Abstract

PARK, KIE JIN. The Atomic Layer Deposition of Noble Metals for Microelectronics Applications. (Under the direction of Dr. Gregory N. Parsons)

The purpose of this research has been to explore noble metals prepared using thermal atomic layer deposition (ALD) for gate electrode applications in CMOS technology. ALD Ruthenium and Rhodium metal films have been focused due to their high work function, low resistivity of their oxidation forms. Study includes 1) ALD Ru process, 2) ALD Ru nucleation behaviors, 3) area-selective ALD Ru process, 4) ALD Ru work function modification, 5) ALD Rh process and work function.

For item 1), ALD Ru films were formed using ruthenocene and oxygen as precursors. ALD window was discovered within 310 to 340°C from ALD Ru growth rate dependence on deposition temperature. Self-limiting reaction behavior was shown from growth rate versus precursor dose time. ALD Ru resistivity was measured to about 20–30µΩ⋅cm and Auger spectroscopy result was consistent with metallic Ru.

For item 2), ALD Ru was deposited on chemical SiO₂, thermal SiO₂, and H-terminated Si surfaces. From thickness vs. ALD cycle, growth rates of Ru on those substrates were similar while as initial nucleation periods were different. Contact angle values of initial substrates showed hydrophilicity was related to the incubation time difference between substrates. ALD Ru Nucleation behavior was investigated on H-terminated Si during incubation period and growth model was proposed.

For item 3), extending ALD Ru nucleation study, area-selective ALD Ru process was demonstrated. Octadecyltrichlorosilane was used to make surface very hydrophobic.
inhibiting nucleation. Metal-oxide-semiconductor (MOS) capacitor was fabricated using selective deposition process and spectroscopic (XPS) and electrical (capacitance-voltage) measurements of the capacitor confirmed the viability of selective deposition. For item 4), ALD Ru work functions on SiO$_2$ and HfO$_2$ was measured and it turned out that Ru work functions on high-k dielectrics are smaller than on SiO$_2$ possibly due to dipole formation at metal/dielectric interface. Organic self-assembled monolayers were applied on high-k dielectric surfaces prior to ALD Ru deposition to modify the dipole at the interface. ALD Ru work functions increased with amine-terminated self-assembled monolayer and decreased with vinyl-terminated monolayer.

For item 5), ALD Rh has rarely been studied even though Rh is a candidate material for PMOS gate electrode. We investigated and developed successful ALD Rh process using Rhodium acetylacetonate and oxygen as precursors. ALD window was found at 280 to 310°C. It was shown that ALD Rh resistivity decreased with deposition temperature having minimum (~10µΩ·cm) at 300°C. XPS result was consistent with metallic Rh.
The Atomic Layer Deposition of Noble Metals for
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_______________________   _______________________
Dr. Carl Osborn                      Dr. Gregory N. Parsons
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This dissertation is dedicated to my wife, Mi Yeon Kim,

my son, John Park,

and my father, Dae Hwan Park, for all their love.

Do not be anxious about anything, but in everything, by prayer and petition, with thanksgiving, present your requests to God. And the peace of God, which transcends all understanding, will guard your hearts and your minds in Christ Jesus – Philippians 4:16-17
Biography

The author was born in Pusan, South Korea. He received his B.S. and M.S. degrees in Chemical Engineering in 1991 and 1993 from Pusan National University. He worked for Kolon Research and Development Center as a senior researcher from the January 1993 to the December 1999. He received his M.S. degree in Electrical Engineering in 2003.
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CHAPTER 1. INTRODUCTION

1.1 Background of atomic layer deposition process

Atomic Layer Deposition (ALD) was first introduced as atomic layer epitaxy (ALE) in the late 1970s by Suntola and co-workers as a method of depositing amorphous and polycrystalline films for thin film electroluminescent (TFFL) displays\(^1{-4}\). III-V compound semiconductors were investigated\(^5,6\) soon after the successful introduction of ALD. Since the mid 1990s, interest in ALD technology has increased rapidly in the silicon-based microelectronics industry. This increase is a direct consequence of the ever-decreasing device dimensions and the increasing aspect ratios in integrated circuits (IC). Traditional thin film deposition techniques such as chemical vapor deposition (CVD) and physical vapor deposition (PVD) are expected to meet major conformality problems during the next few years, and ALD is currently considered a promising alternative candidate to them. At the same time, film thicknesses are shrinking so thin that ALD’s major drawback, the low deposition rate, is becoming less important\(^7\).

In ALD, film growth takes place in a cyclic manner. In the simplest case shown in Figure 1, one cycle consists of four steps: i) introduction of the precursor, ii) purge or evacuation of the reaction chamber, iii) introduction of the reactant, and iv) purge or evacuation. This cycle is repeated as many times as necessary to obtain the desired film thickness. During the precursor pulse, precursor molecules chemisorb, or react with surface groups, saturating the substrate: After the formation of the chemisorbed monolayer, no further adsorption takes place, and the purge periods remove excess precursor and volatile byproduct.
molecules. Under these conditions, film growth is self-limiting. That is, the amount of the film deposited during each cycle is the same and is determined only by the density of the chemisorption or reaction sites at the surface. In an ALD process, a plot of growth rate versus substrate temperature shows a plateau or inflection region in which self-limiting ALD behavior exists\textsuperscript{8,9}. This temperature range is often called the “ALD process window”. At temperatures below this range, excess reactant condensation typically results in a larger growth rate, whereas insufficient activation energy for chemisorption or reaction leads to decreased growth rate. At higher temperatures, film growth rate may be increased by thermal decomposition of reactants or decreased by desorption of desired products or reactants. All of these cases are deviations from the desired self-limiting ALD process. Insufficient dosing of reactants or insufficient purging resulting in gas-phase mixing and reaction of alternate reactants can also keep a process from being ideal self-limiting within the ALD temperature window\textsuperscript{10}. In ideal ALD, the thickness of the film would be determined only by the self-limiting growth reaction that occurs on the surface. As long as enough precursor gas is introduced into the reactor to saturate the surface, deposition of one monolayer would occur each cycle. In reality even when true ALD is achieved, only a fraction of monolayer is deposited each cycle. The non-ideality of the growth rate also depends on several processing parameters. This behavior is sometimes due to steric hindrance of molecular precursors adsorbing on the surface, which leads to saturation at less than one full monolayer of surface coverage \textsuperscript{11}. However, the density of surface adsorption sites is also an important factor since ALD reactions generally occur between
gas-phase species and a specific reactive site on the surface. Decreasing ALD growth rates has also been attributed to reactant desorption.

1.2 Advantages and limits of the ALD process

Atomic Layer Deposition produces individual layers on the atomic level and allows more choices in the type of film deposited including epitaxial, polycrystalline, and amorphous. In addition to this choice, film growth by the sequential deposition of monolayers (as discussed earlier) offers ALD some characteristic advantages over more traditional CVD and PVD techniques. First, in ALD atomic-scale thickness control is achieved because the final film thickness depends only on the number of cycles performed. Second, chemistries used can be highly reactive since precursor and reactant isolated from each other by purge or evacuation steps. This allows for a wider selection of ALD precursors than those available for CVD and lower deposition temperatures. Third, the ALD characteristic of self-limiting surface reactions gives much more uniform films than CVD, especially for films deposited on large-area wafers. This is because in each ALD step film growth stops when the reactants saturate the surface even if reactants have higher flux in some areas of the wafers. During CVD, non-uniformities in the reactant flux along the wafer cause a corresponding variation in the local growth rate. For the same reason, ALD leads to much better conformality than PVD, especially for films deposited on high aspect-ratio structures. In other words, the film growth rate is same over all parts of 3-dimensional structures where PVD cannot provide a conformal film due to self-shadowing. Finally, ALD film is known to have good properties with less damage than PVD film and fewer
impurities than CVD\textsuperscript{18}. Because of these advantages, ALD is considered the most promising deposition technology to replace CVD and PVD in the semiconductor industry for applications that require high conformality and quality such as DRAM (Dynamic Random Access Memory) trench capacitors, back-end interconnect barriers, metal gate electrodes, and high-aspect-ratio vias.\textsuperscript{15,18,19} In spite of the above advantages, ALD has some limitations keeping it from being more prevalent in production. The obvious problem of growing a film one atomic layer at a time is the large number of cycles required to obtain a sufficiently thick films\textsuperscript{20}. In recent applications in microelectronics, however, required film thicknesses have, in many cases, decreased to the low nm range, and this has made the low growth rates of ALD more acceptable. For example, for the 65nm interconnect generation, the Cu diffusion barrier thickness can be no more than 5nm thick, which can be deposited with less than 100 ALD cycles, which could typically be done in several minutes for most cases. Another problem is the deviation from the theoretical monolayer that is form during ALD. An imperfect, partial monolayer usually forms due to steric limitations\textsuperscript{11,16}. Other problems can disrupt the formation of the theoretical monolayer such as residual or desorbing gases\textsuperscript{20}. The desorbed gas can react with the gas entering the chamber, causing unwanted by-products on or above the substrate surface. The growth of polycrystalline films involves nucleation stages similar to those found in other deposition methods that can cause roughening at the surface\textsuperscript{16}. This is less common for epitaxially grown or amorphous films, but may still occur.
1.3 Applications of ALD metals

i) Back-end of line process applications

With the continued scaling down of semiconductor device dimension, now clearly entering the nanoscale node, the need for a deposition technique to produce very conformal, ultrathin films at low growth temperatures has increased. Because of its excellent thickness control and uniformity, ALD metals are of interest especially for back-end technology including Cu-interconnection and diffusion-barrier materials since the deposition of films in back-end technology requires high conformality due to the very high-aspect-ratio structures. For the sub-100nm node, copper has become the primary metal for back-end interconnection metallization because of its low resistivity (1.67µΩ·cm) and resistance to electromigration. However, Cu easily diffuses through the dielectric. Thus, practical applications of Cu metallization require the presence of films that function as diffusion barriers or adhesion/seed layers which are necessary to promote adhesion and prevent diffusion and reaction of the Cu layer with dielectric materials. Metallic tantalum and titanium have been deposited by ALD using metal chlorides and atomic hydrogen produced in remote plasma, and conducting nitrides and related alloys of Ta and Ti are being studied as potential diffusion barriers. Ta-based barrier layers deposited by ALD include TaN deposited. Ti-based barrier layers deposited by ALD include TiN.

ii) Gate electrode applications

Other important applications for metals deposited by ALD include new gate metals for CMOS as well as electrodes for capacitors in memory devices. Gate electrodes in MOS
devices are conventionally made of highly doped polycrystalline silicon (poly-Si). Several issues of poly-Si have been recently encountered due to aggressive scaling. One of them is depletion of the poly-Si gate electrode when the gate stack is biased in inversion, which results in reduced inversion layer charge density. This poly-depletion effect lowers gate capacitance and typically results in an increase of 4-5 Å in the Equivalent Oxide Thickness (EOT) of the gate stack. This effect represents a significant problem as industry targets EOTs of less than 10 Å for sub-65nm CMOS. Other drawbacks to using poly-Si gates arise with further scaling including boron penetration through the dielectric and poly-Si reaction with high-k materials making it less favorable material for the continued use as a gate electrode. Metals for gate materials have several advantages over poly-Si including metals have lower resistivity than poly-Si, no doping is necessary due to excess of electrons in the metal, so no boron penetration will occur, and gate depletion problem is not as significant as poly-Si. From the point view of materials, the work function is an important property for candidate replacement gate electrode materials with work functions near the conduction band edge of Si (4.05eV) and near the valence band edge of Si (5.17eV) for NMOS and PMOS devices, respectively. A single metal gate material with a mid-gap work function for both PMOS and NMOS has been studied and turned out to not be viable due to high threshold voltages. To avoid high threshold voltage, a “dual-metal gate” design in which different metals are used for the PMOS and NMOS devices is a promising solution. Besides the proper work function, prospective metals need to possess several properties including high thermal stability, low resistivity, good adhesion to dielectric, and low reactivity. High-work function (PMOS-compatible) metals, generally
inert elements such as Au and Pt, suffer poor etching and adhesion issues. Low-work function (NMOS-compatible) metals such as Al and Ti often react with the dielectric and form detrimental interface states. From a processing perspective, the choice of deposition technique for the gate metal is also critical as a metal deposition process that does not damage the dielectric layer is desirable. Low impurity concentration is also required because any impurity causes capacitance-equivalent thickness increase and prevents long-term stability. ALD is a promising deposition technique to deal with these constraints.

1.4 Research challenges for metal gate electrodes

Several candidate materials exist for dual metal gates (PMOS and NMOS-compatible). Promising candidates for PMOS include Ru, and Mo for several reasons. A conductive oxide such as RuO$_2$ has also been considered a candidate for PMOS but conductive metal oxides are not of general interest because they could potentially act as a source of oxygen for unwanted silicon oxidation. NMOS metal gate candidates include Ti and Ta (generally in nitrided compounds such as TaSi$_x$N$_y$). Metallic Hf and Zr for NMOS applications appear to be impractical due to high reactivities with dielectric oxides. For a dual metal gate application, processing issues such as extra lithographic steps may also be important obstacles to overcome. One promising approach from a process integration point of view is the idea of depositing one metal over the entire CMOS structure then chemically modifying the metal in one region (either NMOS or PMOS) to change its effective work function (yielding two metallic species with both NMOS and PMOS compatibility). This approach would be similar to the current poly-Si process, in which the same material (poly-
Si) is doped differently in different regions to give the appropriate work functions. It has been shown, for example, that Molybdenum can be changed from a high-work function metal (PMOS) to a low-work function (NMOS) metal with nitrogen implantation. Interdiffusion is another promising technique for adjusting gate work function. Structures in which Ti (NMOS) covers the entire structure and Ni is deposited on top of the Ti only in the PMOS region have been deposited. Upon annealing, the Ni and Ti interdiffuse to form an alloy that is Ni-rich at the dielectric interface and has a PMOS-compatible work function. Metal alloys have also been studied using Ru-Ta alloys, and the metal work function tuning has been achieved by varying the alloy composition. Nanolaminate films by ALD could be a convenient method for controlling the composition and work function of gate metal alloys as well as integrating the deposition processes for both gate dielectric and gate metal films.

Film uniformity and growth rate during ALD greatly depend on the density and nature of surface adsorption sites. Typically, ALD has an initial nucleation period, which is different from cyclic steady state behavior. It is sometimes necessary to modify initial surface properties to shorten the nucleation period. For instance, when depositing high-k dielectrics on silicon using ALD process, surface hydroxyl groups often provide the active sites for precursor adsorption during the initial nucleation period. Since native SiO$_2$ is an undesirable low-k interfacial layer for high-k dielectric applications, the native SiO$_2$ layers are typically etched in a dilute HF solution resulting in a surface (called HF-last) not easily oxidized in air even up to few hours. However, ALD growth generally initiates poorly on HF-last Si, leading to a relatively long initiation ALD period before formation of the first
ALD monolayer.\textsuperscript{61} This initiation period can be shortened by re-oxidizing the HF-last Si surfaces either thermally or chemically.\textsuperscript{62} Another approach might be to nitride the HF-last Si. This approach could passivate the surface against oxidation while still allowing precursor adsorption through the dative bonding mechanism. Similarly, surface pretreatment techniques could be applied to passivate the top surface of high-k against unwanted reactions with ALD metal films grown in our research.

As described in the plan of work section, our research will examine several surface pretreatments mentioned the above. In addition, high-k layer surface terminations with organic monolayers such as alkyls, amines, and alcohols will be examined. Research will include blocking the deposition of ALD metals, patterning the metals, and eventually developing a novel “selective ALD” processes. The work function is a key electrical property for gate electrodes, but the work function of ALD deposited metals is just beginning to be \textsuperscript{ }\textsuperscript{7}ed. The research plan described here for ALD metals focuses on the effects of various surface terminations and substrate pretreatments on the work function values of ALD films. Other challenges and unresolved issues including nucleation and coalescence of ALD films, the extent of surface coverage achieved in an ALD pulse, sufficient dosing of reactants to the substrate, and adequate purging of excess reactants from the system will be also addressed.

1.5 Objective of this work

Our primary objective is to investigate the interface engineering of high-k dielectrics and ALD noble metals for gate electrode application in CMOS technology. Also, we explore
nucleation of ALD metals to understand surface reaction thermodynamics and kinetics. The first goal, therefore, was to develop a thermal ALD process for metal Ruthenium. The second goal was to investigate the nucleation behaviors as well as area-selective process of ALD Ru on dielectric surface. The third goal was to study the electrical properties of ALD Ru and extraction of effective work functions on SiO$_2$ and high-k dielectrics. The fourth goal was to understand the effect of interface dipole at metal/dielectric on metal work function and control metal work function modifying interface from dielectric surface treatments prior to metal deposition organic self-assemble monolayers. The fifth goal was to investigate Rhodium ALD process as alternative gate material. Areas of interest include studying the electrical, material properties, and effective work function of ALD Rh. They also include interface properties and thermal stability of ALD Rh.

1.6 Experimental Approach

Films preparation

ALD Ru and Rh processes were carried out in a home-built hot-wall quartz tube reactor shown in Figure 1.3 using RuCp$_2$ (bis-(cyclopentadienyl)ruthenium) and Rh(acac)$_3$ (rhodium acetylacetonate) as a precursor, respectively. Dry oxygen was used as reactant for both processes. RuCp$_2$ and Rh(acac)$_3$ are solid at room temperature with vapor pressure of ~10mTorr at the bubbler temperature of 80°C and vapor pressure ~20mTorr at the bubbler temperature of 150°C, respectively. The ALD chamber was evacuated to 5x10$^{-6}$ Torr, and the precursor and oxidant gases were introduced into the reactor in separate pulses with an Ar purge between each reactant. Argon was also used as a carrier gas for the precursor
pulse and purity of Ar is 99.999%. During the deposition, the total gas flow rate was constant at 100–300sccm, deposition temperature was 275–350°C, and the chamber was dynamically pumped to maintain pressure at 0.9–1.2 Torr. Flow rate was controlled by needle valve and mass flow controller was not used in this study. Gas line before furnace was kept at 100°C and 160°C with heating tapes for ALD Ru and Rh process, respectively. The valve after precursor cells (bubblers) were always kept at 60–80°C and 150°C to prevent precursors’ condensation at the valve. In case of Rh, since Rh(acac)₃ has high sublimation temperature, precursor condensation is very sensitive to a cold spot in the gas line and valve. Pressure deviation between precursor dose step and Ar gas purge step can indicate precursor condensation in gas line or valve. Compare to Ar purge, precursor dose step shows much smaller pressure suggesting precursor condensation. For substrate holder, 7-inch quartz boat having 5 different positions or 4-inch aluminium boat having 3 different positions was used. During experiment substrate front side of holders were placed at ~3inch and ~5inch inside from furnace inlet for quartz and aluminium boat, respectively. In case of Ru, deposited film was the thickest at second position of quartz boat. This suggests that gas temperature is stabilized at 2nd position and precursor is depleted along with furnace tube length. Unlike Ru, at ALD Rh process due to precursor’s, Rh(acac)₃, high vapor pressure and its intrinsic properties, precursor depletion was detected at 5th position. Rh films at 3rd and 4th position were the thickest and film at 1st position was thinner than 2nd position indicating temperature deviation of gas between furnace inlet and inside. After load samples on substrates into furnace before each ALD process starts, ~30min. was taken in other for entire substrate to obtain thermal equilibrium. Dose times in second for each
cycle was Ar 20-precursor 3-Ar 20-oxygen 6 and Ar 15-precursor 15-Ar 15-oxygen 10 for ALD Ru and Rh, respectively. When sample is unloaded from furnace, N₂ gas was used during system vent process. As substrate, chemical silicon oxide, thermal oxide, H-terminated silicon, PVD hafnium oxide, CVD hafnium oxide, and CVD HfSiOₓ were used. To prepare substrates, silicon surfaces were oxidized by wet chemical treatment (BakerClean® JTB-100), followed by buffered HF acid dip, deionized water rinse, and N₂ flow dry. Silicon was either directly oxidized to form SiO₂, (900°C in air) or coated with thin Hf films by sputtering, followed by thermal oxidation. A micro-slide glass was used to mask parts of substrate to make step through which thickness can be measured using profilometer. Experimental schematic of films preparation using thermal ALD equipment is shown in Figure 1.4. CVD hafnium oxide and hafnium silicate as substrates were provided from Texas Instrument and Sematech. Film continuity was checked to examine metal deposition using voltmeter before further analysis. Deposited film thicknesses were measured using a Tencor Alpha-Step 500 surface profilometer. Film resistivities were measured using 4-point probe station.

Materials characterization

1) X-Ray Photoelectron Spectroscopy (XPS)

XPS was used to determine the chemical states and impurities present in the deposited films. XPS operates by exposing the sample to x-ray photons, causing photoelectron emission from specific energy levels which are characteristic of the elements present in the sample. Therefore, peaks in the detected photoelectron signal over the spectrum of kinetic
energies (which relate to binding energies) correspond to specific elements, thus indicating the presence of impurities such as possible carbon contamination from metallorganic precursors. Peaks corresponding to individual energy levels can also shift to different binding energies depending on the local bonding environments of the atoms involved, and I will use these chemical shifts to determine the oxidation states of species in the deposited films.\textsuperscript{63-65} The primary drawback of XPS is its low throughput, since the analysis chamber must be pumped down to UHV conditions.

Most of XPS analysis were conducted with a system that uses a MgK X-ray source to produce 1253.6 eV photons, and has a resolution of 0.5 eV, detection limit of about 0.5 at\%, and sampling depth of up to 100 Å.

2) Fourier Transform Infrared Spectroscopy (FTIR)

To complement the XPS, FTIR was used for fast characterization of the chemical states of impurities present in the deposited films. This technique operates by exposing the sample to an IR beam and recording the frequencies absorbed by the sample, which correspond to the specific molecular vibrational frequencies of the chemical species present. While less useful for analysis of metals and their oxidation states than XPS, FTIR is more useful for analysis of impurities and their bonding environments, and impurities such as carbon, nitrogen, and hydroxyl groups (possibly due to H\textsubscript{2}O uptake) can be readily studied. A Thermo-Nicolet Magna-750 IR spectrometer with a detection limit of about 1 at\% and detectable wavelengths from 400-4,000 Å was used for this research. Some drawbacks of this technique include poor resolution for thin films (<200 Å thick) and the inability to
examine peaks for metallic species such as hafnium compounds in the available frequency range (although far-IR characterization may also be available through collaborations with other research groups).  

3) Auger Electron Spectroscopy (AES)

As another surface analysis tool, AES was used to measure chemical compositions of deposited films. AES operates by exposing the sample to an incident electron beam, causing emission of Auger electrons from higher energy levels when a core hole is filled. As with XPS, peaks in the kinetic energy spectrum of the emitted electrons correspond to characteristic energy levels of specific elements, thus indicating the presence and relative concentrations of those elements in the sample. However, unlike XPS, relative concentrations are more easily quantified (although less chemical state information is obtained) and the technique is more effectively coupled with ion sputtering, a destructive depth-profiling technique in which the sample surface is eroded away by ion bombardment to characterize changes in chemical composition with depth (generally with a depth resolution as low as 5 Å).  

4) Atomic Force Microscopy (AFM)

To determine the root mean square (RMS) roughness and uniformity of the deposited films, AMF was used. AFM operates by bringing a cantilever-mounted probe tip close enough to the sample surface so that interatomic forces repel the tip, which is scanned across the surface so that the topography is measured by the cantilever deflection. The resulting surface can then be qualitatively examined for evidence of “island” film growth or a
polycrystalline film morphology (possibly indicating the grain size), and the surface roughness can be quantitatively measured through calculation of the RMS roughness. This research utilized a Digital Instruments DI3 model AFM with silicon Veeco Nanoprobe tips (5-10 nm radius of curvature), and RMS roughness values was extracted from 1 μm square scans conducted in tapping mode. Since ALD films are inherently smooth and uniform, uniformly low RMS roughness values (possibly remaining as low as 4-10 Å for films less than 500 Å thick, depending on the material and its morphology) over an entire sample surface would indicate true ALD growth, while non-uniformity and higher roughness values could indicate incomplete dosing of reactants, poor nucleation, or polycrystalline grain growth.

Electrical Characterization

To electrically characterize metal films deposited by ALD, MOS capacitors were fabricated and performed capacitance-voltage (C-V) measurements on them using an HP 4283A LCR meter. To characterize ALD metal films, metal was deposited on thermal SiO2 and Hi-k dielectric on p-type Si (100) wafers, then Al was deposited by evaporation on the top of ALD metal through a shadow mask and the backside of the Si sample to form the electrical contacts of the 2-terminal MOS capacitor structure. The shadow mask patterned capacitor gate dots having areas ranging from 10^{-5}-10^{-3} cm². Then ALD metal was etched off using the Al dots as a hard resist. In case of Ru, reactive ion etching was used and condition was When capacitance vs. voltage sweeps were performed at different frequencies (about 1 kHz – 1 MHz) on these capacitors using a C-V probe station, several qualitative observations
can be made about the equivalent oxide thickness (EOT), the presence of charge in the oxide, and effective work function of ALD metal. In general, the flatband voltage obtained from the C-V curves shifts to more negative voltages with the presence of positive oxide fixed or trapped charges, and to more positive voltages with the presence of negative oxide fixed or trapped charges. Shifts are identified by comparing the observed flatband voltage \( V_{FB} \) to an “ideal” value of \( V_{FB} = \phi_s - \phi_m \), where \( \phi_s \) and \( \phi_m \) are the effective work functions of the semiconductor and the gate metal, respectively. To extract parameters such as \( V_{FB} \), EOT, oxide capacitance \( C_{ox} \), flatband capacitance \( C_{FB} \), a curve-fitting program developed by Prof. J.R. Hauser at NCSU was used. From EOT vs. \( V_{FB} \) obtained from C-V analysis, the effective metal work function was extracted from the intercept of above equation.

1.7 Overview of dissertation

This dissertation has been focused on understanding ALD noble metals processes, nucleations, electrical and material properties as well as interface properties at metal/dielectric CMOS metal gate electrode applications. ALD Ru and Rh processes have been demonstrated successfully using thermal ALD on various dielectrics. ALD Ru nucleation behaviors were studied and novel area-selective deposition was demonstrated to extend of nucleation study. The effective work functions of ALD Ru and Rh were noticed to be different, which may be due to interface dipole either from intrinsic and extrinsic defects. Through interface modification ALD metal/dielectric, effective work function was
shown to be tunable. ALD growth model on H-terminated Si surface was studied and theoretical and experimental data were shown.

Chapter 2 describes demonstration of novel area selective ALD Ru deposition. The growth rate of ALD Ru is similar on various starting surfaces, but the growth initiation differed substantially. Patterned organic monolayers are used to inhibit film nucleation, enabling selective area atomic layer deposition (ALD) of ruthenium on SiO$_2$ and HfO$_2$ surfaces. It was confirmed that OTS could deactivate film growth on thermal silicon oxide and hafnium oxide surfaces by X-ray photoelectron spectroscopy (XPS). Metal-oxide-semiconductor capacitors were fabricated directly using the selective-area process.

Chapter 3 discusses a thermal process for ALD of rhodium using Rhodium(III) acetylacetonate and dry oxygen. The resistivity and XPS of Rh films were measured indicating metallic Rh. Capacitors were formed by selective area ALD of Rh onto SiO$_2$ and HfO$_2$ substrates. The effective work function as-deposited ALD Rh films were measured and observed to be higher on SiO$_2$ than on HfO$_2$ dielectrics.

Chapter 4 presents Organic self-assembled monolayers formed on SiO$_2$ and high-k dielectric surfaces on silicon can be used to modify the effective work function of ruthenium metal films deposited onto the organic layer by atomic layer deposition (ALD). Capacitance measurements of the resulting metal/dielectric/semiconductor stack show that the effective work function of the Ru can decrease by up to 0.6eV, and increase 0.2eV depending on the nature of the organic monolayer.

Chapter 5 we demonstrate the nucleation behaviors of Ru metal films deposited by ALD. ALD Ru films were deposited on chemical SiO$_2$, thermal SiO$_2$, and H-terminated Si. It was
found that hydrophilicity surface gives shorter nucleation incubation period than hydrophobic surface time with similar growth rate. ALD Ru nucleation characteristics on H-terminated Si and thermal SiO$_2$ during the incubation time were studied by XPS and AFM. ALD Ru film showed good thermal stability even after 1000°C annealing from SEM analysis comparing surface structure with as-deposited film. ALD Ru film was found polycrystalline having (002) primary structure on HfO$_2$ and thermal SiO$_2$ and (101) on HfSiO$_x$.

Chapter 6 presents results of Ru ALD nucleation on H-terminated silicon surface using XPS and AFM analysis. Silicon oxide formation was confirmed during ALD cycles from observing emerging Si2p even after 10ALD cycles. Film thickness was measured from XPS Ru3d peak values showing growth rate transient region exists. AFM roughness analysis of ALD Ru films is consistent with growth rate changing upto 100ALD cycles. Based on experimental data, simple ALD growth model was established. It was noticed that theoretical thickness from ALD model fits very well with thickness measured from XPS.
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**Figure caption:**

**Figure 1.1** The schematic of ALD process in the simplest case

**Figure 1.2** (a) The energy band diagram of a N-MOS device showing the depletion layer in the poly-Si gate. (b) The poly-Si gate depletion effect decreases the gate capacitance in the inversion regime as evident in the capacitance-voltage plot. Taken from reference 31

**Figure 1.3** The schematic of home-built hot-wall quartz tube ALD reactor

**Figure 1.4** Experimental schematic of films preparation using thermal ALD equipment
Figure 1.1

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Precursor dose

Reactant dose

Argon Purge

Argon Purge

ligand desorption

`
Figure 1.2

1. Poly-Si gate depletion layer thickness
2. Voltage drop across depletion layer
3. Inversion charge
4. Capacitance ($\mu$F/cm²) vs. Gate Voltage $V_G$ (V)

(a) Diagram showing the layers and voltage potentials.
(b) Graph showing the capacitance variation with gate voltage.

- No gate depletion
- With gate depletion effect
- Accumulation regime
- Inversion regime
Figure 1.3
Kie Jin Park
Figure 1.4

- Vent ALD chamber with N₂
- Open Quick Flange
- Unload substrate holder
- Load substrates on holder
- Close Quick Flange
- Turn on process pump
- Open process gate valve\(^1\)
- Turn off N₂ purge gas
- Wait till chamber pressure gets least 25mTorr
- Close process gate valve and open turbo gate valve\(^2\)
- Turn on a heating tape on for precursor bubble
Wait for 30min.

Close turbo gate valve and open process gate valve
Immediately
Turn process start on

Change butterfly valve switch to automatic
and program dose times and ALD cycle

Wait till Ar process completes

Turn on process start on

Wait till ALD process completes (process automatically finishes)

Change butterfly valve switch to open

Wait till chamber pressure gets least 25mTorr

Close process gate valve and open turbo gate valve

Wait for 1min.

Close turbo gate valve

Vent ALD chamber with N₂

自动控制由Labview程序

程序默认允许Ar流量30秒。

手动

*1: Process gate valve: Gate valve to process pump

*2: Turbo gate valve: Gate valve to turbo pump
CHAPTER 2. Microcontact Patterning of Ruthenium Gate Electrodes by Selective Area Atomic Layer Deposition


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Abstract

Patterned octadecyltrichlorosilane monolayers are used to inhibit film nucleation, enabling selective area atomic layer deposition (ALD) of ruthenium on SiO₂ and HfO₂ surfaces using bis-(cyclopentadienyl)ruthenium and oxygen. X-ray photoelectron spectroscopy indicated that OTS could deactivate film growth on thermal silicon oxide and hafnium oxide surfaces. The growth rate of ALD Ru is similar on various starting surfaces, but the growth initiation differed substantially. Metal-oxide-semiconductor capacitors were fabricated directly using the selective-area process. Capacitance measurements indicate the effective work function of ALD Ru is 4.84±0.1eV on SiO₂, and the effective work function is reduced on HfO₂/SiO₂ layers.
2.1 Introduction

Improved control of interface reactions during thin film processing is critical for advanced electronic and optical devices. Ruthenium is of interest for advanced metal/oxide/semiconductor (MOS) transistor gate electrodes to reduce poly-silicon depletion effects and as nucleation layer for copper interconnect layers.\(^1\) Ruthenium is considered a viable candidate for p-type MOS devices because it has a vacuum work function near the conduction band edge of silicon, good thermal stability, and low resistivity of the oxidation phase.\(^2\)

Microcontact-printed organic monolayer resists have previously been used for selective area atomic layer deposition (ALD) of oxides\(^3\)\(^-\)\(^5\) and for chemical vapor deposition (CVD) of metals.\(^6\) A previous report demonstrates selective area digital CVD Ru using patterned photoresist.\(^7\) In this work, selective deposition of Ru is demonstrated using contact printed self assembled monolayer resists by ALD processing. Also in this work, spectroscopic characterization is used to demonstrate selectivity, and the effect of processing on the monolayer structure is analyzed. Selective deposition enables direct formation of Ru/HfO\(_2\)(SiO\(_2\))/Si capacitor stacks, and the effective work function of ALD Ru is characterized on HfO\(_2\) and SiO\(_2\) dielectrics. A key problem for metals in CMOS is methodology to enable integration of two different metal work functions. Techniques to integrate two different metals in nanoscale device fabrication include selective modification of a metal, for example by interdiffusion\(^8\)\(^,\)\(^9\) or by silicide formation\(^10\), or by metal alloy formation.\(^11\) We suggest here that selective area ALD is a possible alternate route to dual-metal gate integration.
2.2 Experimental

ALD Ru was carried out in a home-built hot-wall quartz tube reactor using RuCp₂ (bis-(cyclopentadienyl)ruthenium) as a precursor and dry oxygen. RuCp₂ is solid at room temperature with vapor pressure of ~10 mTorr at the bubbler temperature of 80°C. To prepare substrates, silicon surfaces were oxidized by wet chemical treatment (BakerClean® JTB-100), followed by buffered HF acid dip, deionized water rinse, and N₂ flow dry. Silicon was either directly oxidized to form SiO₂, (900°C in air) or coated with thin Hf films by sputtering, followed by thermal oxidation. For example, the Hf based films with equivalent oxide thickness (EOT) of 30Å consisted of 11Å of sputtered hafnium followed by oxidized in N₂ (with ~20ppm O₂) at 600°C for 1 min. These conditions likely resulted in growth of HfO₂ with some interfacial HfSiOₓ and/or SiO₂. The samples are referred to here as HfO₂/SiO₂ films.

To prepare the patterned organic monolayer an elastomeric stamp was made of polydimethylsiloxane (PDMS) solution and a curing agent. The mold patterns for the PDMS stamps were micron-scale line/space photoresist and metallic dots made by physical vapor deposition of aluminum through a shadow mask. A solution of OTS (octadecyltrichlorosilane) in dry hexane (10 mM) was used as the “ink”. The OTS solution was applied to the PDMS stamp by spin coating, and the inked stamp was dried in nitrogen flow for 30s. The stamp was then brought into contact with the clean substrate and held in place for 30-60s. The resulting OTS films were characterized by water contact angle analysis, scanning force microscopy and X-ray photoelectron spectroscopy (XPS). For some measurements, OTS was also deposited by directly exposing the oxidized silicon to
its solution at room temperature. Resulting films showed a static contact angle with water to be between \(<90\) and \(110^\circ\), consistent with a range of film quality, from relatively poorly packed \((<90^\circ)\), to highly packed \((110^\circ)\) films.\(^{13,14}\) Films with contact angle \(\geq 90^\circ\) show similar results in inhibiting deposition. After exposure to 300 cycles of Ru ALD, the OTS monolayers generally showed reduced contact angle \((<80^\circ)\), indicating monolayer degradation. The results suggest that Ru nucleation is not as sensitive to quality of the monolayer surface as observed for Hf or Zr oxide\(^{15}\) and Ti based \(^{13}\) film deposition. This may be due to the higher oxygen affinity of Hf, Zr, and Ti where these metals are more likely to penetrate the monolayer and react with oxide present at the Si/monolayer interface. The OTS-patterned substrates were rinsed in hexane and deionized water, then dried with nitrogen flow before being loaded into the ALD reactor. The ALD chamber was evacuated to \(5\times10^{-6}\) Torr, and the precursor and oxidant gases were introduced into the reactor in separate pulses (3 and 6 sec, respectively) with a 20 second Ar purge between each reactant. Argon was also used as a carrier gas for the RuCp\(_2\) pulse. During the deposition, the total gas flow rate was constant at 100sccm, and the chamber was dynamically pumped to maintain pressure at 1.2 Torr. Under these conditions, self limiting growth was observed at temperatures between \(\sim310^\circ\) and \(350^\circ\)C corresponding to \(\sim1\AA\) per deposition cycle, which is larger than \(0.5\AA/\text{cycle}\) reported previously for Ru ALD.\(^{16}\) This difference is under investigation. The resulting Ru films were characterized by surface profilometry to determine thickness, and XPS was used to determine the film chemical composition. Capacitance vs. voltage (CV) was measured using an HP 4284A LCR meter at 1MHz using p-type silicon substrates with doping levels of \(1.5\times10^{18}\ \text{cm}^{-3}\).
2.3 Results and Discussion

Figure 2.1 shows Ru film thickness vs number of ALD cycles for deposition on HfO$_2$/SiO$_2$, SiO$_2$, and hydrogen-terminated silicon (HF-last) surfaces. For deposition on the HF-last, no film was observed by eye after 100 cycles for the conditions used. Also, on the OTS surface, no film was observed by XPS (vide infra) for up to 300 cycles studied. The inset in Figure 2.1 is an optical image of a selectively deposited Ru capacitor on HfO$_2$/SiO$_2$ using the OTS monolayer resist. The deposited thickness per cycle was similar on SiO$_2$, HfO$_2$/SiO$_2$, and Si-H, but the intercepts show different values, consistent with different incubation times for growth on these surfaces. However, details of growth incubation require more investigation of thin (<100Å) layer growth. Figures 2.2(a) and 2(b) show XPS spectra after 150 cycles of selective ALD Ru at 325 °C on clean SiO$_2$ and on SiO$_2$ covered with microcontact-stamped OTS. Figure 2(b) shows that the Ru 3p peaks are not observed on the OTS covered regions after ALD, indicating good selectivity to Ru growth with this monolayer surface (static contact angle for this sample was 92° before Ru deposition). The measured Ru 3p$^{1/2}$ and 3p$^{3/2}$ peak positions at 484 and 462eV, and the width of the peaks are consistent with the presence of several Ru oxidation states from elemental Ru to mildly oxidized RuO$_x$. Presence of RuO$_x$ is confirmed by the existence of the O1s peak, although it is possible that most of the O is confined to the surface. Because of overlap of C1s and Ru3d peaks, it is difficult to calibrate the XP spectrum energy scale to compensate for surface charge. The spectrum from the Ru film shows a small signal from the Si substrate peak at 98.7eV, close to the expected value of 99.3eV.
Figure 2.3(a) shows CV characteristics of capacitors formed using selective area Ru deposition. For comparison, some capacitors (shown in figure 3(b)) were formed using blanket Ru followed by sputtered Al through a shadow mask and Ru dry etching. Before measurement, all capacitors received a post-metal anneal consisting of N$_2$:H$_2$=10:1 at 400°C for 30min. The CV behavior of the selective ALD Ru capacitor shows a flatband voltage ($V_{FB}$) of -0.2V and equivalent oxide thickness of 30Å as determined using the Hauser CV fitting procedure. For the sputtered Al / ALD Ru capacitor, $V_{FB}$ is -1.5V, consistent with a larger concentration of positive fixed charge in the dielectric induced by the Al sputter process that is not completely removed by the post-metal anneal.

A key question for advanced gate metals is the effective work function in a capacitor structure. The CV curves were analyzed for a range of dielectric film thickness, and the results of $V_{FB}$ versus EOT are shown in Figure 2.4. For the HfO$_2$/SiO$_2$ samples, determination of the effective work function ($\phi_{eff}$) from CV data must consider the effect of charge at the SiO$_2$/Si interface, as well as charge at any internal interface in the dielectric stack. The data presented in Figure 2.4 is not sufficient to unambiguously differentiate these interface charge densities, but the linear fit indicates that the bulk charge is relatively small in these films. For the case of Ru on SiO$_2$, the intercept $\phi_{ns} = \phi_{eff} - \phi_s$ where $\phi_s$ is the semiconductor work function. In this case, $\phi_{eff}$ is determined to be 4.84±0.1eV. The slope shows a high positive charge density at the Si/SiO$_2$ interface. The more negative intercept for Ru on HfO$_2$/SiO$_2$ suggests a somewhat smaller $\phi_{eff}$ at the (HfO$_2$)/Ru interface, which is consistent with a different interface dipole due to differences in dielectric screening and charge neutrality levels in SiO$_2$ and HfO$_2$. For the Ru films reported here, Auger
analysis indicates O/Ru ratio of ~3% and resistivity values ranged from 35 to 20µΩ⋅cm. An effective work function of 5.1eV has been reported for CVD Ru on HfO₂, where the Ru contains a higher concentration of oxygen.⁷

Another problem with metal gate integration in complementary MOS technology is the potential need for two different metal gate materials for adjacent n-type and p-type MOS transistors. Processes that can selectively place one metal on a predetermined area of a substrate may provide a possible route to dual metal gate processing, to eliminate the need for a potentially damaging metal etch step. Alternate passivating approaches, beyond the OTS monolayer demonstrated here, would be helpful to further simplify processing requirements.

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Reference


Figure captions

**Figure 2.1** Ruthenium film thickness vs. number of ALD cycles as deposited on HfO$_2$, SiO$_2$ and Si-H (HF-last) surfaces, compared to deposition on OTS covered substrate. The data point at zero thickness for growth on Si-H is determined from visual inspection. The data point at zero thickness for growth on OTS is determined from XPS. Visual inspection shows clear selectivity on OTS for all conditions studied (up to 300 cycles). The error bar for each substrate represents typical measurement error (±5%) of profilometer. The inset shows an optical image of a selectively deposited Ru (100µm diameter) metal on HfO$_2$.

**Figure 2.2** (a) Survey scan, and (b) Ru Ru3p region from XPS analysis of a SiO$_2$ partially covered with OTS after 150 Ru ALD cycles at 325ºC.

OTS: region with OTS covered, ALD Ru: Ru covered after on HfO$_2$ and SiO$_2$ compared to deposition on OTS covered substrate.

**Figure 2.3** Capacitance-Voltage behaviors of MOS capacitors

(a) Selectively deposited ALD Ru MOS

(b) Conventionally processed MOS

**Figure 2.4** $V_{FB}$ versus EOT for Ru/SiO$_2$/Si and Ru/HfO$_2$/Si Capacitors.

Quality of fittings (R): 0.9, the doping density of p-type Si: $1.5 \times 10^{18}$/cm$^3$, $\phi_{ms}$: the work function difference between metal and silicon substrate
Figure 2.2
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(a)

(b)

Ru3p

OTS

ALD Ru

N(E)/E

Binding Energy (eV)

490 485 480 475 470 465 460 455

1200 1000 800 600 400 200 0

N(E)/E

Ru3p/C1s

C(KLL) O(KVV)

Si2s Si2p

OTS

ALD Ru

Binding Energy (eV)
Figure 2.3
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(a) $V_{FB} = -0.2\text{V}$

(b) $V_{FB} = -1.5\text{V}$
Figure 2.4
Kie Jin Park

\[ \Phi_{ms} = -0.4V \]

\[ \Phi_{ms} = -0.26V \]

\( N_f = 9.2 \times 10^{11} \text{ /cm}^2 \)

\( N_f = 2.73 \times 10^{12} \text{ /cm}^2 \)
CHAPTER 3. Atomic Layer Deposited Rhodium for PMOS Gate Electrode Applications

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Abstract

A thermal process for atomic layer deposition (ALD) of rhodium was investigated using Rhodium(III) acetylacetonate (Rh(acac)\textsubscript{3}) and dry oxygen. For these precursors, atomic layer deposition was observed with ~0.9Å per deposition cycle within a temperature window from 275 to 310°C. The resistivity of Rh films was observed to decrease with increasing deposition temperature, and a resistivity of ~10\(\mu\)Ω⋅cm was obtained at 300°C. X-ray photoelectron spectroscopy showed carbon content below the detection limit (0.5 at.%) and a few at.% of oxygen, consistent with low resistivity metallic Rh. Deposition onto patterned photoresist resulted in selective area growth, and capacitors were formed by selective area ALD of Rh onto SiO\textsubscript{2} and HfO\textsubscript{2} substrates. Capacitance vs. voltage measurements were used to extract the effective work function of the metal in the capacitor structure, and for as-deposited ALD Rh films, the effective workfunction was observed to
be 5.43eV and 5.25eV on SiO₂ and HfO₂ dielectrics, respectively. These values are 0.5eV larger than for ALD ruthenium films deposited in the same reactor, and the results suggest that Rh may be a possible candidate for a metal gate electrodes in p-type transistor devices.
3.1 Introduction

Metals are of interest for advanced metal/oxide/semiconductor (MOS) transistor gate electrodes to reduce poly-silicon depletion effects. Noble metals are considered viable candidates for PMOS devices because it has a vacuum work function near the conduction band edge of silicon, good thermal stability, and low resistivity of the oxidation phase. Noble metals, including Pt, Ru, Ir and Pd have been formed by atomic layer deposition (ALD) for applications as gate metal electrodes and as nucleation layers for copper interconnect layers. In recent work, the effective work function, $\Phi_{\text{m, eff}}$, of ALD Ru has been measured to be 4.7-4.9eV, which is below the value of 5.2eV desired for PMOS metal gates. Moreover, the value of $\Phi_{\text{m, eff}}$, on high-k dielectrics (4.7eV) is generally somewhat lower than on SiO$_2$ (~4.9eV), making implementation into high-k gate stacks more challenging. This article presents initial results of thermal ALD rhodium deposited by rhodium(III) acetylacetonate (Rh(acac)$_3$) and dry oxygen, including composition and electrical characterization in metal oxide semiconductor (MOS) capacitors. Selective deposition of Rh using patterned photoresist has been characterized, and it enables direct formation of Rh/HfO$_2$(SiO$_2$)/Si capacitor stacks. The effective work function of ALD Rh is characterized on HfO$_2$ and SiO$_2$ dielectrics.

3.2 Experimental

ALD Rh process was carried out in a home-built hot-wall quartz tube reactor using Rh(acac)$_3$ as a precursor and dry oxygen. Rh(acac)$_3$ is solid at room temperature with vapor
pressure of ~20mTorr at the bubbler temperature of 150°C. The ALD chamber was evacuated to 5x10^{-6} Torr, and the precursor and oxidant gases were introduced into the reactor in separate pulses (15 and 10 sec, respectively) with a 15 second Ar purge between each reactant. Argon was also used as a carrier gas for the Rh(acac)$_3$ pulse. During the deposition, the total gas flow rate was constant at 300sccm, and the chamber was dynamically pumped to maintain pressure at 0.9 Torr. ALD Rh films were deposited on chemical vapor deposited HfO$_2$ and thermally grown SiO$_2$. Under these conditions, self limiting growth was observed at temperatures between ~275º and 310ºC corresponding to ~0.9Å per deposition cycle, consistent with a previous report. The resulting Rh films were characterized by surface profilometry and atomic force microscopy to determine thickness and surface roughness, and X-ray photoelectron spectroscopy (XPS) was used to determine the film composition. The film resistivity was measured with a four-point probe, and capacitance vs. voltage (CV) was measured using an HP 4284A LCR meter at 1MHz using p-type silicon substrates with doping levels of 7x10^{17} and 3x10^{15} cm$^{-3}$ for SiO$_2$ and HfO$_2$, respectively.

3.3 Results and Discussion

Figure 3.1 shows ALD Ru film growth rate vs. deposition temperature on HfO$_2$. All other process conditions were held fixed using values given above. The plateau in growth rate vs. temperature is typical of self-limiting ALD film growth, where the self limiting reaction proceeds, in this case, between about 275 and 310 ºC. The lower growth rate at lower temperature is consistent with the reaction being limited by precursor adsorption, and
the higher rate at elevated temperature is consistent with precursor dissociation in a chemical vapor deposition process. Figure 3.2 shows Rh film thickness vs number of ALD cycles for deposition on HfO$_2$ using a fixed growth temperature of 300°C. An error bar obtained from ±1 standard deviation of multiple measurements per one sample is included. A linear relation is observed between Rh film thickness and ALD cycle number, and the slope gives a growth rate of ~0.9 Å/cycle. XPS spectra of ALD Rh deposited on silicon oxide are shown in Figure 3.3, where approximately 10 Å of the top surface was sputtered in the UHV chamber prior to XPS analysis to remove adventitious surface oxygen and carbon. The measured Rh 3d$^{3/2}$ and 3d$^{5/2}$ peak positions at 312.5 and 307.7 eV having 2:3 of the ratio peaks, and no C1s and very small O1s peaks are consistent with metallic Rh film. The spectra are referenced to the adventitious carbon peak at 285 eV measured before surface sputter cleaning. The sensitivity of XPS is about 0.5% and atomic ratio of O/Rh in ALD Rh film is ~ 0.09. The oxygen sensitivity factor is small in XPS, making oxygen content is difficult to quantify. Figure 3.4 shows Rh film resistivity as a function of deposition temperature. Resistivity decreases with increasing temperature and reaches a minimum of 10 µΩ⋅cm at 300°C, consistent with the bulk resistivity of Rh of 4.3 µΩ⋅cm.

Figure 5 (a) and (b) show CV characteristics of capacitors formed using Rh on HfO$_2$ and SiO$_2$. To form capacitors, photoresist (~1 µm) was first deposited on SiO$_2$ and HfO$_2$ and patterned, then hard-baked at 100°C for 5 min. Films were then transferred into the deposition chamber and heated at the deposition temperature for 15 min before deposition was initiated. After 200 cycles, deposition was visible on the oxide, with no visible deposition on the photoresist, consistent with inhibited Rh nucleation on the organic
This selective-area deposition eliminated the need for Rh etching, and the CV behavior could be evaluated directly upon removal of the samples from the reactor system. Resulting CV curves (Figure 3.5) show typical metal-oxide-semiconductor behavior, with a flatband voltage ($V_{FB}$) and equivalent oxide thickness (EOT) determined using the Hauser CV fitting procedure. To extract the effective work function of the gate electrode in the metal/oxide/semiconductor stack, the flat band voltage ($V_{FB}$) was measured for several capacitors with various equivalent oxide thickness. $V_{FB}$ is plotted versus EOT in Figure 3.6 for ALD Rh on HfO$_2$ and SiO$_2$. The effective work functions of as-deposited ALD Rh on HfO$_2$ and SiO$_2$ were extracted to 5.43 and 5.25eV from the intercept values of $V_{FB}$ vs EOT. From the slopes of $V_{FB}$ vs EOT, it was observed that a negative fixed charge density ($1.5 \times 10^{12}$ cm$^{-2}$) at the Si/HfO$_2$ interface and a positive fixed charge density ($8.1 \times 10^{11}$ cm$^{-2}$) at Si/SiO$_2$ interface. Also included in Figure 3.6 are results from CV analysis of ruthenium films deposited in the same reactor system, using similar dielectric materials. It is interesting to note that the slopes of the lines are the same, but the intercepts shift up by ~0.5eV, consistent with an effective workfunction that is 0.5eV larger for Rh than for Ru. The high values of effective workfunction observed for Rh meet the values required for PMOS metal gate electrodes. It is important to note that metal gate electrodes typically have to undergo a high temperature anneal in device processing, and the effect of anneals on materials properties are currently under investigation. Figure 3.7 shows atomic force microscope images of ALD Rh films after 150 cycles on HfO$_2$, SiO$_2$, and H-terminated Si substrates. The surface roughness of the ALD Rh on H-terminated Si surface was much bigger than on HfO$_2$ and SiO$_2$, similar to that observed for Ru ALD which indicates a
strong dependence of the surface energy of the initial starting surface in determining the nature of nucleation in Rh ALD.

We gratefully acknowledge support from SEMATECH and the Semiconductor Research Corporation (SRC) under the Front End Processing Research Center.
Reference

5 T. Aaltonen, J. Hamalainen, M. Ritala, and M. Leskela, in ALD of Rhodium, RhO2, and IrO2, San Jose, CA, 2005.
Figure captions

Figure 3.1 ALD Ruthenium film growth rate vs. deposition temperature as deposited on CVD HfO₂ substrate

Figure 3.2 Rhodium film thickness vs. number of ALD cycles deposited on HfO₂

Figure 3.3 XPS analysis of ALD Rh film on SiO₂
(a) Rh3d (b) O1s (c) C1 after 150 Rh ALD cycles at 300 ºC.

Figure 3.4 Resistivity of ALD Rhodium and Ruthenium films vs. deposition temperature

Figure 3.5 Capacitance-Voltage behaviors of selectively deposited ALD Rh MOS capacitors
(a) on CVD HfO₂
(b) on SiO₂

Figure 3.6 V FB versus EOT
(a) Rh/SiO₂/Si and Ru/SiO₂/Si
(b) Rh/HfO₂/Si and Ru/HfSiOₓ/Si
Quality of fittings (R): 0.9, p-type silicon substrates with doping levels of 7x10¹⁷ and 3x10¹⁵ cm⁻³ for SiO₂ and HfO₂, respectively.
**Figure 3.7** AFM images of ALD Rh films on (a) CVD HfO2, (b) SiO2, and (c) H-terminated surface
Figure 3.1
Kie Jin Park

![Graph showing growth rate (Å/cycle) vs. temperature (°C) for different processes and pressures. The graph includes markers for ALD and CVD, with a pressure of 0.9 Torr.]
Figure 3.2
Kie Jin Park

![Graph showing the relationship between ALD cycle and thickness (Å). The graph is linear with data points and error bars indicating variability.](image-url)
Figure 3.3
Kie Jin Park

(a) Rh3d

(b) C1s

(c) O1s
Figure 3.4
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Rhodium

Ruthenium

Resistivity (µΩ·cm)

ALD Temperature (°C)
Figure 3.5
Kie Jin Park

(a)

(b)
Figure 3.6
Kie Jin Park

(a) Flatband Voltage (V) vs. EOT (nm) for Rhodium and Ruthenium,
(b) Flatband Voltage (V) vs. EOT (m) for Rhodium and Ruthenium.
Figure 3.7
Kie Jin Park

(a) 

(b) 

(c)
CHAPTER 4. Work Function Tuning in MOS Capacitors with Atomic Layer Deposition of Ru onto Self-Assembled Organic Monolayer

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Abstract

Organic self-assembled monolayers formed on SiO$_2$ and high-k dielectric surfaces on silicon can be used to modify the effective work function of ruthenium metal films deposited onto the organic layer by atomic layer deposition (ALD). Ruthenium films deposited by ALD using bis-(cyclopentadienyl) ruthenium and oxygen at 325°C are found to nucleate and grow on several organic surface monolayers including 3-aminopropyltriethoxysilane (APS) and undecenyl tricholosilane (UDS). Capacitance measurements of the resulting metal/dielectric/semiconductor stack show that the effective work function of the Ru can decrease by up to 0.6eV, and increase 0.2eV depending on the nature of the organic monolayer. The shifts are consistent with expected dipoles present at the organic/dielectric interface.
4.1 Introduction

It is well known that the processes governing nucleation of Ru during atomic layer deposition (ALD) depend strongly on the nature of the precursors used for deposition and the substrate surface.\textsuperscript{1,2} For the case of deposition from ruthenocene, surfaces that are more hydrophobic, such as Si-H, methyl-terminated organic monolayers, or some photoresist surfaces, tend to inhibit nucleation and can allow for selective area deposition. Nucleation is less inhibited on more hydrophilic surfaces such as SiO\textsubscript{2} and HfO\textsubscript{2}, although more understanding of how to achieve well defined two-dimensional growth is a current topic of research\textsuperscript{3-5}

Metal gate electrodes are also being actively researched as possible replacements to current polycrystalline silicon gates used in metal/oxide/semiconductor transistor devices. Metal gates can eliminate charge depletion effects in polycrystalline silicon and thereby increase the overall gate capacitance. Significant challenges for metal gate electrodes include defining viable gate electrode materials with Fermi levels near the valence and conduction band of silicon (4.0 and 5.2 eV, respectively), and identifying fabrication pathways to allow integration of two different gate materials into the device manufacturing process flow. To achieve optimum material performance, there is interest in methods to modify and tune the effective work function of advanced metal gates. Various approaches for tuning the effective metal work function have been studied, including nitrogen implantation\textsuperscript{6}, interdiffusion\textsuperscript{7,8}, alloy formation\textsuperscript{9}, and nanolaminate structures.\textsuperscript{10-13} It is well known that an adsorbate on a clean metal surface will alter the energy required for electron extraction from that surface\textsuperscript{14}(i.e. the effective metal work function $\Phi_{m,\text{eff}}$). Also, if the adsorbate
carries a dipole moment, the change in effective work function upon adsorption will depend on the magnitude and direction of that dipole moment.\textsuperscript{15,16} For this article, we investigated possible mechanisms associated with work function modulation of ruthenium metal. Specifically, the shift in effective metal work function in MOS structures was studied by introducing organic monolayers or chemical pretreatment at the metal/insulator interface before metal deposition by ALD. Many of these processes and materials are not likely candidates for inclusion in MOS device fabrication. However, the viability of achieving work function modulation of a metal by careful deposition of that metal onto an organic surface is demonstrated.

4.2 Experimental

ALD Ru was carried out in a home-built hot-wall quartz tube reactor using RuCp\textsubscript{2} (bis-(cyclopentadienyl)ruthenium) as a precursor and dry oxygen. RuCp\textsubscript{2} is solid at room temperature with vapor pressure of \textasciitilde 10 mTorr at the bubbler temperature of 80\textdegree C. Silicon was either directly oxidized to form SiO\textsubscript{2}, (900\textdegree C in air) or coated with thin Hf films by sputtering, followed by thermal oxidation. These conditions likely resulted in growth of HfO\textsubscript{2} with some interfacial HfSiO\textsubscript{x} and/or SiO\textsubscript{2}. The samples are referred to as HfO\textsubscript{2}/SiO\textsubscript{2} films. CVD HfSiO\textsubscript{x} on silicon substrates was used as dielectric layers in capacitors for interface modification experiments.

Solutions of 1\% 3-aminopropyltriethoxysilane (APS) and 0.1\% undecenyltrichlorosilane (UDS) in dry toluene were prepared and deposited by directly exposing HfSiO\textsubscript{x} to its solution at room temperature before ALD Ru process. The resulting APS and UDS films
were characterized by water contact angle analysis, and attenuated total reflection-fourier transform infrared spectroscopy (ATR-FTIR).

Resulting films showed contact angles with deionized water to be 35° and 47° for APS with two different HfSiOₓ pretreatments and 95° for UDS surface. After exposure to 150 cycles of Ru ALD, Ru films were obtained on top of APS and UDS. For chemical pretreatment of HfSiOₓ surface before ALD Ru process, HfSiOₓ on Si was exposed in 1N nitric acid aqueous solution for 15hrs at room temperature.

The APS and UDS treated substrates were sonicated in toluene, and then dried with nitrogen flow before being loaded into the ALD reactor. The ALD chamber was evacuated to 5x10⁻⁶ Torr, and the precursor and oxidant gases were introduced into the reactor in separate pulses (3 and 6 sec, respectively) with a 20 second Ar purge between each reactant. Argon was also used as a carrier gas for the RuCp₂ pulse. During the deposition, the total gas flow rate was constant at 100 standard cubic centimeters per minute (sccm), and the chamber was dynamically pumped to maintain pressure at 1.2 Torr. Capacitance vs. voltage (CV) was measured using an HP 4284A LCR meter at 1MHz using p-type silicon substrates with doping levels of 1.5x10¹⁸ cm⁻³ for SiO₂ and HfO₂ substrates and 1.5x10¹⁵ for HfSiOₓ substrate.

**4.3 Results and Discussion**

The CV curves for ALD Ru capacitors on SiO₂, HfO₂/SiO₂, and HfSiOₓ were analyzed for a range of dielectric film thickness, and the results of flatband voltage (V_{FB}) versus equivalent oxide thickness (EOT) using the Hauser CV fitting procedure¹⁷ are shown.
in Figure 4.1. If there is minimal bulk charge in the dielectric, then $V_{FB}$ is expected to be linearly related to EOT shown in equation (1)

$$V_{FB} = \phi_{ms} - \frac{1}{\varepsilon_{ox}} Q_E O T,$$  \hspace{1em} (1)

where the intercept is a measure of the effective metal work function in the capacitor structure. From the intercepts of Figure 1, the effective work functions of ALD Ru were found to be 4.84eV, 4.7eV, and 4.68eV on SiO$_2$, HfO$_2$, and HfSiO$_x$, respectively. The effective work function of ALD Ru on Hf based dielectrics is somewhat smaller than on thermal oxide, possibly due to differences in interface dipoles of Ru on Hf based dielectrics and SiO$_2$. This is consistent with expected trends in work function shift caused by MIGS. Effective work function changes with fermi pinning parameter (S) which depends on the electronic component of the dielectric constant $\varepsilon_\infty$ in equation (2) from MIGS model. $S$ value of HfO$_2$ is known lower than SiO$_2$.

$$\Phi_{m,\text{eff}} = \Phi_{\text{CNL,d}} + S(\Phi_{m,\text{vac}} - \Phi_{\text{CNL,d}}),$$ \hspace{1em} (2)

where $\Phi_{m,\text{eff}}$, $\Phi_{m,\text{vac}}$, $\Phi_{\text{CNL,d}}$ are effective metal work function, vacuum metal work function, and charge neutrality level potential in the dielectric layer.\textsuperscript{18} Another possibility might be interface dipole from extrinsic state created from oxygen vacancy (O$_v$) or chemical bonding at metal/dielectric interface.\textsuperscript{19} In this case, electronegativity difference between Si-Ru and Hf-Ru or Si-O$_v$-Ru and Hf-O$_v$-Ru makes dipole. Since Hf has smaller electronegativity than Si, Hf-base dielectrics/Ru have bigger negative dipole in Ru than SiO$_2$/Ru so that effective Ru work function on Hf-based dielectrics is smaller.
Hafnium silicate films were exposed to a nitric acid treatment before ALD Ru deposition, and $V_{FB}$ versus EOT for these films is compared to that for untreated films in Figure 4.2. The intercept for the treated surface gives $\Phi_{m,eff} = 4.5$eV suggesting dipole change at metal/dielectric interface by nitric acid treatment. Larger positive pole pointing toward dielectric compare to untreated surface is believed formed due to the nitric acid treatment. ATR-FTIR spectra of APS and UDS are shown in Figure 4.3. Results of CV analysis for the APS and UTS treated surfaces are shown in Figure 4.4. The APS treated surface shows an increase in $\Phi_{m,eff}$ to be about 4.8~4.95eV which is ~ 0.1-0.25eV larger than the untreated sample. On the other hand, the UTS treated surface shows $\Phi_{m,eff}$ to be about 4.1eV, which is a full 0.6eV less than the untreated surface. A common process in device fabrication is to anneal MOS capacitors after gate electrode formation in forming gas at 400~450°C. Figure 4.5 shows that Ru deposited on APS and UTS were exposed to forming gas anneal, and the results showed significant changes in the CV curves, likely due to decomposition of the organic layers. It is also important to note that the organic monolayer likely undergoes some reaction and modification during the metal ALD process. The detailed mechanisms associated with work function modulation, and the particular relation to monolayer structure are not clearly understood. Nevertheless, it is concluded that the work functions shifts from nitric acid treatment and organic monolayers attachment caused the net interface dipole changes by intrinsic state and/or extrinsic states at the metal/dielectric interface. Permanent dipole moment of attached molecules also affect work function shift.\textsuperscript{14} It is known that amine terminated organosilane molecule has dipole
moment directing dielectric.\textsuperscript{20} This is consistent with decreasing effective Ru work function by APS.

This work has demonstrated the use of organic monolayer integration into MOS processing for tuning the effective work function of advanced metal gate electrodes. While the processes described are not suitable for direct introduction into CMOS device processing, the chemical mechanisms associated with interface dipole modification at the molecular level may lead to future processes or device structures to extend electronic device performance or functionality.

We acknowledge support from SEMATECH and the Semiconductor Research Corporation, and support from NSF under CTS - 0072784.
Reference


Figure captions

**Figure 4.1** $V_{FB}$ versus EOT for Ru/SiO$_2$/Si, Ru/HfO$_2$/Si, and Ru/HfSiO$_x$/Si Capacitors. The intercept gives $\Phi_{m,\text{eff}} = 4.84\text{eV on } \text{SiO}_2$, $4.7\text{eV HfO}_2$, $4.68\text{eV HfO}_2$ surfaces

**Figure 4.2** $V_{FB}$ vs EOT for Ru on HfSiO$_x$ films with nitric acid pretreatment steps before metallization. The nitric acid pretreated HfSiO$_x$ shows a change in intercept consistent with a 0.2eV decrease in effective metal work function

**Figure 4.3** ATR-FTIR spectrums of monolayers on HfSiO$_x$

(c) 3-aminopropyltriethoxysilane (APS)

(d) Undecenyltrichlorosilane (UDS)

**Figure 4.4** $V_{FB}$ vs EOT for Ru on HfSiO$_x$ films with two different organic layer pretreatment steps before metallization. The APS monolayer shows a change in intercept consistent with 0.1~0.4eV increases in effective metal work function, and the UTS monolayer shows a 0.6eV decrease in $\Phi_{m,\text{eff}}$

**Figure 4.5** $V_{FB}$ vs EOT after post metallization annealing for Ru on HfSiO$_x$ films with a APS monolayer before metallization.

Post metallization annealing: $N_2:H_2 = 10:1$, 400°C x 30min.
Figure 4.1
Kie Jin Park

![Graph showing flatband voltage vs. EOT for different EOT values on SiO2, HfO2, and HfSiOx layers.](image)

- $N_f = -1.49 \times 10^{12} \text{ /cm}^2$
- $N_f = 9.2 \times 10^{11} \text{ /cm}^2$
- $N_f = 2.73 \times 10^{12} \text{ /cm}^2$
Figure 4.2
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-0.23
-0.42

No pretreatment
Nitric acid pretreated

Flatband Voltage (V)
EOT (nm)

0 2 4 6 8 10 12

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Figure 4.3
Kie Jin Park
Figure 4.4
Kie Jin Park

![Graph showing the relationship between Flatband Voltage (V) and EOT (nm) for different treatments.](image-url)
Figure 4.5
Kie Jin Park

![Graph with x-axis labeled EOT (nm) and y-axis values ranging from -0.5 to 1.5, showing scattered data points.](image-url)
CHAPTER 5. The Nucleation Characteristics of Ruthenium Metal Film by Atomic Layer Deposition

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Abstract

The nucleation behaviors of Ru metal films were studied deposited by atomic layer deposition (ALD) using Ruthenocene precursor and oxygen reactant. ALD Ru films were deposited on chemical SiO\textsubscript{2}, thermal SiO\textsubscript{2}, and H-terminated Si. It was found that hydrophilicity surface gives shorter nucleation incubation period than hydrophobic surface time with similar growth rate. ALD Ru nucleation characteristics on H-terminated Si and thermal SiO\textsubscript{2} during the incubation time were studied by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). XPS Ru 3p analysis suggests ALD Ru growth rates are changing during nucleation incubation period. SiO\textsubscript{2} formation was observed from XPS Si 2p during incubation period on H-terminated Si surface. ALD Ru film showed good thermal stability even after 1000°C annealing from SEM analysis comparing surface structure with as-deposited film. ALD Ru film was found polycrystalline having (002) primary structure on HfO\textsubscript{2} and thermal SiO\textsubscript{2} and (101) on HfSiO\textsubscript{x}. 

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5.1 Introduction

Metallic gates have been studied as alternate gate electrodes for poly-Si in CMOS devices. Ruthenium is of interest for a potential material for PMOS gate metal because of its high vacuum work function (4.7~5.2eV), good thermal stability, and low resistivities of its oxidation phase.\textsuperscript{1,2} Ru also has been considered to be for capacitor electrodes in dynamic random access memories (DRAMs)\textsuperscript{3-6} and in ferroelectric random access memories (FRAMs).\textsuperscript{7,8}

Ru films by physical vapor deposition (PVD)\textsuperscript{9,10} and chemical vapor deposition (CVD)\textsuperscript{11-13} have been studied. However, the trend of CMOS devices requires more conformal and less impurity thin film. It has been reported that atomic layer deposition (ALD) process has high conformality and control of film thickness due to its self-limiting process.\textsuperscript{14} Although ALD Ru process has been reported\textsuperscript{15}, ALD Ru film nucleation behaviors have rarely been studied. In this paper, we report substrate dependence on ALD Ru film nucleation behaviors such as surface roughness, growth rate, and nucleation incubation time. Surface hydrophilicity was found to have interesting relations with ALD Ru nucleation behaviors. On H-terminated Si surface having longest incubation time among surfaces used in our study, ALD Ru nucleation during initial nucleation period was investigated by X-ray photoelectron spectroscopy (XPS). Surface roughness propagation of ALD Ru by AFM was consistent with XPS analysis. Polycrystalline structures of ALD Ru on HfO\textsubscript{2}, HfSiO\textsubscript{x}, and SiO\textsubscript{2} were determined from X-ray diffraction analysis (XRD).
5.2 Experimental

ALD Ru was carried out in a flow-type tube reactor using bis-(cyclopentadienyl)ruthenium (RuCp₂) as a precursor and oxygen. RuCp₂ is solid at room temperature with vapor pressure of ~10mTorr at the bubbler temperature of 80°C. The processing pressure and substrate temperature were fixed at 1.2 torr and 325°C, respectively. The process gas flow rates were 100 standard cm³ per minute (sccm). Ar gas was used as carrier gas and purging gas between precursor and reactant doses. Substrates used are thermal SiO₂ (grown at 900°C in air), chemical SiO₂ prepared by SC1 solution 16, and H-terminated Si formed by 1% HF acid dip. Initially, silicon surfaces were oxidized by wet chemical treatment (BakerClean® JTB-100), followed by buffered HF acid dip, deionized water rinse, and N₂ flow dry. Another set of surfaces was dielectric substrates including thermal SiO₂, HfO₂, and CVD HfSiO₃. HfO₂ on silicon substrate was formed with Hf films by sputtering, followed by thermal oxidation in N₂ (with ~20ppm O₂) at 600°C for 1 min. 17 The ALD Ru film thicknesses on different substrates were measured using a Tencor Alpha-Step 500 surface profilometer. The roughness and grain size comparison of ALD Ru films on various substrates were measured from AFM and SEM. Contact angles to find out initial substrate hydrophilicity before ALD process were characterized using deionized water. ALD Ru films were deposited on H-terminated Si surface with 0, 10, 40, 70, 100, 150 cycles and analyzed with XPS and AFM for investigation of incubation nucleation. To find out crystalline structures of ALD Ru on various dielectric surfaces, XRD 2θ scan was done. To observe annealing effect on ALD Ru film, forming gas annealing in N₂:H₂=10:1 at 400°C for 30 minutes, and rapid thermal annealing (RTA) in N₂.
atmosphere at 1000°C for 10 second were done on HfSiOₓ surface, followed by SEM image analysis compare to as-deposited ALD Ru film.

5.3 Results and Discussion

Figure 5.1 shows Ru film thickness vs. number of ALD cycles for deposition on chemical SiO₂, thermal SiO₂, and H-terminated Si surface. It was observed that ALD Ru film growth rates for all three substrates are similar by the slopes of curves. The ALD Ru on H-terminated substrate has longer initial nucleation period than on thermal and chemical SiO₂ surfaces; the x-intercepts for the different substrates, shown in Figure 1, define the “nucleation incubation time” which is the cycle where film start to grow with a constant growth rate. Water contact angle of chemical SiO₂ surface is smaller than that of thermal SiO₂ and that of H-terminated Si surface is biggest as expected indicating the most hydrophobic surface. As a result, Figure 5.2 shows that incubation time of ALD Ru is proportional to water contact angle of initial substrate. In other words, ALD Ru incubation time for hydrophobic substrate is longer than that for hydrophilic substrate. AFM and SEM images show that ALD Ru film on chemical SiO₂ surface has smaller grain and smoother than on H-terminated Si surface shown in Figure 5.3. XPS Ru 3p₃/₂ peaks for ALD Ru films on H-terminated Si deposited from 0, 10, 40, 70, 100, and 150 ALD cycles were measured shown in Figure 5.4 (a). It was observed that the Ru 3p₃/₂ peak intensity at 100 ALD cycle was much bigger than at 70 cycles and peak intensities up to 70 cycles from 10 cycles increase relatively slowly. XPS Si 2p peaks at 99.8eV for silicon substrate are decreased with ALD Ru cycles shown in Figure 5.4 (b). Starting from 10 ALD cycles, Si2p
peaks at ~103eV appear and increase with ALD cycles suggesting SiO$_2$ formation during ALD Ru process. Figure 5.5 shows ALD cycle versus Ru film thickness measured from profilometer and XPS. Thickness from XPS peak values were calibrated Ru 3p$_{3/2}$ peak at 150 cycle corresponding to 60Å. This result suggests ALD Ru growth rate changes with ALD cycles until about 100 cycles and becomes constant afterward. Figure 5.6 shows RMS roughness by AFM for ALD Ru films on H-terminated Si surface and thermal SiO$_2$ deposited at various ALD cycles. ALD Ru film roughness increases with ALD cycle very sharply up to 100 and 50 cycles for H-terminated Si and thermal SiO$_2$, respectively. This is consistent with smaller incubation time of ALD Ru on SiO$_2$ than on H-terminated Si surface. Anealing effect on ALD nucleation was investigated as shown in Figure 5.6. Figure 5.7 shows that as-deposited ALD Ru film has fine grain size of crystalline and secondary microstructures. After annealed at 400°C in forming gas, the secondary structure disappears and primary microstructure gets bigger. ALD Ru has no film discontinuity even after 1000°C annealing in N$_2$ atmosphere though the microstructure becomes much bigger indicating Ru film agglomeration. As expected ALD Ru is polycrystalline film shown in Figure 5.8 and has primary (002) structure top of HfO$_2$ and thermal SiO$_2$ while (101) structure is primary on HfSiO$_x$.

5.4 Conclusion

The nucleation behaviors of ALD Ru metal films using Ruthenocene precursor and oxygen reactant on chemical SiO$_2$, thermal SiO$_2$, and H-terminated Si were studied. ALD Ru growth rate was similar with substrates while nucleation incubation time depends on
surface hydrophilicy. Si 2p analysis of XPS for ALD Ru on H-terminated Si surface confirmed the formation of thermal SiO\textsubscript{2} during ALD process. ALD Ru growth rate was found to change during incubation period from XPS Ru 3p analysis. ALD Ru thickness measured from XPS Ru 3p was consistent with profilometer giving smooth fitting in the plot of Ru thickness versus ALD cycle. ALD Ru roughness both on H-terminated Si and SiO\textsubscript{2} propagated sharply during the ALD cycle reaches the incubation period indicating nucleation mechanisms are different between during incubation period and constant growth rate period. Crystalline structure of ALD Ru on various dielectrics was examined by XRD. Difference in crystalline structure between on HfO\textsubscript{2} and SiO\textsubscript{2} and on HfSiO\textsubscript{x} was observed which needs further investigation. ALD Ru tends to agglomerate during annealing. Nevertheless, no ALD Ru film discontinuity of was found even up to 1000°C annealing confirming excellent thermal stability of ALD Ru film as promising candidate materials in CMOS high temperature processes.

5.5 Acknowledgements

SEMATech and the Semiconductor Research Corporation (SRC) under the Front End Processing Research Center funded this work, which is gratefully acknowledged.
Reference


Figure captions

Figure 5.1 ALD cycle versus Ru film thickness deposited on chemical SiO₂, thermal SiO₂, and H-terminated Si

Figure 5.2 Water contact angle of substrates versus nucleation incubation time

Figure 5.3 SEM and AFM images for ALD Ru deposited on chemical SiO₂, thermal SiO₂, and H-terminated Si

Figure 5.4 XPS spectrum of ALD Ru deposited on H-terminated Si surface at 0, 10, 40, 70, 100, and 150 cycles
(a) Ru₃p (b) Si₂p

Figure 5.5 ALD Ru thickness by XPS and profilometer vs. cycle on SiO2 and Si-H surfaces

Figure 5.6 AFM RMS for ALD Ru deposited on thermal SiO₂ and H-terminated Si function of ALD cycle

Figure 5.7 SEM images as-deposited, forming gas annealed, RTA annealed ALD Ru films
Forming gas annealing: N₂:H₂ = 10:1, 400°C x 30 minutes
**Figure 5.8** SEM and XRD analysis for ALD Ru films deposited on HfO$_2$, HfSiO$_x$, and thermal SiO$_2$
Figure 5.1
Kie Jin Park

[Graph showing the relationship between ALD Ru Thickness and ALD cycle, with a label indicating ~1 Å/cycle.]
Figure 5.2
Kie Jin Park

![Graph showing the relationship between contact angle and incubation time (cycle).](image-url)
Figure 5.3
Kie Jin Park
Figure 5.4
Kie Jin Park

(a) Ru 3p and Si 2p peaks for various ALD cycles. (b) Si 2p peaks for different ALD cycles.
Figure 5.5
Kie Jin Park

![Graph showing Ru thickness vs. ALD cycle. The graph compares the thickness measured by profilometry and XPS methods, with data points for H-terminated and Therm-SiO₂ surfaces.](image-url)
Figure 5.6
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![Graph showing RMS (nm) vs. ALD cycle for different conditions (on SiO2 and on H-terminated Si). The graph includes data points and curves indicating the variation in RMS with ALD cycles.](image-url)
Figure 5.7
Kie Jin Park

As-deposited  As forming gas annealed (400°Cx30min)  1000°C annealed (10sec, Ar)
Figure 5.8
Kie Jin Park

On HfO₂  On HfSiOₓ  On SiO₂
CHAPTER 6. ALD Ruthenium Growth Model on Si-H Surface

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Abstract

Ruthenium becomes an important material candidate for interconnect and front-end application, lately. Atomic layer deposition has been one of the fastest growing technologies for past decades due to its process nature of excellent conformality and thickness control ability. Ru ALD nucleation on H-terminated silicon surface was studied using X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) analysis. Silicon oxide formation was confirmed during ALD cycles from observing emerging Si2p even after 10ALD cycles. Film thickness was measured from XPS Ru3d peak values showing growth rate transient region exists. AFM roughness analysis of ALD Ru films is consistent with growth rate changing up to 100ALD cycles. ALD Ru growth model on Si-H surface including detail reaction mechanism was proposed and rate constants for each reaction were extracted. The ALD growth model was extended to SiO\textsubscript{2} surface.
Ruthenium is of interest for copper diffusion barrier and PMOS metal gate electrodes application. Atomic layer deposition (ALD) is growing technology due to its excellent conformality and low impurity contents as well as good thickness control ability. Although several ALD Ru processes were reported and nucleation behaviors are known depending on surface properties as well as process conditions, Ru nucleation behaviors are current topic of research. Especially, ALD Ru film nucleation during incubation period has rarely been studied. Here we investigate Ru ALD nucleation on H-terminated silicon surface using X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) analysis and propose ALD growth model.

ALD Ru was carried out in a flow-type tube reactor using bis-(cyclopentadienyl)ruthenium (RuCp₂) as a precursor and oxygen. RuCp₂ is solid at room temperature with vapor pressure of ~10 mTorr at the bubbler temperature of 80°C. The processing pressure and substrate temperature were fixed at 1.2 torr and 325°C, respectively. The process gas flow rates were 100 standard cm³ per minute (sccm). Ar gas was used as carrier gas and purging gas between precursor and reactant dose. H-terminated Si was formed by wet chemical treatment (BakerClean® JTB-100), followed by 1% HF acid dip, N₂ flow dry. The ALD Ru film thicknesses for 200, 250, 300cycles were measured using a Tencor Alpha-Step 500 surface profilometer. The roughness of ALD Ru films were measured from AFM. ALD Ru films deposited with 0, 10, 40, 70, 100, 150cycles were analyzed with XPS.
Figure 6.1 shows Ru film thickness measured from profilometer vs. number of ALD cycles for deposition on H-terminated Si surface. The x-intercept shown in Figure 1 suggests the existence of Ru ALD nucleation incubation time on H-terminated surface. XPS Ru 3p\(_{3/2}\) peaks for ALD Ru films on H-terminated Si deposited from 0, 10, 40, 70, 100, and 150 ALD cycles were measured shown in Figure 2 (a). It was observed that the Ru 3p\(_{3/2}\) peak intensity at 100 ALD cycle was much bigger than at 70 cycles and peak intensities up to 70 cycles from 10 cycles increase relatively slowly. Figure 2 (b) shows Ru 3p\(_{3/2}\) peak values vs. ALD cycles indicating that ALD Ru growth rate is changing. Figure 3 shows ALD Ru thicknesses measured from XPS and profilometer versus cycle. Thicknesses from XPS Ru 3p\(_{3/2}\) peak values were calibrated assuming 90 cycles of incubation time. XPS Si 2p peaks at 99.8eV for silicon substrate are decreased with ALD Ru cycles shown in Figure 4. Starting from 10 ALD cycles, Si2p peaks at ~103eV appear and increase with ALD cycles suggesting SiO\(_2\) formation during ALD Ru process. Figure 5 shows RMS roughness by AFM for ALD Ru films on H-terminated Si surface deposited at various ALD cycles. ALD Ru film roughness increases with ALD cycle very sharply up to 100 for H-terminated Si. It is known that cyclopentadienyl ligands in Ru(Cp)\(_2\) are oxidized by oxygen following equation (1).\(^8\)

\[
\text{Ru(Cp)}_2 + \frac{25}{2}\text{O}_2 \rightarrow \text{Ru} + 5\text{H}_2\text{O} + 10\text{CO}_2
\]  

(0)

However, ALD Ru growth rate including nucleation incubation period and cyclic steady state ALD region need to be clarified. Based on the data we obtained, assuming no physisorption process exists, ALD growth model for Ru ALD on H-terminated silicon
surface was proposed. Figure 6 shows the schematic of the growth model. Until ALD cycle arrives a full Ru covered surface, during oxygen dose $O_2$ is consumed for silicon oxide formation and Ru(Cp)$_2$ ligand oxidation. Ru(Cp)$_2$ adsorbs on top of silicon oxide surface and RuO during Ru(Cp)$_2$ dose. Once Ru atoms cover surface, $O_2$ and Ru(Cp)$_2$ are consumed for deposition and ALD Ru grows with a constant growth rate. Following reactions can be expressed for the growth model assuming no physisorption involved in reactions and reverse reaction rates of each reaction steps are much lower than adsorption and ignored since substrate temperature is not significantly high.\textsuperscript{9,10} Si-H is oxidized at $O_2$ dose providing Ru(Cp)$_2$ adsorption site and at this stage hydrogen is assumed to stay on surface due to low substrate temperature (equation (2) and (3)).\textsuperscript{11}

\[
\theta_{\text{Si-H}} + \frac{1}{2}O_2 \rightarrow \theta_{(\text{H})\text{Si-O}} \quad (2)
\]

\[
\text{RuCp}_2 + \theta_{(\text{H})\text{Si-O}} \rightarrow \theta_{[\text{RuCp}_2]^*} \quad (3)
\]

Equation (4) and (5) are combustion reactions, where cyclopentadienyl ligands are oxidized into H$_2$O and CO$_2$ by oxygen.

\[
\text{RuCp}_2 + 3\theta_{O^*} \rightarrow \frac{1}{3}\theta_{\text{Ru}} + a\text{H}_2\text{O} + b\text{CO}_2 + \text{other product} \quad (4)
\]

\[
\theta_{[\text{RuCp}_2]^*} + c\text{O}_2 \rightarrow \theta_{\text{Ru}} + d\text{H}_2\text{O} + e\text{CO}_2 + \text{other product} \quad (5)
\]

Equation (6) shows oxygen diffuses at $O_2$ dose into Ru subsurface, which was observed by Quartz Microbalance Analysis from previous result.\textsuperscript{8}

\[
\theta_{\text{Ru}} + \frac{3}{2}O_2 \rightarrow 3\theta_{O^*} \quad (6)
\]
\( \theta_{(H)Si-O}, \theta_{[Ru(Cp)2]^*} \) and \( \theta_{Ru} \) are surface coverage of oxidized silicon, Ru(Cp)\(_2\) adsorbate, and Ru. \( x_1, x_2, x_3, x_4, \) and \( x_5 \) are conversion for each reaction. The proposed growth model includes above five reactions during ALD Ru growth. After a full coverage of Ru on surface, reaction from eq. (4) at Ru(Cp)\(_2\) dose and reaction from eq. (6) at O\(_2\) dose only take place. Assuming one monolayer thickness of Ru is 3 Å. At \( n \) ALD cycle, thickness \( T \) becomes \( T = 3 \sum_{i=1}^{n} \theta_{Ru}^{(n)} \). Figure 7 shows experimental Ru thickness on Si-H from XPS and profilometer and theoretic data from model for thickness vs. ALD cycle. For model, as fitting parameters conversion values \( x_1, x_2, \) and \( x_5 \) for each reaction were used. Resulting rate constants were \( k_1 = 3.5 \times 10^{-3} \text{torr}^{-0.5} \cdot \text{sec}^{-1} \) and \( k_2 = 0.3 \text{torr}^{-1} \cdot \text{sec}^{-1} \). \( k_3, k_4, \) and \( k_5 \) are very high value since \( x_3 = x_4 = 1 \) (combustion reaction) and \( x_5 = 1 \) from data fitting. This suggests that Si-H surface oxidation step and Ru(Cp)\(_2\) adsorption step on Si-O site are rate control steps for ALD Ru growth. As a result, during incubation period ALD Ru growth rate on Si-H are controlled by Si-H oxidation and adsorption of Ru(Cp)\(_2\) on Si-O site. As Si-H and Si-O sites decrease and Ru site increases, growth rate increases. Once only Ru atoms cover the surface, growth rate becomes constant. The growth model was extended to ALD Ru on SiO\(_2\) including equation (7), (8), (9), and (10) from growth model for Si-H surface because silicon substrate oxidation step doesn’t exists. Another assumption made was surface is covered only Si-O initially.

\[
\text{RuCp}_2 + \theta_{\text{Si-O}} \xrightarrow{x_2} \theta_{[\text{RuCp}_2]^*} \tag{7}
\]

\[
\text{RuCp}_2 + 3\theta_{O} \xrightarrow{x_5} \frac{1}{3} \theta_{Ru} + a\text{H}_2\text{O} + b\text{CO}_2 + \text{other product} \tag{8}
\]
Figure 8 shows experimental Ru thickness on SiO₂ from XPS and profilometer and theoretic data from model for thickness vs. ALD cycle. Rate constants were extracted into $k_2 = 0.18 \text{ torr}^{-1} \cdot \text{ sec}^{-1}$ and $k_5$ is very high since $x_5=1$. Compare to growth on Si-H, $k_2$ is smaller in SiO₂ indicating Ru(Cp)₂ adsorption on Si-O is slower than Ru(Cp)₂ adsorption on (H)Si-O. This indicates, similarly in Si-H surface, Ru(Cp)₂ adsorption reaction on Si-O site is rate determining step during incubation period.

SEMA TECH and the Semiconductor Research Corporation (SRC) under the Front End Processing Research Center funded this work, which is gratefully acknowledged.
Reference


Figure captions

Figure 6.1 ALD cycle versus Ru film thickness deposited on H-terminated Si

Figure 6.2 (a) XPS Ru3p of ALD Ru deposited on H-terminated Si surface at 0, 10, 40, 70, 100, and 150 cycles (b) Ru3p3/2 peak values vs. ALD cycle

Figure 6.3 Ru thickness measured from XPS Ru3p3/2 peak and profilometer vs. ALD cycle

Figure 6.4 XPS Si2p of ALD Ru deposited on H-terminated Si surface at 0, 10, 40, 70, 100, and 150 cycles

Figure 6.5 RMS roughness by AFM for ALD Ru deposited on H-terminated Si function of ALD cycle

Figure 6.6 Schematic of ALD Ru growth model on H-terminated Si surface

Figure 6.7 Comparison of ALD Ru growth by experimental and model on H-terminated Si surface

Figure 6.8 Comparison of ALD Ru growth by experimental and model on SiO$_2$
Figure 6.1
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![Graph showing the relationship between Thickness (Å) and ALD cycle. The graph displays a linear trend with increasing thickness corresponding to an increase in ALD cycles.]
Figure 6.2
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(a) Ru 3p

(b) XPS Ru 3p$_{3/2}$ Peak (CPS)
Figure 6.3
Kie Jin Park

Ru Thickness (Å)

ALD Cycle
Figure 6.4
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![Graph showing Si and SiO₂ peaks with binding energy in eV on the x-axis and CPS (A.U.) on the y-axis. The graph compares peak intensities at different cycles.]
Figure 6.6
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After a full coverage of Ru on substrate

CO₂+H₂O + other by-products

Residual ligands oxidized and excess oxygen formed

Ru(Cp)₂

CO₂+H₂O + other by-products

Oxidize ligands oxidized by excess oxygen

C₅H₅  Ru  C₅H₅  Ru  C₅H₅

Ru on Ru and RuCp₂⁺ on (H)Si-O

RuCp₂⁺ adsorption on (H)Si-O

Oxidize surface and ligands

O₂

Oxidize surface

Ru(Cp)₂

Initial nucleation period

Si
Figure 6.7
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![Graph showing the relationship between ALD cycles and thickness (Å). The graph includes experimental data points and a model line.](image-url)
Figure 6.8
Kie Jin Park

![Graph showing the relationship between ALD Cycles and Thickness (Å). The graph includes a line of best fit and experimental data points.]
Appendix is a reprint of a manuscript published in Journal of Vacuum Science and Technology A

**Appendix. Bulk and Interface Charge in Low Temperature Silicon Nitride for Thin Film Transistors on Plastic Substrates**

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**Abstract**

We report bulk and interface charge densities in silicon nitride thin films deposited by plasma chemical vapor deposition from NH$_3$/N$_2$/SiH$_4$ mixtures, at temperatures compatible with flexible plastic substrates. Bulk and interface charges are independently determined from measurements of flat band potential as a function of film thickness for a range of substrate temperatures and gas compositions. Increasing NH/SiH bond ratio in the deposited films (determined from infrared absorption) leads to a more positive interface charge and more negative bulk charge, and the trend in interface charge is consistent with a relation between charge and stress at the Si/SiN$_x$ interface. As substrate temperature is decreased from 250 to 50°C, the leakage is observed to decrease, the interface charge decreases, and the bulk charge changes from negative to net positive.
I. Introduction

Hydrogenated amorphous thin film transistors (TFT’s) were developed in the 1970s\(^1\), and are now widely used as switching elements in active matrix liquid crystal displays. Materials for TFT’s are typically formed on large glass sheets at ~300°C using plasma enhanced chemical vapor deposition (PECVD), and the processes and materials used now are very similar to those developed for the original devices. There is growing demand for fast-responding lightweight displays that can withstand rugged treatment and extreme exposure conditions. Organic TFT materials are attractive for lightweight rugged displays, in part because organics can be processed at low temperature on low cost flexible plastic substrates. Inorganic materials will likely offer advantages over organic materials in some applications, and more detailed insight into electrical properties of inorganic materials formed at low temperature will be helpful.

Amorphous\(^2\)\(^3\) or polycrystalline\(^4\) silicon TFT’s can compatible with lower temperature processing to enable integration onto plastic substrates\(^5\)\(^-\)\(^8\). Initial analysis of stability of low temperature TFT materials suggests reasonable possibilities for future improvements\(^8\). However, large area electronic fabrication using flexible substrate technology will require of significant new challenges in low temperature materials processing and integration. For example, a critical problem for low temperature TFT’s is the quality of the gate dielectric. Of particular interest are leakage current, charge trap density in the film bulk, and the charge at the dielectric/semiconductor interface. Hydrogenated silicon nitride is the common gate insulator in amorphous silicon TFT’s
because electronic defect structure at the amorphous silicon/silicon nitride interface does not severely pin the semiconductor Fermi level. Silicon nitride, however, does have a significant bulk trap state density that limits device performance and stability. Silicon nitride can generally be processed by plasma CVD at low temperature (<150°C) with reasonably low leakage currents. This article addresses the issue of bulk and surface charge density in silicon nitride, and how they are affected by deposition temperature. The characterization of bulk and surface charge density will be important to improve transistor performance to advance low temperature silicon and organic transistor processing technologies.

II. Experiment

A. Materials Preparation

Films were prepared in a capacitively coupled RF (13.56 MHz) load-locked PECVD system. The electrode area is 30 x 35 cm² with a spacing of 3 cm, and the system is capable of depositing uniform nitride films over 900 cm². The process gases were introduced through a showerhead array of 0.5 mm-diameter orifices in the RF-powered electrode. For electrical characterization studies, silicon substrates (1.0 Ω·cm n-type) were cleaned with 1% HF solution to remove organic impurities and the native oxide layer before being loaded into the reactor. The effects of process gas composition and substrate temperature on the silicon nitride properties were investigated. Initially, the silane gas flow rate was varied from 5 standard cubic centimeters per minute (sccm) to 20
sccm while maintaining NH₃ at 75 sccm and N₂ at 575 sccm. The ammonia/silane ratio therefore ranged from 3.75 to 15. Substrate temperature was fixed at either 150°C or 250°C. For another set of runs, substrate temperatures varied over 50 to 350°C with a constant gas composition ratio of SiH₄/NH₃/N₂=7.5/75/575. For all runs described here, processing pressure and RF power was kept at 0.4 Torr and 150W, respectively.

Some of the resulting silicon nitride films were also evaluated in thin film transistor structures formed on flexible polyimide. Tri-layers formed at higher temperature (250°C) delaminated during lithographic processing, presumably due to thermal shrinkage of the polyimide and differences in thermal expansion coefficients between the polyimide and the inorganic layers. Lower temperature processed films showed good stability during further processing.

B. Low temperature SiNₓ Characterization

Films were characterized using Fourier transform infrared spectroscopy (FTIR), capacitance vs. voltage (CV), and current vs. voltage (IV) measurement. For IR analysis, samples were deposited on high resistivity (>10 Ω·cm), double-side polished Si (100) substrates, and measured using a Nicolet Magma 750 spectrometer in the transmission mode with a 4 cm⁻¹ resolution. For CV and IV measurement, metal/insulator/semiconductor capacitors were formed using silicon substrates with doping levels of 4x10¹⁵ cm⁻³ and Al contacts evaporated through a shadow mask, forming dots ~7 x 10⁻⁴ cm². For IV measurement, the gate was biased positively, and the ramp rate was 5 V/s. Dielectric constant (κox) was extracted from accumulation capacitance using
the known physical thickness and electrode area. Film thicknesses were obtained using a Tencor Alpha-Step 500 surface profilometer. For each sample, several (>5) measurements were made, and values were uniform typically within ±5%. The dielectric constants for the films deposited at 150°C typically ranged from 5 to 6, and they were higher (6 to 8) for films deposited at 250°C. High temperature stoichiometric silicon nitride is expected to have a dielectric constant of ~7.0. A lower value at lower temperature suggests a lower density in those films.

III. Results and Data Analysis

The infrared absorption spectra of silicon nitride film deposited with various NH$_3$/SiH$_4$ ratios at 150°C and 250°C are shown in Figures 1(a) and (b), respectively. The features of interest include N-H bond stretching mode at 3300 cm$^{-1}$, Si-H bond stretching mode at 2140 cm$^{-1}$, N-H$_2$ bond bending mode at 1550 cm$^{-1}$, N-H bond bending mode at 1180 cm$^{-1}$, and Si-N bond stretching mode at 830 cm$^{-1}$. For both temperatures, NH bond density is observed to increase with decreasing SiH bond density as NH$_3$/SiH$_4$ ratio is increased. Figure 1(c) shows the infrared absorption spectra for films deposited at various temperatures when NH$_3$/SiH$_4$ is fixed at 10/1. The data shows that as substrate temperature is increased, both NH and SiH bond densities decrease, and there is a related increase in SiN bond stretching intensity with increasing temperature. For all IR spectra the film thickness ranged from 900Å to 1100Å and the spectra in Fig. 1 are normalized for thickness.
The films shown in Figure 1 were characterized electrically, and the results are shown in Figure 2. Figures 2(a) and (b) are logarithmic plots of current density versus electric field measured at room temperature for films deposited at 150°C and 250°C, respectively. Comparing the data in Figures 1 and 2, the leakage current density generally decreases with increasing NH/SiH bond ratio observed in the IR. Figure 2(c) shows IV results for films deposited at various temperatures with NH₃/SiH₄ gas flow ratio fixed at 10 and NH/SiH ≈ 1. At applied electric field between 4×10⁶ and 1×10⁷ V/cm, the leakage current appears to decrease with decreasing substrate temperature. Figure 3 shows capacitance-voltage results for films in Figure 2. Figures 3(a) and (b) show the change in flatband voltage (related to net dielectric charge) for films deposited with various gas flow ratio (and various resulting NH/SiH bond density) at 150 and 250°C, respectively. The expected work function difference, $\phi_{MS}$, between the Al and n-type silicon used here, zero fixed charge in the dielectric would result in $V_{FB} = -0.04V$. For most films studied, $V_{FB}$ was significantly shifted negative, indicating positive fixed charge, and the negative shift generally increases with an increase in the NH/SiH ratio. It is interesting to note that for the sample with NH/SiH = 3.54, the flatband shift is less than for the film with NH/SiH = 1.0, indicating a decrease in net fixed charge at higher NH/SiH due to charge compensation (shown below). Figure 3(c) shows capacitance vs. voltage results for films deposited at different temperatures at a fixed flow ratio NH₃/SiH₄ = 10. All films show $V_{FB}$ more negative than the zero charge value, consistent with positive fixed charge, but the magnitude of the shift decreases with decreasing film deposition temperature. It is also important to note that the
shift of the CV curve measures only the net fixed charge, and a low net fixed charge could result from compensated positive and negative fixed charges.

By characterizing the thickness dependence of CV curves and flatband voltage shifts, the total charge distribution (i.e. interface vs. bulk charge densities) can be determined. If the total bulk charge density \( Q_{BC}, \text{q/cm}^3 \) in a film is constant, increasing the film thickness will lead to an increase in the total amount of charge, and therefore an increase in the \( V_{FB} \) shift. However, if the charge is located primarily at or near the silicon/dielectric interface \( Q_{IC}, \text{q/cm}^2 \), an increase in film thickness will not change the total charge. For fixed \( Q_{IC} \) the measured flatband voltage is expected to change with thickness because of changes in \( C_{ox} \). Therefore, considering bulk \( Q_{BC} \) and interface \( Q_{IC} \) charge densities, the measured flatband voltage will change with thickness as given in equation (1).\(^{11}\) This relationship assumes that \( Q_{BC} \) is distributed uniformly through the film bulk.

\[
V_{FB} = \phi_{MS} - \frac{Q_{IC}}{K_s \epsilon_o} t_{ox} - \frac{Q_{BC}}{2K_s \epsilon_o} t_{ox}^2
\]  

Flatband voltage is measured for several values of film thickness, and Figure 4 shows plots of \( V_{FB} \) vs. film thickness and the resulting fit to equation (1). Values for \( Q_{IC} \) and \( Q_{BC} \) are extracted from the fits, and \( Q_{BC} \) is multiplied by \( t_{ox} \) to normalize to a film.
thickness of 1000Å (close to the typical physical thickness of 900-1100Å) to more easily compare bulk and interface charge densities (q/cm²).

Figure 5(a) shows values of $Q_{IC}$ and $Q_{BC} \cdot t_{ox}$ (determined from the fits in Figure 4) vs. NH/SiH ratio (from the IR data in Figure 1) for films deposited at 150°C. A typical error bar obtained from the quality of the fits (±1 standard deviation) is included. At the lowest NH/SiH ratio measured, $Q_{IC}$ and $Q_{BC} \cdot t_{ox}$ have a similar magnitude ($\sim 2 \times 10^{12}$ /cm²), but interface charge is negative, whereas the bulk charge is positive. Increasing NH/SiH results in a change in sign for both bulk and interface charge. At NH/SiH near 1.0, bulk and interface charge are both positive, but increasing NH/SiH leads to more negative charge in the film bulk, and more positive charge at the film/semiconductor interface. Therefore, at higher NH/SiH bond density, the net fixed charge (interface and bulk) decreases, and the $V_{FB}$ shifts more positive toward the expected ($Q=0$) $V_{FB}$ value, even though the interface charge is becoming more positive and the bulk charge is becoming more negative. Considering the bulk and interface charge density in these films, the decrease in leakage current with increasing NH/SiH ratio is likely related to charge screening effects, where the charge in the film decreases the field dropped across the dielectric, and is not entirely due to an improvement in film insulating quality.

The results in Figure 5(b) shows values of bulk and interface charge extracted from the CV data from films deposited with NH₃/SiH₄ ratio = 10 (and NH/SiH ≈ 1) plotted vs. substrate temperature. As the substrate temperature increases, the interface charge becomes more positive and the bulk charge becomes more negative. The magnitude of
the changes are similar consistent with net charge compensation. This charge compensation apparently does not improve leakage current, as shown in Figure 2 where leakage current increases with increasing deposition temperature. Therefore, the increased charge density in these films is possibly linked to an increased density of hopping related defect states.

The detailed relations between bonded hydrogen distribution, defect structure and charge density are not clear. Interface charge density may be related to stress at the Si/SiNx interface built in during film deposition\(^\text{12}\), where stress can enhance the rate of defect generation. Stress measurements indicate that tensile stress in SiNx films increases monotonically for films with similar NH/SiH ratio as used here\(^\text{13}\), consistent with the increase in interface charge shown in Figure 5(a). It is important to note that optimum dielectrics for transistor applications should minimize \(Q_{\text{IC}}\) and \(Q_{\text{BC}}\) to decrease charge scattering during both electron and hole transport along the semiconductor/dielectric interface. Therefore, the effects of film structure and bulk and interface charge densities need to be balanced to determine the optimum material processing conditions for devices.

**IV. Summary and Conclusions**

The thickness dependence of CV data from silicon nitride films deposited by PECVD from \(50^\circ\text{C}-250^\circ\text{C}\) has been fit to an expected model to independently extract bulk and interface charge densities. Comparisons with IV and IR transmission results indicate that a
decrease in apparent leakage current with increasing NH/SiH ratio is likely related to a combination of charge screening and an improvement in insulating quality. Films with larger NH/SiH ratios also show more positive interface charge and higher negative bulk charge densities, and the interface charge density is suspected to increase with increasing stress at Si/SiNₓ interface. As deposition temperature is decreased from 250 to 50°C, the concentration of both positive and negative fixed charge is found to decrease and some improvement in leakage current is observed.
Reference


Figure captions

**Figure 1.** Infrared absorption spectra for PECVD SiN$_x$ films containing different NH/SiH ratio at (a) T = 150°C and (b) T = 250°C, with (c) different temperature for NH$_3$/SiH$_4$ = 10

**Figure 2.** Current density vs. electric field for SiN$_x$ deposited with different NH/SiH ratio at (a) T = 150°C and (b) T = 250°C, with (c) different temperature

**Figure 3.** C/C$_{ox}$ vs. voltage plots for nitride films deposited with different NH/SiH ratio at (a) T = 150°C and (b) T = 250°C, with (c) different temperature. Note the change in the flatband voltage (V$_{FB}$) with changing NH/SiH and deposition temperature

**Figure 4.** Plots of flat band voltage versus the nitride thickness at (a) different NH/SiH ratio at T = 150°C, and with (b) different temperature at NH$_3$/SiH$_4$ = 10. The symbols are experimental data, and the solid and dashed lines are best fits to equation (1) in the text.

**Figure 5.** The charge variation in the interface and bulk film for the films deposited with (a) different NH/SiH ratio at T = 150°C, and with (b) different temperature at NH$_3$/SiH$_4$ = 10
Figure 1
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(a) Temperature = 150°C SiN

(b) Temperature = 250°C SiN

(c) NH₃/SiH₄ = 10

Temperature (°C)

Absorbance

Wavenumber (cm⁻¹)
Figure 2
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(a) Temp. = 150°C
NH/SiH = 0.3
0.62
1.0
3.54

(b) Temp. = 250°C
NH/SiH = 0.18
0.69
0.81
1.13

(c) NH₃/SiH₄ = 10
Temperature (°C) = 250
50
150
Figure 3
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(a) C/Cox vs. Voltage (V)

(b) C/Cox vs. Voltage (V)

(c) C/Cox vs. Voltage (V) with Temperature (°C)
Figure 4
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(a) NH/SiH

(b) NH$_3$/SiH$_4$ = 10
Figure 5
Kie Jin Park

(a) Temp. = 150°C

(b) NH₃/SiH₄ = 10