broader range of structural changes in dielectric needed to quantify its effect on the resistivity change of Ru films. Towards this goal, we have successfully grown bilayer SiO$_2$ films of various crystallinity on 20 nm Ru(0001) films. The Ru(0001) samples compatible with the in-situ measurement of resistivity in van der Pauw geometry have been made and successfully annealed under UHV condition without any change in film thickness, which is a crucial requirement for the study of the effect of structural change on surface characteristics of Ru interface. The future goal for this project is to study the correlation between the resistivity change of Ru films and the structural change of SiO$_2$ encapsulation.
APPENDIX A: SUPPORTING INFORMATION FOR CHAPTER 5
**XPS study of sample series 3**

Figure A1: XPS spectra for Ru 3d (a), O 1s (b), and Si 2p (c) for the same sample following the second (green), fourth (blue), and fifth (brown) stage of sample processing. Ru$^0$ and Ru$^{\delta+}$ correspond to metallic ruthenium and ruthenium oxide (RuO$_2$), respectively.
Figure A1 represents the characteristic XPS spectra of Ru 3d, O1s, and Si 2p collected from the same sample following the second, fourth, and fifth steps in an 11-steps sequential process, explained in chapter 5. Those three representative steps depict the nature of the chemical state of the Ru interface upon annealing at different annealing environments. The entire Ru 3d binding energy region is fitted with two peaks for ruthenium associated with metallic ruthenium (Ru$^0$) and oxidized ruthenium (Ru$^{\delta+}$), and one peak for carbon (C1s). We noted the large variations in both the position and intensity of the C 1s features needed to fit our data as a function of condition accurately.

While transitioning from step 4 (Ar/H$_2$ annealing) to step 5 (air annealing), we observed that C 1s position is shifted to lower binding energy (BE) by ~1 eV. Interestingly, a similar effect is also noted in both the O 1s and Si 2p data. This combination of data is consistent carbon on or within the SiO$_2$ layer present at the interface of the Ru changing work-function as the interfacial oxidation state of the metal transitions from Ru to RuO$_2$, which then results in equivalent band-bending shifts to the BEs associated with all elements present within the insulating oxide layer. Since oxidation is known to increase the work function of Ru, band-bending effects near the surface are expected to concomitantly decrease the BE of core levels in the supported oxide when oxidizing the Ru metal,
Figure A2: Comparison between RuO$_x$ thickness from XRR and Ru$^{5+}$/Ru$^0$ from XPS. Ru$^0$ represents the metallic ruthenium whereas, Ru$^{5+}$ is associated with the oxidized component of Ru, consistent with RuO$_2$.

The trend of change in Ru-oxide's thickness formed on the surface of Ru is consistent with the XPS derived Ru$_{oxide}$:Ru$_{metal}$ ratio.
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