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Area-selective Atomic Layer Deposition of Silicide and Oxides Using Inherent Substrate Dependent Processes

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UNIVERSITY OF CALIFORNIA SAN DIEGO

Area-selective Atomic Layer Deposition of Silicide and Oxides Using Inherent Substrate Dependent Processes

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy

in

Materials Science and Engineering

by

Jong Youn Choi

Committee in Charge:

Professor Andrew C. Kummel, Chair
Professor Prabhakar Bandaru
Professor David P. Fenning
Professor Ivan K. Schuller
Professor Wei Xiong

2019
The Dissertation of Jong Youn Choi is approved, and it is acceptable in quality and form for publication on microfilm and electronically:

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Chair

University of California San Diego

2019
DEDICATION

To my God who has guided my life until now and to my family for all the prayers, love and support during my graduate studies.
EPIGRAPH

A man’s heart plans his way, but the LORD directs his steps.

*Proverbs 16:9*
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<tbody>
<tr>
<td>Å</td>
<td>angstrom</td>
</tr>
<tr>
<td>AC</td>
<td>alternating current</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>ALD</td>
<td>atomic layer deposition</td>
</tr>
<tr>
<td>AS-ALD</td>
<td>area-selective atomic layer deposition</td>
</tr>
<tr>
<td>BE</td>
<td>binding energy</td>
</tr>
<tr>
<td>CB</td>
<td>conduction band</td>
</tr>
<tr>
<td>$C_{\text{max}}$</td>
<td>maximum capacitance</td>
</tr>
<tr>
<td>CV</td>
<td>capacitance voltage</td>
</tr>
<tr>
<td>CVD</td>
<td>chemical vapor deposition</td>
</tr>
<tr>
<td>DC</td>
<td>direct current</td>
</tr>
<tr>
<td>$D_{\text{it}}$</td>
<td>density of interface traps</td>
</tr>
<tr>
<td>DMADMS</td>
<td>Bis(dimethylamino)dimethylsilane</td>
</tr>
<tr>
<td>eV</td>
<td>electron volt</td>
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<tr>
<td>EOT</td>
<td>equivalent oxide thickness</td>
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<tr>
<td>Eq.</td>
<td>equation</td>
</tr>
<tr>
<td>FGA</td>
<td>forming gas anneal</td>
</tr>
<tr>
<td>GV</td>
<td>conductance voltage</td>
</tr>
<tr>
<td>HV</td>
<td>high vacuum</td>
</tr>
<tr>
<td>I</td>
<td>electric current</td>
</tr>
<tr>
<td>IMPM</td>
<td>inelastic mean free path</td>
</tr>
<tr>
<td>KE</td>
<td>kinetic energy</td>
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x
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<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tr>
<td>L</td>
<td>Langmuir</td>
</tr>
<tr>
<td>MOSCAP</td>
<td>metal oxide semiconductor capacitor</td>
</tr>
<tr>
<td>MOSFET</td>
<td>metal oxide semiconductor field effect transistor</td>
</tr>
<tr>
<td>nm</td>
<td>nanometer</td>
</tr>
<tr>
<td>pA</td>
<td>picoamps</td>
</tr>
<tr>
<td>PBN</td>
<td>pyrolitic boron nitride</td>
</tr>
<tr>
<td>STM</td>
<td>scanning tunneling microscopy</td>
</tr>
<tr>
<td>TMDS</td>
<td>tetramethyldisilazane</td>
</tr>
<tr>
<td>UHV</td>
<td>ultra-high vacuum</td>
</tr>
<tr>
<td>V</td>
<td>volts</td>
</tr>
<tr>
<td>VB</td>
<td>valence band</td>
</tr>
<tr>
<td>$V_{fb}$</td>
<td>flatband voltage</td>
</tr>
<tr>
<td>$V_{th}$</td>
<td>threshold voltage</td>
</tr>
<tr>
<td>XPS</td>
<td>x-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>$\nu$</td>
<td>frequency</td>
</tr>
<tr>
<td>$\Phi_{spec}$</td>
<td>spectrometer work function</td>
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PUBLICATIONS

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C. F. Ahles, J. Y. Choi, S. Wolf, and A. C. Kummel "Selective Etching of Silicon in Preference to Germanium and Si\textsubscript{0.5}Ge\textsubscript{0.5}" ACS Appl. Mater. Interfaces, 2017, 9, 20947.

S. W. Park, J. Y. Choi, S. Siddiqui, B. Sahu, R. Galatage, N. Yoshida, J. Kachian, A. C. Kummel "Formation of atomically ordered and chemically selective Si-O-Ti monolayer of Si\textsubscript{0.5}Ge\textsubscript{0.5}(110) for a MIS structure via H\textsubscript{2}O\textsubscript{2}(g) functionalization" Journal of Chemical Physics, 2017, 146, 052808.

FIELD OF STUDY

Major Field: Materials Science and Engineering

Studies in Surface Science and Physical Chemistry
Professor Andrew C. Kummel
ABSTRACT OF THE DISSERTATION

Area-selective Atomic Layer Deposition of Silicide and Oxides Using Inherent Substrate Dependent Processes

by

Jong Youn Choi

Doctor of Philosophy in Materials Science and Engineering

University of California San Diego, 2019

Professor Andrew C. Kummel, Chair

For the last three decades, the semiconductor industry continued to grow in all aspects such as the device performance, power efficiency, data process speed, manufacturing yield and costs. One of the most important factors that made this big stride possible was a scaling of metal-oxide-semiconductor field effect transistors (MOSFETs), the fundamental and core component of microelectronic devices. The miniaturization of MOSFETs allowed for the integration of billions of transistors into a single microprocessor
chip, and currently the industry is looking into the issues of fabricating MOSFETs to further scale down to a sub-10 nm node using three-dimensional features.

A significant challenge of fabricating MOSFETs at the sub-10 nm node is the patterning process, which requires excellent spatial uniformity, a detailed positioning of material, and perfect thickness control. To avoid the technical complexity and limitation of a conventional top-down patterning technique, lithography, a new approach of patterning MOSFET components should be developed.

In this work, selective deposition of molybdenum silicide (MoSi$_x$), molybdenum silicate (MoSiO$_x$) and hafnium oxide (HfO$_x$) were demonstrated using selective atomic layer deposition, a bottom-up approach of nanoscale patterning for MOSFETs. Selectivities were obtained by the difference in the chemical reactivity of precursors between the different substrates of interest. The deposition was performed in a self-limiting manner or carefully controlled decomposition of the precursor which provides conformality with a sub-nanoscale thickness control. In sum, this study focuses on the inherently selective deposition processes based on the surface chemistry and the engineering techniques for selectivity enhancements which can be integrated into three-dimensional MOSFET fabrication processes.
Chapter 1

Introduction

1.1 Atomic Layer Deposition (ALD) and patterning Metal Oxide Semiconductor Field Effect Transistors

As Metal-oxide-semiconductor field effect transistors (MOSFETs) were scaled down to sub-10 nm node using three-dimensional features, a precise control of film thickness and conformality while maintaining the required electrical, physical and chemical qualities became substantial. [1,2] Therefore, atomic layer deposition (ALD) is employed since ALD provides a spatial conformality with atomic-scale thickness control by the self-limiting reactions of alternately dosed precursors.

For the patterning process, the conventional lithography technique met a limitation in resolution for sub-10 nm features due to a restricted focal plane of the X-ray source and imperfect alignment of the patterning masks. Three-dimensional MOSFETs (FinFets) in particular require a multi-patterning lithography process (i.e. double patterning) which has insufficient structural quality and resolution due to a memory effect originating from a chemical damage from reactive ion etching and structural complexity in mask alignment. [3-6] To overcome the complexity and limitations of the conventional top-down lithography scheme, ALD-enabled nanopatterning has been gaining attention to achieve higher resolution. For example, a spacer defined double patterning (SDDP) process employs a “spacer” to pattern an underlying film to the sub-10 nm in three-dimensions as shown in Fig. 1.1. [7,8] The pattern of the spacer is transferred to the underlying film; therefore, the spacer film is deposited using ALD to accomplish the high-resolution
features. In sum, implementing ALD is critical to achieve good film qualities and to enable a high-resolution patterning for the MOSFET components in three-dimensions.

1.2 Area-selective Atomic Layer Deposition

Area-selective Atomic Layer Deposition (AS-ALD) is a bottom-up approach of the patterning technique which leverages the advantages of ALD and the spontaneous positioning of a depositing film. The selectivity is obtained by the preferential reactions between the precursors and the target surface where a film grows. In contrast, the precursors show non-reactivity with the unwanted surface where the film should not be grown. Since the ALD selectivity relies on the chemical reactivity of the surface, surface modification is often employed using passivation or activation. [9,10] Another approach is to remove nucleation from the unwanted surface by adding plasma etching during the deposition. [11] However, adding the passivation or activation layers may require another process of selective removal of residual passivants or activants after the selective deposition is complete. The plasma process also necessitates damage control of the films and substrates from reactive ion etching and residual by-products.

AS-ALD using inherently substrate-dependent processes has a benefit of not using any preceding steps such as passivation or activation, or any additional plasma steps because it only utilizes the intrinsic differences in reactivity of the starting substrates. Therefore, the choice of the precursors and the substrate preparation are important for the intrinsic selective processes. [12-14] A comparison between the conventional patterning and ALD enabled patterning is depicted in Fig. 1.2.
1.3 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is the main surface characterization technique employed to study the chemical compositions and chemical states of the substrates and thin films by analyzing the photo-emitted electrons from the samples. XPS can effectively investigate a surface coverage and saturation of chemisorbates within the topmost 1-3 nm of the sample by a quantitative analysis of the XPS spectra. The chemical states of the elements provide information about the other elements that they are bonded to; therefore, the empirical formula can be obtained. The composition of the XPS includes a monochromatic X-ray source, a multichannel hemispherical analyzer and a spectra acquisition software. An Al anode (Kα = 1486.7 eV) was used as a monochromatic X-ray source. As this characteristic X-ray irradiates a sample, the core level electrons are emitted from the sample atoms having a kinetic energy of the following equation:

\[ E_{kinetic} = E_{hv} - E_{binding} - \Phi_{spec} \]

where \( E_{kinetic} \) is the kinetic energy of the electron, \( E_{hv} \) is the energy of the incident X-ray, \( E_{binding} \) is the binding energy of the electron, and \( \Phi_{spec} \) is the work function of the spectrometer. [15] The photoemitted electrons are collected by a multichannel analyzer where the incoming electrons pass through the lenses and the fixed voltage (pass energy) applied to the hemisphere. [16] The electrical current from the collected electrons are amplified by a factor of \( 10^8 \) in an electron multiplier (Channeltron) and the counts of electrons are plotted as a function of \( E_{binding} \) in the form of spectrum. A schematic of XPS is shown in Fig. 1.3.
1.4 Scanning Tunneling Microscopy

Scanning Tunneling Microscopy (STM) was employed to investigate the morphology of MoSi$_x$ in the Chapter 2. STM is a powerful surface imaging tool using the quantum tunneling effect of an electron between an atomically sharp tip (i.e. tungsten) and the topmost atom on the surface of interest by applying a bias to the tip. The STM tip sweeps around the surface only a few angstroms away by fine control of the tip using a piezoelectric feedback loop while maintaining a constant tunneling current between the sample and the tip. [17] The current from the tunneled electrons are amplified and processed by a control unit to record the data in the form of image. This technique allows mapping of morphology at atomic resolution in two different modes of filled states and empty states depends on the relative bias of the sample surface in respect to the tip. For example, a positively biased tip attracts the electrons from the filled orbitals of the atoms of the sample surface, resulted in a filled state imaging mode. For the MoSi$_x$/Si surface in Chapter 2 the surface morphologies were obtained using the filled state imaging mode of in-situ STM. This allowed us to investigate an as-deposited and in-situ annealed MoSi$_x$ surface without oxidizing metallic MoSi$_x$ by exposing the film into an ambient air. A schematic of a simplified STM circuit is shown in Fig. 1.4.

1.5 Atomic Force Microscopy

Atomic Force Microscopy (AFM) is employed to investigate a surface morphology of a deposited film in a sub-nanometer resolution. The components of AFM are a probe, a laser, a detector and feedback loop as described in Fig. 1.5. A sharp tip ($\Phi < 30$ nm) attached to an end of a cantilever, which oscillates near its resonance frequency, is used as
a probe. A laser constantly shines the back of the cantilever and a laser beam is reflected to the detector where the amplitude of the oscillation is measured. When the tip approaches to the sample close enough to interact with the surface with an atomic scale forces such as Van der Waals forces, the amplitude of the cantilever’s oscillation changes. The change in amplitude of the oscillation is used for feedback loop device to control the distance between the cantilever and the sample operated by a piezoelectric controller. In this study, AFM was employed to characterize the MoSiOₓ and HfOₓ surfaces in Chapter 3 and Chapter 4.
Figure 1.1 A comparison between the (a) double patterning and (b) spacer defined double patterning (SDDP) processes.
Figure 1.2. A comparison of the (a) conventional patterning (Lithography) and (b) ALD enabled patterning (Selective ALD) processes.
Figure 1.3. A schematic of X-ray Photoelectron Spectroscopy.
Figure 1.4. A schematic of the simplified Scanning Tunneling Microscopy circuit.
Figure 1.5. A schematic of Atomic Force Microscopy.
1.6 References

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Chapter 2

Selective atomic layer deposition of MoSi\textsubscript{x} on Si (001) in preference to Silicon Nitride and Silicon Oxide

2.1 Abstract

Highly selective deposition of MoSi\textsubscript{x} on Si in preference to SiO\textsubscript{2} and SiN\textsubscript{x} was achieved via atomic layer deposition (ALD) using MoF\textsubscript{6} and Si\textsubscript{2}H\textsubscript{6} at 120°C. The selectivity was enabled by the lack of chemical reactivity between the reactants and the SiO\textsubscript{2} and SiN\textsubscript{x} substrates. In contrast, MoF\textsubscript{6} nucleated in a self-limiting manner on H-terminated Si, and a following Si\textsubscript{2}H\textsubscript{6} exposure reduced MoF\textsubscript{x} to Mo\textsuperscript{0} which is consistent with Mo-Si bond formation. X-Ray photoelectron spectroscopy (XPS) revealed that the 5 ALD cycles of MoF\textsubscript{6} and Si\textsubscript{2}H\textsubscript{6} selectively deposited a substoichiometric MoSi\textsubscript{2} film on the Si substrate in contrast to previous results showing a nearly pure Mo deposition. Extra Si\textsubscript{2}H\textsubscript{6} doses on the substoichiometric MoSi\textsubscript{2} film incorporated more Si into the film without disturbing the inherent selectivity over SiO\textsubscript{2} and SiN\textsubscript{x}. A depth-profiling study showed that the bulk of the film has Si/Mo = 1.7 – 1.9 with <10% F and O impurities. The data is consistent with higher pressure Si\textsubscript{2}H\textsubscript{6} doses inducing silicide formation instead of metal deposition. To verify selectivity on the nanoscale, the selective deposition of MoSi\textsubscript{x} was investigated on a patterned Si wafer containing three-dimensional (3D) nanoscale SiO\textsubscript{2} and SiN\textsubscript{x} features. Cross-sectional transmission electron microscopy (TEM) showed that selective MoSi\textsubscript{x} deposition was achieved on nanoscale 3D structures. AFM documented that there were less than 10 nuclei/\textmu m\textsuperscript{2} on SiO\textsubscript{2}; since SiO\textsubscript{2} has \sim 10\textsuperscript{6}/\textmu m\textsuperscript{2} OH groups, this corresponds to an intrinsic selectivity of about 10\textsuperscript{6}:1 between the OH groups on SiO\textsubscript{2} and
Si-H groups on Si. This inherent substrate-dependent selectivity for silicide deposition allows the elimination of pre-positioning of passivants.

2.2 Introduction

Exact positioning of materials on nanoscale devices is required to manipulate atomic-scale properties for next-generation nanoelectronics [1-3]. For semiconductor fabrication, detailed positioning of materials with excellent conformality and stoichiometry is required to meet the demand for cost, yield, and throughput [4]. As metal-oxide-semiconductor field effect transistors (MOSFETs) are scaled to less than <10 nm channel length, there is a need to overcome the constraints originating from top-down processes such as damage from reactive ion etching and structural complexity in alignments on three-dimension (3D) surfaces [3-6].

Recently, as MOSFET devices have been fabricated in 3D structures (FinFETs), there has been increasing interest in area-selective deposition on the nanoscale while maintaining conformal film quality since area-selective atomic layer deposition (ALD) eliminates patterning steps and complexity particular to 3D devices such as lithography onto 3D structures [6]. It has been demonstrated that selective ALD can be accomplished using self-assembled monolayers (SAMs) as passivation layers [7-9]. The passivation layers block or eliminate surface functional groups that are reactive towards ALD precursors so that selectivity can be obtained; however, this necessitates the selective deposition of the passivation layer. Furthermore, often the passivation layers must be selectively removed after the selective deposition [10]. Therefore, an alternative method to obtain selectivity has been suggested which is to utilize substrate-dependent reactivity of
ALD precursors [11-14]. B. Kalayan et al.[14] reported the intrinsic substrate-dependent selectivity of W metal deposition on Si over SiO₂ using WF₆ and SiH₄. The inherent substrate selectivity was ascribed to only H-terminated Si readily being reactive to WF₆(g) to form SiF₄(g) products since Si-O bonds are stable enough not to be attacked by WF₆ [13,24]. B. Kalayan et al. suggested that by adding a H₂ carrier gas with WF₆ during the deposition process, the selectivity window (number of ALD cycles over which selectivity is retained) could be improved. It was hypothesized that the ALD by-product HF passivated the –OH nucleation sites on SiO₂ in the form of SiOₓFᵧ which is not reactive towards WF₆.

Transition metal disilicides such as TiSi₂, CoSi₂ and MoSi₂ are capable of reducing the electrical resistance at the contact regions and tuning the contact work function in MOSFETs [15,16]. It is important to reduce the parasitic resistance since the performance of scaled devices with <10 nm channel length can be strongly affected by parasitic resistance. The conventional methods to form silicides involve a high temperature anneal after metal deposition onto Si or by direct deposition of silicides using evaporation or co-sputtering [17]. These methods readily form silicides of the desired stoichiometry, but they may not be applicable to complicated 3D structures due to the Si consumption, poor step coverage and insufficient thickness control for scaled devices. There have been several studies on W or Mo metal ALD using WF₆ or MoF₆ and SiH₄ or Si₂H₆ but little is documented on ALD of silicide [14,18]. K. Bernal-Ramos et al. carried out CoSi₂ ALD on H-terminated Si (111) at 140°C using an organometallic Co precursor (t-Bu-AllylCo(CO)₃) and trisilane (Si₃H₈) [19]. NbSi deposition was achieved by T. Proslier et al. using NbF₅ and Si₂H₆ at a deposition temperature of 150 – 400°C [20]. Using MoF₆ and Si₂H₆ as the reactants, D. Seghete et al. studied the nucleation and growth characteristics of Mo metal
ALD between 90–150°C using a quartz crystal microbalance [18]. It was hypothesized that Si₂H₆ acts as a sacrificial reducing agent for MoF₆ and leaves reduced Mo metal as a final product which was previously suggested in W metal ALD or CVD using WF₆ and SiH₄ [14,28]. While the inherent selectivity of metal deposition on Si over thermally grown pristine SiO₂ was previously reported using MoF₆ or WF₆, in 3D architectures (FinFETs), selective silicide growth on Si over SiO₂ as well as SiNₓ or SiON which are ion damaged is also required. Selective silicide deposition on Si over ion damaged SiNₓ or SiON is a critical challenge in 3D nanostructures.

The objective of the present study is to quantify on the nanoscale the selective deposition of MoSiₓ on Si in preference to SiO₂, SiON and SiNₓ using the inherent substrate selectivity of MoF₆ and Si₂H₆. The selectivity on planar samples was quantified with X-ray photoelectron spectroscopy (XPS) as well as atomic force microscopy (AFM) in order to count the number of unwanted nuclei on SiO₂, while the selectivity on 3D nanoscale structures was probed by both XPS and transition electron microscopy (TEM). To achieve stoichiometric MoSi₂, additional Si insertion after the ALD cycles was performed by dosing Si₂H₆ onto the Mo rich MoSiₓ film. The resistivity of the MoSiₓ film was obtained by using 4-probe electrical measurements.

2.3 Experimental

Four types of samples were employed: P-type Si (100) (Boron-doped, Virginia Semiconductor), thermally grown SiO₂ on Si (100) (University Wafer), SiON (Applied Materials) and patterned samples having Si, SiO₂ and SiNₓ. The SiON in this study is Si₃N₄ which has been subjected to reactive ion etching and plasma ashing in oxygen during
fabrication, and therefore contains oxygen; this mimics the conditions of Si$_3$N$_4$ after processing in integrated 3D nanoscale devices. The samples were diced into 12 mm × 3 mm pieces and degreased with acetone, methanol and deionized (DI) H$_2$O. The native oxide on Si was removed by immersing the degreased samples into a 0.5% HF(aq) solution for 30 seconds. For consistency in cleaning procedure, the SiO$_2$, SiON and patterned samples were subjected to the same cleaning procedure. The samples were blow-dried using high purity N$_2$ gas. Two or three samples out of the Si, SiO$_2$, SiON and patterned sample were loaded together on a single sample holder to expose the samples to the same ALD conditions. The samples were loaded into a load lock chamber pumped by a turbo molecular pump and backed by a mechanical pump. The base pressure of the load lock was ~2.0×10$^{-7}$ Torr. Subsequently, the samples were transferred in-situ to an ultra-high vacuum chamber with a base pressure of ~3.0×10$^{-10}$ Torr pumped by an ion pump and titanium sublimation pump. The ultra-high vacuum chamber was equipped with a monochromatic XPS (XM 1000 MkII/SPHERA, Omicron Nanotechnology), STM (Omicron Nanotechnology) and annealing system using a pyrolytic boron nitride (PBN) heater.

The samples were first annealed at 120°C in the ultra-high vacuum chamber and the chemical composition of the samples were determined using XPS. Afterwards, the samples were transferred in-situ to a home-made reaction chamber having a base pressure of ~5.0×10$^{-7}$ Torr. For MoSi$_x$ deposition, MoF$_6$ (Synquest Laboratories, 99%) and Si$_2$H$_6$ (Air Liquide, 99.99%) precursors were employed.

During the ALD cycles, a constant purge of N$_2$ (80 mTorr) was used, and the pressure of this purge was controlled using a leak valve. The MoF$_6$ and Si$_2$H$_6$ doses were regulated using pneumatic valves controlled by a LabView program. An expansion volume
was employed for the MoF₆ and Si₂H₆ doses. This consisted of filling a secondary volume with MoF₆ or Si₂H₆ and dosing the precursors from their respective secondary volumes. The fill/dose times for the MoF₆ were 40ms/50ms and for Si₂H₆ the fill/dose times were 18ms/18ms. The exposures of MoF₆ and Si₂H₆ were calculated in terms of Langmuirs (L) where 1 L = 1 × 10⁻⁶ Torr × 1 sec. The pressure spikes during the exposures were monitored using a Convectron gauge in the reaction chamber. The doses were 1.8 MegaL for MoF₆ and 4.2 MegaL for Si₂H₆ with a 2-minute wait time between the doses. The samples were heated using a pyrolytic boron nitride (PBN) heater, and the temperature was maintained at 120°C. The chamber walls were maintained at 80°C. After the deposition cycles, the samples were transferred in-situ to the ultra-high vacuum chamber for XPS and STM. For the XPS measurement, the X-rays were generated by an Al Kα anode (1486.7 eV). XPS data was acquired using constant analyzer-energy (CAE) with a step width of 0.1 eV and a pass energy of 50 eV. The XPS detector was at 60° to the sample normal (30° take-off angle from the sample surface) with a detector-acceptance angle of 7°. XPS spectra were analyzed after correcting each peak area with its respective relative sensitivity factor using a Casa XPS v.2.3 program. All of the chemical components in this work were normalized to the sum of all components. STM was performed with a sample bias of -1.8 V and a constant current of 200 pA.

To investigate the elemental composition of the bulk of the film, Ar⁺ sputtering was performed in conjunction with XPS. A lens voltage of 5kV with a beam current of 1.2 µA at 6.0×10⁻⁷ Torr of Ar was employed; since a raster was used to cover the full sample area, the current density was approximately 1.2 uA/50 mm². The MoSiₓ sample was maintained
at 25°C during sputtering to minimize any thermal desorption of SiH$_3$F$_y$ or SiF$_4$ compounds from the surface.

2.4 Results and Discussion

2.4.1 XPS of MoF$_6$ and Si$_2$H$_6$ saturation on Si and selectivity in preference to SiON

Fig. 2.1(a) shows the XPS chemical composition of the HF cleaned Si surface before and after sequential doses of MoF$_6$ and Si$_2$H$_6$ at 120°C (note: the raw XPS spectra are presented in the supplement). After the HF clean, all the Si was in an oxidation state of 0 with 9% O and 12% C contamination which was most likely due to adventitious hydrocarbon adsorption during the sample transfer into vacuum. HF(aq) is known to eliminate native oxide on Si and leaves the Si surface H-terminated [21]. Note that the yellow bars (Si 2p) in Fig. 2.1 indicate the total amount of Si while the gray bars (Si (0)) indicate the amount of Si which is in an oxidation state of 0 (Si$^0$). The amount of Mo$^0$ (Mo (0), the purple bars) and the total amount of Mo (Mo 3d, the pink bars) were also plotted separately to emphasize the amount of pure MoSi$_x$. After the 5.4 MegaL of MoF$_6$ at 120°C, 14% Mo and 38% F were deposited on the HF cleaned Si surface. After an additional 5.4 MegaL of MoF$_6$ at 120°C were dosed, the Mo concentration increased from 14% to 16% and the F concentration increased from 38% to 42%. This small increase in Mo and F content after an additional 5.4 MegaL of MoF$_6$ shows that the reaction of MoF$_6$ on HF cleaned Si is self-limiting. (Also see Fig. 2.14) After the Si surface was saturated with MoF$_x$, the ratio of F/Mo was 2.6 and all of the Si was in an oxidation state of 0. Sequential doses of 4.2 MegaL of Si$_2$H$_6$ and 42 MegaL of Si$_2$H$_6$ indicate that the Si$_2$H$_6$ reaction also saturates on the MoF$_x$ covered Si surface. It is shown below that with a thicker sub-
stoichiometric MoSi\textsubscript{2} film, additional Si can be forced onto the surface. However, the Si\textsubscript{2}H\textsubscript{6} reacts in a self-limiting manner on a thinner (monolayer) film of Mo. After saturation of Si\textsubscript{2}H\textsubscript{6}, the Si content was 59\% and F decreased to 10\%. Since the substrate is Si, this increase of the Si content after dosing Si\textsubscript{2}H\textsubscript{6} could be partially ascribed to the substrate since F desorption occurred in the form of SiH\textsubscript{x}F\textsubscript{y} or SiF\textsubscript{4}. However, attenuation of the Mo after Si\textsubscript{2}H\textsubscript{6} dose was observed which is consistent with the deposition of Si. The deposition of Si was also demonstrated by previously published studies using WF\textsubscript{6} and Si\textsubscript{2}H\textsubscript{6} or MoF\textsubscript{6} and Si\textsubscript{2}H\textsubscript{6} chemistry [14,18]. The half cycles of Si\textsubscript{2}H\textsubscript{6} dosed onto a WF\textsubscript{6} or MoF\textsubscript{6} saturated surface; for the Mo chemistry, the reaction was described as:

$$MoF_5^* + Si_2H_6(g) \rightarrow MoSiH_{x}F_{3-x}^* + SiH_{2-x}F_{2+x}(g) + 2H_2(g) \quad (x = 0, 1 \text{ and } 2)$$

where the asterisks indicate surface species. The authors pointed out that the subsequent WF\textsubscript{6} or MoF\textsubscript{6} doses react with the deposited SiH\textsubscript{x}F\textsubscript{y} species to form W or Mo metal again.

The reaction of MoF\textsubscript{6} and Si\textsubscript{2}H\textsubscript{6} on H-terminated Si demonstrates the potential for MoSi\textsubscript{x} ALD on Si-H terminated Si; conversely, for the same series of MoF\textsubscript{6} and Si\textsubscript{2}H\textsubscript{6} saturation doses on SiON, no reaction was observed. (see Fig. 2.1(b)). It should be noted that while this sample was nominally SiON, XPS showed only negligible amounts of N on the surface and so this sample is mostly ion damaged SiO\textsubscript{x}. After the first 3 pulses of MoF\textsubscript{6}, 8\% F and negligible Mo (<1\%) were observed. For the rest of the saturation doses, the SiON surface remained unreactive to both MoF\textsubscript{6} and Si\textsubscript{2}H\textsubscript{6}. This inherent chemical selectivity of SiO\textsubscript{2} (not SiON) was reported earlier using WF\textsubscript{6} and SiH\textsubscript{4} for W metal ALD on Si vs. SiO\textsubscript{2} [13,14,23]. Kalanyan et al. used SiH\textsubscript{4} as a sacrificial reducing agent for W deposition, and the substrate dependent selectivity was explained by the thermodynamically unfavorable reaction between WF\textsubscript{6} and stable Si-O bonds of pristine
SiO₂. A similar mechanism is consistent with the selectivity of MoF₆ and Si₂H₆ on Si vs. SiON despite Si₂H₆ being more reactive than SiH₄ and SiON being a less stable film than SiO₂. While the SiON used in this study is ion damaged, the Si is in oxidation states of +3 and +4 and the data is consistent with these strong Si-O, Si-N, SiO-H bonds precluding the Si from forming bonds to Mo. (see Fig. 2.10). DFT models by Kwon et al. show that the stronger SiO-H bond compared to Si-H can raise the activation barrier and enthalpy of reaction for ALD [30].

In Fig. 2.2, the XPS spectra of Si 2p and Mo 3d for the HF cleaned Si sample are shown to compare the oxidation states at each experimental step. After the first 5.4 MegaL of MoF₆, the Si 2p peak remained at an oxidation state of 0 which is consistent with Si-Mo bond formation. The Mo 3d peaks appeared at multiple oxidation states which indicates that the surface species are MoFx with x = 4, 5 and 6. (black line) The additional 5.4 MegaL of MoF₆ did not change the oxidation states of the Si 2p or the Mo 3d peaks. (blue line) These results are consistent with the formation of Si-Mo-Fx at the surface. It is noted that the F/Mo ratio was 2.6 after the MoF₆ saturation dose from XPS. (Fig. 2.1(a)) while the Mo is in oxidation states of 4-6; therefore, it is possible that there is some Mo-O bond formation. A small shoulder peak at a higher binding energy (103 eV) on the Si 2p XPS peak appeared after a 4.2 MegaL of Si₂H₆ dose. (red line) This is consistent with Si-F or Si-O formation. The Mo 3d spectra shows that after a single Si₂H₆ dose, all of the Mo is reduced to Mo⁰ with a binding energy of 227.4 eV. This is consistent with the formation of a monolayer of MoSiₓ and the transfer of any residual oxygen or fluorine from Mo to Si in the form of Si-O and Si-F bonds. A possible simplified reaction of MoF₆ and Si₂H₆ could be described as:
\[ \text{MoF}_6(g) + 1.5\text{Si}_2\text{H}_6(g) \rightarrow \text{MoSi}_2(s) + \text{SiF}_4(g) + 3.5\text{H}_2(g) + 2\text{HF}(g) \]

2.4.2 Selectivity of MoSi\textsubscript{x} in preference to SiO\textsubscript{2} and stoichiometry

ALD characteristics of MoSi\textsubscript{x} on the Si substrate and the inherent selectivity over the SiO\textsubscript{2} and SiN\textsubscript{x} substrates were verified via XPS of MoSi\textsubscript{x} deposition on a patterned sample. Fig. 2.3 shows the chemical composition of a set of three samples: HF cleaned Si, HF cleaned SiO\textsubscript{2} and HF cleaned patterned sample (note: the raw XPS spectra are presented in Fig. 2.12). The three samples were loaded together on a single sample holder to ensure that they were exposed to identical deposition conditions. The Si and SiO\textsubscript{2} samples allowed verification of selectivity during deposition on the patterned sample. The patterned sample had SiO\textsubscript{2} layers sandwiched by SiN\textsubscript{x} on top of the Si substrate as shown in Fig. 2.3(d). It is noted that the SiN\textsubscript{x} on the patterned sample was actually SiON since it was ion damaged and ashed in O\textsubscript{2} during fabrication. As shown in Fig. 2.3(a), a 30 s HF clean removed the native oxide on Si. The thermally grown SiO\textsubscript{2} was 300 nm thick and so the 30 s of HF clean did not change the elemental composition or oxidation states of SiO\textsubscript{2}. The HF cleaned patterned sample showed a mixture of SiN\textsubscript{x}, SiO\textsubscript{x} and Si\textsuperscript{0}. Even though there were Si and SiO\textsubscript{2} samples loaded together to monitor the selectivity of the patterned sample, the blanket films might not be the same as 3D nanostructure features due to the high aspect ratio as well as damage from the patterning processes. Employing a patterned sample in XPS allowed selectivity determination on the nanoscale on realistic surface because the Si\textsuperscript{0} component could be distinguished from SiO\textsubscript{2} or SiN\textsubscript{x} from XPS. If MoSi\textsubscript{x} was deposited selectively on the patterned sample, it was expected that only the attenuation of this Si\textsuperscript{0} component from the mixture of SiO\textsubscript{2} and SiN\textsubscript{x} would be observed. (See Fig. 2.12)
XPS was performed after 5 ALD cycles of MoF$_6$ and Si$_2$H$_6$ at 120°C as shown in Fig. 2.3(b). XPS showed a surface composition of 32% Mo and 10% Si with 39% F on the Si sample which shows a MoF$_x$ rich surface. This is in contrast to a surface closer to MoSi$_2$ after the first ALD cycles. Even though a monolayer of MoSi$_2$ was able to be deposited on Si in the ALD saturation experiments described in Fig. 2.1 and Fig. 2.2, consecutive ALD cycles did not produce stoichiometric MoSi$_2$. The formation of Si deficient MoSi$_x$ could be due to the surface SiH$_x$F$_y$ species desorbing during the fluorosilane elimination process and due to residual Mo-F bonds which are not readily removed by standard Si$_2$H$_6$ dosing [18,20,22]. For the first 1-3 monolayers, there is an excess of Si from the substrate present to assist in fluorine desorption in the form of SiH$_x$F$_y$ or SiF$_4$, but for thicker films Mo-F surface bonds may persist since the only available Si is from the gaseous Si$_2$H$_6$. The overall fluorosilane elimination chemistry using MoF$_6$ and Si$_2$H$_6$ is consistent with one of two chemical reactions:

$$MoF_6(g) + Si_2H_6(g) \rightarrow Mo(s) + 2SiH_3F(g) + 2H_2(g)$$

or

$$2MoF_6(g) + 1.5Si_2H_6(g) \rightarrow 2Mo(s) + 2SiF_4(g) + SiHF_3(g) + 3.5H_2(g) + 2HF(g)$$

It is noted these processes are limited to the first 1-3 monolayers, since cross sectional TEM studies of the patterned sample shows Si substrate depletion of about 1 nm. For the ALD cycles remote from the surface, the depth profile studies below show that the MoF$_x$ is just a surface layer and not a bulk film. There was no MoSi$_x$ deposition on the SiO$_2$ substrate consistent with highly selective ALD. On the patterned sample, XPS showed that 5% Mo was deposited, and the Si$^0$ was attenuated to 1%. (The raw XPS peaks are shown in Fig. 2.12(c)) The fraction of N and O at the surface did not change significantly during ALD.
on the pattern sample. The data is consistent with Si-deficient MoSi$_x$ being deposited selectivity on the 6% of Si$^0$ (The grey bar in Fig. 2.3(a)) on the patterned sample. This selectivity on the pattern samples is consistent with three aspects of the XPS study: (1) There was MoSi$_x$ deposition on the Si sample but not on the SiO$_2$ sample. (2) After the MoSi$_x$ deposition, only the Si$^0$ (not the higher oxidation state Si peaks from Si-N and Si-O) was attenuated on the patterned sample. (3) Numerically, $\sim$4% Mo deposition on the patterned sample with 6% Si$^0$ is proportional to having 32% Mo on the Si sample with 54% Si$^0$ on the HF clean surface.

To form MoSi$_2$, the three samples were exposed to an additional 25.2 MegaL (6 pulses) of Si$_2$H$_6$ at 120°C. (Fig. 2.3(c)) After the extra Si$_2$H$_6$, Si increased to 20% on the Si substrate consistent with Si being incorporated into the film or on the surface. These extra Si$_2$H$_6$ doses did not decrease the selectivity for deposition on Si versus SiO$_2$.

### 2.4.3 Post deposition anneal effect on MoSi$_x$ composition

The substrate selectivity of the MoSi$_x$ deposition with respect to SiON along with the effect of post deposition anneal on film composition were investigated. It should be noted that this SiON is actually Si$_3$N$_4$ which has been ashed with an O$_2$ plasma and so this models patterned sample sidewalls after RIE etching. The SiON was loaded into the chamber along with Si and SiO$_2$ for calibration. Fig. 2.4(a) shows that the SiON surface is composed primarily of SiN$_x$ after the HF clean. After the 5 cycles of MoSi$_x$ ALD followed by an additional 25.2 MegaL of Si$_2$H$_6$, there was 24% Mo and 18% Si on HF cleaned Si while less than 1% Mo was detected on the SiO$_x$ and SiN$_x$ surfaces as shown in Fig. 2.4(b) (Note, the raw XPS spectra are presented in the supplement). Subsequently, the three
samples were annealed at 520°C for 3 mins which decreased F from 25% to 3% on the Si substrate. The 520°C PDA also reduced all of the Mo to Mo⁰ on the Si substrate and decreased the Si/Mo ratio from 0.75 to ~0.5 at the surface. This is consistent with the desorption of surface F in the form of SiHF₃ or SiF₄. The XPS analysis of the high temperature anneal indicates that the F could be removed from the film by the post anneal which may be needed for practical application in MOSFETs [25-27].

2.4.4 Topography of the MoSiₓ film and selectivity

Using an in-situ STM and ex-situ AFM, the surface topographies were investigated after the deposition and the high temperature anneal on the Si and SiO₂ samples. A separate sample of HF cleaned Si after 20 cycles of MoF₆ and Si₂H₆ was prepared for the in-situ STM. Fig. 2.5(a) shows the STM image of MoSiₓ/HF cleaned Si sample. The MoSiₓ film was atomically flat and conformal with an RMS roughness of 2.8 Å. This sample was annealed in-situ at 500°C for 3 mins in the ultra-high vacuum chamber at a pressure of ~5.0×10⁻¹⁰ Torr. After the 500°C anneal, the film became flatter with an RMS roughness of 1.7 Å shown in Fig. 2.5(b). There was no agglomeration at the surface. Another sample of MoSiₓ/HF cleaned Si after 5 ALD cycles at 120°C followed by an in-situ 550°C anneal was taken into an ex-situ furnace for a 900°C spike anneal in 5% H₂ balanced with N₂. After the 900°C spike anneal, AFM was used to obtain the surface morphology. The film retained a sub-nanoscale RMS roughness of 4.75 Å demonstrating that the MoSiₓ film has very good thermal stability up to 900°C. (see Fig. 2.5(c))

Fig. 2.5(d) shows an ex-situ AFM image of the SiO₂ surface after dosing 5 ALD cycles at 120°C followed by an in-situ 550°C anneal for 3 minutes in order to confirm the
selectivity by counting the number of nuclei on the surface. The density of nuclei was 9 nuclei/µm² which confirms the very good selectivity over SiO₂. P.C. Lemaire et al. [13] studied the relationship between inherent substrate selectivity and hydroxyl density during tungsten (W) ALD using WF₆ and SiH₄. They reported that an increase in the surface OH density on SiO₂ provokes earlier nucleation of W on SiO₂ (selectivity loss) via a reaction of W-ALD reactants with the surface hydroxyls. The authors also stated that pre-dosing the Si-OH terminated SiO₂ with SiH₄ induces earlier W nucleation by forming a Si monolayer on SiO₂. In present study, Si₂H₆ was employed which is more reactive than SiH₄ due to the weak Si-Si bond; therefore it is likely that Si₂H₆ will react with Si-OH sites on SiO₂ above a threshold exposure. To estimate the selectivity of MoSiₓ deposition between H-terminated Si versus OH terminated SiO₂, the surface OH density of the thermally grown SiO₂ was assumed to be ~2 OH/nm² as reported by R. Mueller et al. [29] Assuming MoSiₓ deposition on H-terminated Si was 100%, there were only ~10 nuclei/µm² out of ~2×10⁶/µm² (2 OH/nm²) hydroxyls on SiO₂ which is consistent with more than 10⁶ selectivity between Si-H groups and hydroxyls on SiO₂. Parson et al.[14] reported for the ALD of W using WF₆ and SiH₄, ~450 nuclei/µm² after 30 cycles of W ALD which is about 50× greater than in the present study. There are one two previous reports of similar selectivity for any selective ALD or CVD process. Chang et al.[24] studied the CVD of W by a mixture WF₆+H₂+SiH₄ and measured the W particles on SiO₂; while they observed a low particle density (20 particles/cm²), the particles were ~2 µm² in size and therefore at least 10³ larger is mass than the particles in the present study (~1.4×10⁻³ µm² in size with ~2 nm height). The high selectivity in the present study is consistent with careful control
of wall temperature and using short high pressure \( \text{Si}_2\text{H}_6 \) pulses and longer purge cycles to avoid CVD.

### 2.4.5 Depth profile XPS in conjunction with \( \text{Ar}^+ \) sputter

A depth profile study was performed to determine the internal composition of the MoSi\(_x\) film. Fig. 2.6 (a) shows XPS of MoSi\(_x\)/HF cleaned Si after sequential sputtering experiments (Addition raw XPS spectra are presented in the supplement). The MoSi\(_x\) film was deposited on HF cleaned Si at 120°C using 5 ALD cycles of MoF\(_6\) and Si\(_2\)H\(_6\) without additional Si\(_2\)H\(_6\) incorporation. As the sputtering time increased, the MoSi\(_x\) film became thinner until the underlying Si substrate was exposed. The first 10 mins of sputtering decreased the F from 35% to 8% while the Mo shifted from a mixture of oxidized Mo and Mo\(^0\) to pure Mo\(^0\). The data is consistent with the surface F being bonded primarily to Mo. Following consecutive sputtering cycles, the amount of Si increased and the amount of Mo decreased. Furthermore, the amount of Si\(^0\) (gray bars) increased together with the total Si (yellow bar) and reached a maximum at 43% after 100 mins of a total sputtering time. The Si\(^0\)/Mo\(^0\) ratio was employed to distinguish the pure MoSi\(_x\) phase because as shown by Wagner et al. as well as Brainard and Wheeler in the pure MoSi\(_x\) phase, both Mo and Si are bonded to each other and have an oxidation state of 0 consistent with minimal charge transfer between Mo and Si in the silicide. [32,33] After removal of the silicon oxide and MoF\(_x\) species at the surface, the percentage of Si\(^0\) exceeded that of Mo\(^0\). The Si\(^0\)/Mo\(^0\) ratio in the bulk of the MoSi\(_x\) film was 1.41 which corresponds to a Si-deficient MoSi\(_x\) film. It is noted that in the center of the film the Si/Mo ratio is 1.77 therefore, in the absence of background O\(_2\)/H\(_2\)O, it is possible the Si\(^0\)/Mo\(^0\) ratio would be closer to 2.
Fig. 2.6 (b) shows the raw XPS spectra of Si 2p corresponding to each XPS measurement in Fig. 2.6 (a). The Si peak at 99.2 eV increased and broadened to higher binding energy after the 4\textsuperscript{th} sputtering cycle. In contrast, the energy of the of Mo peak corresponded to Mo\textsuperscript{0} after each sputtering cycle. (Fig. 2.11) The data is consistent with the bulk MoSi\textsubscript{x} film being mostly Si\textsuperscript{0} and Mo\textsuperscript{0} in the form of MoSi\textsubscript{x}, while the top surface and the bottom interface was rich in SiO\textsubscript{x}. The top SiO\textsubscript{x} is consistent with contamination from the chamber environment while the bottom interfacial oxide is consistent with the imperfect ex-situ HF clean. The sub-stoichiometric oxide at the bottom interface did not affect the deposition and film quality indicating that the inherent selectivity of the MoSi\textsubscript{x} ALD is sensitive to the quality of the SiO\textsubscript{2}. Fig. 2.6 (c) shows the percentages of the chemical components obtained from the XPS measurement in Fig. 2.6 (a). After the 2\textsuperscript{nd} sputtering cycle (40 mins of total sputtering time), F decreased to below 3\% and eventually reached 0\%. O in the bulk of the film was <10\% but slowly increased to 15\% at the MoSi\textsubscript{x}-Si interface which is consistent with the existence of an interfacial oxide layer.

2.4.6 Incorporation of Si\textsubscript{2}H\textsubscript{6} for stoichiometry using depth profile XPS

To understand the effect of the additional Si\textsubscript{2}H\textsubscript{6} doses on the Si/Mo ratio of MoSi\textsubscript{x} film, XPS depth profiling was performed on a MoSi\textsubscript{x} film which had the additional Si incorporation. An additional 6 pulses (25.2 MegaL) of Si\textsubscript{2}H\textsubscript{6} were dosed at the end of the 5 ALD cycles of MoF\textsubscript{6} and Si\textsubscript{2}H\textsubscript{6} at 120\°C followed by an anneal at 530\°C for 3 mins on dry cleaned Si. This dry clean process uses a downstream plasma of NF\textsubscript{3} and NH\textsubscript{3} with Ar as a carrier gas [31]. Fig. 2.7(a) presents a series of depth-profile XPS after each experimental step. After the 6×Si\textsubscript{2}H\textsubscript{6}/5ALD cycles, there were 28\% F, 20\% Si, and 28\%
Mo at the surface. F on the surface was mostly removed after the 530°C anneal and the Mo was all reduced to Mo$^0$ which was consistent with the desorption of F in the form of SiH$_x$F$_y$ or SiF$_4$ from the surface as presented in Fig. 2.4(c). The Si/Mo ratio was 0.89 at this step. In comparison, the Si/Mo ratio of the MoSi$_x$ film without the extra Si$_2$H$_6$ doses was only 0.33. (see Fig. 2.7(b)) After removing the surface oxide contamination, the Si$^0$/Mo$^0$ in the bulk was 1.32 (Si/Mo = 1.96) for MoSi$_x$ with extra Si$_2$H$_6$ pulses. This was comparable to the Si$^0$/Mo$^0$ = 1.41 (Si/Mo = 1.77) in the bulk of MoSi$_x$ without extra Si$_2$H$_6$ incorporation as depicted in Fig. 2.7(c). The ratio of Si$^0$/Mo$^0$ indicates the stoichiometry of the pure MoSi$_x$ component. This is important for the electrical properties as contact materials in MOSFETs. In this context, the notation of Si$^0$/Mo$^0$ indicates the ratio between Si and Mo at oxidation states of 0; conversely, Si/Mo indicates the ratio of the total amount of Si to total amount of Mo in the film including Si and Mo atoms boned to F and O and therefore having higher oxidation states. These results are consistent with the extra Si$_2$H$_6$ pulses increasing the Si content at the Si-deficient MoSi$_x$ surface after the ALD cycles. In contrast, the Si/Mo ratios in the bulk of the MoSi$_x$ films were close to stoichiometric MoSi$_2$. Fig. 2.7(d) shows the XPS percentage of each chemical component in the function of the Ar$^+$ sputter time which is consistent with the MoSi$_x$ formation in bulk of the film.

Previous studies reported Si$_2$H$_6$ and SiH$_4$ to be sacrificial reactants to reduce metal fluorides for pure metal deposition [14,18,20,22,28]. D. Seghete et al. previously reported Mo metal deposition on Al$_2$O$_3$ using MoF$_6$ and Si$_2$H$_6$ at 130°C with almost complete removal of Si from the Mo metal film as determined by Auger Electron Spectroscopy (AES) [18]. Even though identical reactants were used at a very similar temperature, there was a significant difference in the Si$_2$H$_6$ dosing conditions. For pure Mo metal deposition
with minimal Si impurities, 1.5 MegaL of Si$_2$H$_6$ was introduced into a high vacuum reaction chamber for 60 s at a constant pressure of 25 mTorr using a leak valve. In the present study, 4.2 MegaL of Si$_2$H$_6$ was introduced within 6 seconds using a pneumatic valve. This is about 3 times larger Si$_2$H$_6$ exposure within 10 times shorter dosing time thus a 30× higher partial pressure during the ALD dose. The 30× higher instantaneous pressure during dosing may allow a precursor mediated Si$_2$H$_6$ chemisorption layer to remain on the surface long enough to react with the Mo to incorporate more Si into the film. This self-limiting Si CVD component can also explain the larger growth rate of MoSi$_x$ (1.2 nm/cycle) in the present study versus that of pure Mo metal (0.6-0.7 nm/cycle) at a similar process temperature. However, the possibility of the thermal decomposition of Si$_2$H$_6$ during the ALD cycles were excluded since the thermal decomposition of Si$_2$H$_6$ did not occur below 360°C. (See Fig. 2.15) It is noted that an alternative explanation is provided by D. Seghete et al.[18] which is the reaction is sufficiently exothermic that the high pressure Si$_2$H$_6$ dosing raises the surface temperature during reaction.

2.4.7 Electrical property (resistivity) of the MoSi$_x$ film

The resistance of the MoSi$_x$ film was measured using a 4-point probe measurement. For the electrical measurement, updoped Si (001) with >10000 ohm·cm resistance was used as a substrate. For the electrical measurement, 10 cycles of MoSi$_x$ ALD at 120°C was deposited on an HF cleaned intrinsic (semi-insulating) Si sample followed by an in-situ 550°C anneal for 3 minutes and a 900°C spike anneal in 5% H$_2$ balanced in N$_2$. Ni dots were deposited as a probe contact. Fig. 2.8 shows the resistance of the film versus the
current. The resistance was 110 Ohm and, using an infinite sheet approximation, the resistivity could be calculated as:

\[ \rho = ktR_{\text{max}} = (4.53) \times (10 \times 10^{-7}) \times (110) = 498 \mu\Omega\text{cm} \]

where \( k \) is a constant, \( t \) is thickness and \( R_{\text{max}} \) is the measured maximum resistance.

2.4.8 Cross-sectional TEM of a patterned sample after MoSi\textsubscript{x} selective deposition

A cross-sectional TEM study was performed on the patterned sample to confirm the selectivity of MoSi\textsubscript{x} on the nanostructured pattern. On the HF cleaned patterned sample, 5 cycles of MoSi\textsubscript{x} ALD followed by an additional 25.2 MegaL of Si\textsubscript{2}H\textsubscript{6} were dosed at 120°C. The elemental composition of this sample at each deposition step is shown in Fig. 2.3 (a-c). Fig. 2.9 (a-b) presents the cross-sectional TEM images of the patterned sample before and after MoSi\textsubscript{x} deposition. The TEM image shows complete selectivity of MoSi\textsubscript{x} deposition only on Si but not on SiN\textsubscript{x} nor SiO\textsubscript{2} without damaging Si substrate by etching. (See Fig. 2.9 (c-d)) The thickness of the MoSi\textsubscript{x} film deposited on Si was \( \sim 6.3 \) nm after the 5 ALD cycles followed by an additional 25.2 MegaL which gives a growth rate of 1.2 nm/cycle. This higher than expected growth rate was observed by D. Seghete et al.[18] and ascribed to extra Mo deposition due to the decomposition of MoF\textsubscript{6} from a highly exothermic reaction between MoF\textsubscript{6} and H-Si species. In addition, a direct reaction between the H-terminated Si substrate and MoF\textsubscript{6} could be also attributed to the high growth rate by consuming Si from the substrate. The reaction between the MoF\textsubscript{6}(g) and Si(s) could be:

\[
\text{MoF}_6(g) + 2\text{Si} - \text{H}(g) \rightarrow \text{Si} - \text{MoF}_2(s) + 2\text{SiHF}_3(g) + \text{HF}(g)
\]
or

\[
\text{MoF}_6(g) + 2\text{Si}(s) \rightarrow \text{Si} - \text{MoF}_2(s) + \text{SiF}_4(g)
\]
, where Si-H(s) indicates H terminated Si surface and Si-MoF$_2$(s) indicates the MoF$_2$ surface species bonded to the Si atoms of the surface. However, extra Si$_2$H$_6$ pulses of high pressure after 5 cycles may incorporated more Si into the film which is consistent with the high growth rate because the consumption of Si from the surface on patterned samples was very small as shown in Fig. 2.9. Due to the high growth rate per cycle of MoSi$_x$ ALD, 5 ALD cycles is sufficient for contact materials. There was 2.8 nm of an interface oxide layer between the MoSi$_x$ film and the Si substrate which is consistent with the results in Fig. 2.6. This could be improved by an in-situ clean such as a plasma clean at the sample preparation step.

2.5 Conclusions

Selective atomic layer deposition of sub-stoichiometric MoSi$_2$ was achieved by an inherently selective process on hydrogen-terminated Si versus thermally grown SiO$_2$, ion damaged SiON, and SiN$_x$. This inherent selectivity is based on the favorable reactivity of MoF$_6$ and Si$_2$H$_6$ on H-Si but not on SiO$_2$ or SiN$_x$ since Si-O, Si-N, and SiO-H bonds are strong enough that they cannot be cleaved by either precursor at 120°C. Both MoF$_6$ and Si$_2$H$_6$ showed self-limiting behavior which allowed deposition of a highly conformal and smooth film with a root mean square (RMS) roughness of 2.8 Å. Post-annealing in ultra-high vacuum at 500°C for 3 minutes further decreased the RMS roughness to 1.7 Å. The quality of the film was preserved even after a 900°C spike anneal in an H$_2$/N$_2$ environment which is consistent with very good thermal stability. A depth profiling XPS study revealed that the bulk of the MoSi$_x$ film is close to stoichiometric MoSi$_2$ (Si/Mo = 1.7 – 1.9) with <10% oxygen and fluorine. The surface of the MoSi$_x$ film after 5 ALD cycles showed a
highly Si-deficient MoSi$_x$ surface with Si/Mo ratio of 0.33 and this Si/Mo ratio at the surface could be improved to 0.89 by pulsing extra Si$_2$H$_6$. The selectivity of MoSi$_x$ was examined on nanoscale patterned features of SiO$_2$ and SiN$_x$. The cross-sectional TEM imaging shows that the selectivity is retained on the nanoscale and that MoSi$_x$ can be selectively deposited on Si without substrate consumption. A large growth rate of 1.2 nm/cycle allows only 5 ALD cycles to be sufficient for its purpose as a contact material. This inherently selective MoSi$_x$ deposition would obviate the need for lithography on complicated 3D MOSFET structures (FinFETs). The selectivity for Si-H bonds vs SiO-H bonds exceeds $10^6$ showing that with careful choice of precursor, extreme selectivity is possible on the nanoscale even without the use additional passivation layers. The study also showed that ALD of silicide versus metal could readily be switched while retaining selectivity by changing the partial pressure during the ALD pulse of the reductant.

2.6 Acknowledgements

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Chapter 2, in part or in full, is a reprint of the material as it appears in the Applied Surface Science. J. Y. Choi, C. F. Ahles, R. Hung, N. Kim, and A. C. Kummel, "Selective atomic layer deposition of MoSi$_x$ on Si(001) in preference to Silicon Nitride and Silicon Oxide" Applied Surf. Sci., 2018, 462, 1008–1016. The dissertation author was the primary investigator and author of this paper.
2.7 Supplemental Materials

An experiment was performed to study the saturation behavior of MoF$_6$ on HF cleaned Si. Fig. 2.14(a) below shows the elemental composition of HF cleaned Si followed by different amounts of MoF$_6$ doses at $120^\circ$C. Mo coverages on HF cleaned Si were 12.3%, 13.9% and 15.8% after 0.25 MegaL, 5.4 MegaL, and 10.8 MegaL of MoF$_6$ doses respectively. Fig. 2.14(b) shows $\Delta$Mo coverage/$\Delta$dose size at each experiment corresponding to Fig. 2.14(a). Even though the Mo coverage increases as the amount of dose increases, the increase per MegaL of dose is only substantial for the 0.25 MegaL dose. Since the sizes of the dose for the next two experiments are 20 times larger, the increases of Mo coverage per MegaL of doses are negligible. This is consistent with the saturation of MoF$_6$.

To investigate if there was a contribution of Si$_2$H$_6$ decomposition to the growth rate, Si CVD (chemical vapor deposition) was performed on HF cleaned Si and HF cleaned SiON using Si$_2$H$_6$. Fig. 2.15 below shows the elemental composition of HF cleaned Si and HF cleaned SiON followed by Si$_2$H$_6$ doses at $360^\circ$C and $500^\circ$C. 3 MegaL of Si$_2$H$_6$ was dosed at $360^\circ$C and Si$_2$H$_6$ did not react with Si-H surface nor the SiON surface. The Si percentage went up from 76% (HF cleaned Si) to 87% (After dosing 3 MegaL Si$_2$H$_6$ at $360^\circ$C); however, this is due to reduction of C contaminants from the heating to $360^\circ$C since no change was observed on SiON. After the 10 MegaL Si$_2$H$_6$ dose at $500^\circ$C, both Si and SiN$_x$ surfaces were completely covered with Si showing 99% Si and 98% Si respectively. This is consistent with the Si CVD by thermal decomposition of Si$_2$H$_6$. This is consistent with the absence of Si$_2$H$_6$ thermal decomposition at the deposition temperature of $120^\circ$C.
Fig. 2.16 is a cross-sectional TEM image after 20 cycles of MoF$_6$ and Si$_2$H$_6$ at 120°C on HF cleaned Si. The MoSi$_x$ film thickness was 17.7 nm which correspond 0.88 nm/cycle. This is smaller than the growth rate (1.2 nm/cycle) that we obtained from 5 ALD cycles followed by extra Si$_2$H$_6$ pulses. The higher growth rate for the first 5 ALD cycles is consistent with the hypothesis that the larger growth is due to the direct reaction between Si substrate and MoF$_6$ or from extra Si incorporation into the film after the 5 ALD cycles. The absence of substrate consumption in the cross-sectional images of the patterned samples (Fig. 2.9) implies that the substrate consumption is limited to < 1 nm.
2.8 Figures

Figure 2.1. XPS of MoSi\textsubscript{x} film selectively grown on HF cleaned Si versus degreased SiON after a cycle of saturating doses of MoF\textsubscript{6} and Si\textsubscript{2}H\textsubscript{6}. (a) 2 sets of 5.4 MegaL of MoF\textsubscript{6} were dosed on HF cleaned Si at 120°C. XPS showed saturation of Mo at 16%. Afterward, 4.2 MegaL and an additional 42 MegaL of Si\textsubscript{2}H\textsubscript{6} were dosed onto the MoF\textsubscript{6}-saturated Si surface at 120°C; Si was saturated at 59%. (b) The same amounts of MoF\textsubscript{6} and Si\textsubscript{2}H\textsubscript{6} were dosed on the degreased SiON at 120°C. Degreased SiON showed an inherent non-reactivity to both MoF\textsubscript{6} and Si\textsubscript{2}H\textsubscript{6} and had <1% Mo detected on the surface.
Figure 2.2 Oxidation States from XPS peaks of Si 2p and Mo 3d at each experimental step on HF cleaned Si. (a) Si 2p peaks after sequential MoF$_6$ and S$_2$H$_6$ doses shows that Si remained in oxidation state of 0 after the 10.8 MegaL of MoF$_6$ at 120°C (blue line) which is consistent with Mo-Si bond formation and no Si-F bonds being present on the surface. After the 4.2 MegaL S$_2$H$_6$ dose at 120°C (red line), most of the Si stayed in an oxidation state of 0. This is consistent with the formation of a monolayer of MoSi$_2$. A small oxidized Si peak emerged at higher binding energies which might be SiH$_x$F$_{4-x}$ ($x = 2$ or 3) or SiO$_x$ at the surface. (b) Mo 3d peaks after sequential MoF$_6$ and S$_2$H$_6$ doses shows that the Mo 3d peaks existed in multiple oxidation states after the saturation dose of MoF$_6$. (black and blue line) After a Si$_2$H$_6$ dose (red line), all of the Mo was reduced and the peak was centered at 227.4 eV which is consistent with MoSi$_2$ formation.
Figure 2.3. XPS chemical composition of Si, SiO₂ and a patterned sample after 5 ALD cycles of MoSiₓ and subsequent further Si₂H₆ dosing. (a) Chemical composition of HF cleaned Si, SiO₂ and patterned sample. (b) 5 ALD cycles of MoF₆ and Si₂H₆ at 120°C selectively deposited Si-deficient MoSiₓ on Si and not on SiO₂. The Si⁰ component of the patterned sample was also selectively attenuated by the MoSiₓ deposition. (c) After an additional 25.2 MegaL (6 pulses) of Si₂H₆, more Si was incorporated onto the MoSiₓ surface. Selectivity with respect to SiO₂ was maintained during the additional Si₂H₆ pulses. (SiO₂ had 0% Mo and 0% Si⁰ throughout the ALD process). (d) A schematic of HF cleaned Si, SiO₂ and patterned samples loaded together on a single sample holder along with a diagram of a patterned sample showing its features.
Figure 2.4. XPS chemical composition of selective MoSi$_x$ deposition on HF cleaned Si vs SiO$_2$ and SiON with 520°C PDA for 3 mins. (a) Chemical composition of Si, SiO$_2$ and SiON after the HF clean. (b) MoSi$_x$ was selectively deposited only on Si after the 5 ALD cycles of MoSi$_x$ followed by the additional 6 pulses (25.2 MegaL) of Si$_2$H$_6$ at 120°C. (c) Post-deposition anneal was performed at 520°C for 3 mins. The PDA removed F from the MoSi$_x$ film and reduced all of the Mo to Mo$^0$. (d) A schematic of HF cleaned Si, SiO$_2$ and SiON samples loaded together on a single sample holder.
Figure 2.5. Surface morphology of Si samples after each stage of ALD and PDA and SiO$_2$ sample after ALD and PDA. (a) After 20 ALD cycles of MoSi$_x$ on HF cleaned Si, STM shows an atomically flat and conformal surface with an RMS roughness of 2.8 Å. (b) After the PDA at 500°C for 3 mins, the film got smoother and the RMS roughness decreased to 1.7 Å. (c) 5 cycles of MoSi$_x$ ALD on HF cleaned Si was subjected to the in-situ 550°C anneal followed by an ex-situ spike anneal at 900°C. The film did not show agglomeration, and the RMS roughness was 4.75 Å which demonstrates the thermal stability of the MoSi$_x$ film. (d) AFM image of SiO$_2$ showed only a few MoSi$_x$ nuclei on the surface after the 5 cycles of MoF$_6$ and Si$_2$H$_6$ at 120°C followed by the 550°C anneal for 3 mins which is consistent with the high selectivity.
Figure 2.6. Depth profiling XPS study of the MoSi$_x$ film. (a) A series of Ar$^+$ sputtering experiments were performed in conjunction with XPS on HF cleaned Si after the 5 cycles of MoF$_6$ and Si$_2$H$_6$ at 120°C. (b) XPS peaks of Si 2p after sequential Ar$^+$ sputtering shows that the bulk of the MoSi$_x$ film consisted mostly of Si$^0$. (c) The chemical composition of the film is plotted versus Ar$^+$ sputter time on Si after 5 cycles of MoF$_6$ and Si$_2$H$_6$ at 120°C. A lens voltage of 5kV with a beam current of 1.2 µA at 6.0×10$^{-7}$ Torr of Ar was employed.
Figure 2.7. Depth profiling XPS study of the MoSi$_x$ film with extra Si$_2$H$_6$ doses. (a) A series of Ar$^+$ sputtering experiments were performed in conjunction with XPS on dry cleaned Si after 5 cycles of MoF$_6$ and Si$_2$H$_6$ followed by additional 6 pulses (25.2 MegaL) of Si$_2$H$_6$ at 120°C. (b) Surface composition after 5 ALD cycles of MoF$_6$ and Si$_2$H$_6$ with and without extra Si$_2$H$_6$ pulses is compared. Si/Mo ratios were 0.33 for 5 ALD and 0.89 for 5ALD + 6×Si$_2$H$_6$ which is consistent with Si incorporation on the surface. (c) Bulk composition of MoSi$_x$ with and without extra Si$_2$H$_6$ pulses is compared after getting rid of the surface contaminations using Ar$^+$ sputter. Si/Mo ratios were 1.77 for 5 ALD and 1.96 for 5ALD + 6×Si$_2$H$_6$. (d) The chemical composition of the film is plotted versus Ar$^+$ sputter time on Si after 5 cycles of MoF$_6$ and Si$_2$H$_6$ followed by additional Si$_2$H$_6$ pulses at 120°C. A lens voltage of 5kV with a beam current of 1.2 µA at 6.0×10$^{-7}$ Torr of Ar was employed.
Figure 2.8. 4-probe measurement after Ni deposition on the 900°C annealed MoSiₓ/Si. Using an infinite sheet model approximation, the resistivity of the MoSiₓ film is estimated to be 498 µΩcm.
Figure 2.9. Selective ALD on a patterned sample. (a) Cross-sectional TEM image of the patterned sample before the deposition. (b) Cross-sectional TEM image of the HF cleaned patterned sample after 5 cycles of MoF$_6$ and Si$_2$H$_6$ at 120°C with a continuous N$_2$ purge. 6.34 nm of MoSi$_x$ was selectively deposited only on Si and not on SiO$_2$ nor SiN$_x$. (c) Magnified Si region of the patterned sample before the deposition. (d) Magnified Si region of the patterned sample after the MoSi$_x$ deposition shows that MoSi$_x$ was deposited without damaging Si substrate by etching.
Figure 2.10. Oxidation states from XPS peaks of Si 2p and O 1s of degreased SiON at each experimental step of MoF$_6$ and Si$_2$H$_6$ doses. (a) Si 2p peaks show oxidation states of +3 and +4 which are consistent with strong Si-O, Si-N and Si-OH bonds. (b) O 1s peaks are positioned at 533.8 which is consistent with Si-O.
Figure 2.11. Depth profiling XPS study of the MoSi$_x$ film. XPS peaks of Mo 3d after sequential Ar$^+$ sputter cycles show that the Mo 3d peak stays at a 0 oxidation state.
Figure 2.12. XPS spectra of Si 2p, Mo 3d, O 1s, F 1s, C 1s and N 1s on (a) HF cleaned Si, (b) HF cleaned SiO$_2$ and (c) HF cleaned patterned sample at each step of MoSi$_x$ deposition.
Figure 2.13. XPS spectra of Si 2p, Mo 3d, O 1s, F 1s, C 1s and N 1s on (a) HF cleaned Si, (b) HF cleaned SiO\(_2\) and (c) HF cleaned SiON at each step of MoSi\(_x\) deposition followed by 520°C anneal for 3 mins.
Figure 2.14. Saturation study of MoF$_6$ on HF cleaned Si. (a) The elemental composition of HF cleaned Si followed by different amount of MoF$_6$ doses. (b) Change of Mo coverage per MegaL of dose for each experiment of MoF$_6$ dose.
Figure 2.15. Chemical Vapor Deposition of Si via $\text{Si}_2\text{H}_6$ decomposition. (a) HF cleaned Si was exposed to $\text{Si}_2\text{H}_6$ doses at 360°C and 500°C. (b) HF cleaned SiON was exposed to $\text{Si}_2\text{H}_6$ at 360°C and 500°C. Both surfaces were completely covered with Si at 500°C consistent with the $\text{Si}_2\text{H}_6$ decomposition at 500°C.
Figure 2.16. Cross-sectional TEM image after 20 cycles of MoSi$_x$ ALD on HF cleaned Si. 17.7 nm of MoSi$_x$ was deposited which corresponds to a growth rate of 0.88 nm/cycle.
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Chapter 3

Highly Selective Atomic Layer Deposition of MoSiO$_x$ Using Inherently Substrate-Dependent Processes

3.1 Abstract

A resistive MoSiO$_x$ film was deposited with high selectivity on Si in preference to SiO$_2$ and SiN using MoF$_6$, Si$_2$H$_6$ and O$_2$ as reactants. Two different approaches were demonstrated via thermal atomic layer deposition (ALD). First, ALD of MoSiO$_x$ by sequential dosing of MoF$_6$, Si$_2$H$_6$ and O$_2$ (ABC-type) at 200$^\circ$C followed by an ex-situ post-deposition anneal (PDA) in O$_2$ at 350$^\circ$C was performed. The growth of the film using the ABC-type deposition was limited to $\sim$5.25±0.5 nm because the insulating film inhibits the MoF$_6$ and Si$_2$H$_6$ ALD reaction. The second method was to grow MoSi$_x$ at 120$^\circ$C and employ a post-deposition anneal in O$_2$/He at 350$^\circ$C (AB+C-type) to form MoSiO$_x$. The selectivity of this process on Si versus SiO$_2$ was perfect for 10 nm of deposition on Si, as there were no nuclei or particle formation observed on the SiO$_2$ surface by atomic force microscopy (AFM). The high selectivity can be obtained due to the inherent inability of MoF$_6$ to react SiO$_2$ and SiN surfaces. Transmission electron microscopy (TEM) of a nanoscale-patterned sample demonstrated that the highly selective MoSiO$_x$ can be achieved and be integrated into three-dimensional nanoscale structures.

3.2 Introduction

As metal-oxide-semiconductor field effect transistors (MOSFETs) are scaled to sub-10 nm nodes with three-dimensional features, it becomes a significant challenge to
enhance the feature density and quality in patterning processes. Conventional patterning processes such as photolithography and e-beam lithography rely on multiple steps of resist patterning. These processes involve a combination of deposition and lithography followed by wet and plasma etching, which might lead to imperfect alignment and low resolution issues. [1,2] Additionally, some metals such as Cu and Co are not easy to etch. [3-5] Area selective atomic layer deposition (ALD) is of great interest in multi-patterning processes since it provides conformality, spatial uniformity and selectivity. Selective oxide deposition might simplify self-aligned double patterning (SADP) by depositing on side walls of the lithographically defined mandrel without depositing on the bottom layer (see Supplement, Fig. 3.11). In the multiple patterning processes, sharp self-aligned selective deposition is required not only to pattern the sub-10 nm features but also to reduce the need for lithography. [1,6]

Selective ALD of oxides is challenging since strongly oxidizing co-reactants can induced reactions on any surface. For example, the most commonly used oxygen sources for metal oxide deposition are H$_2$O, H$_2$O$_2$, O$_2$ plasma and ozone (O$_3$) which can physisorb or chemisorb onto semiconductor, insulator, and metallic surfaces initiating ALD nucleation. [7-12] One technique for selective deposition of oxides with these strong oxidants is to add passivants or plasma etching steps every cycle or every couple of cycles to prevent any nucleation leading to selectivity loss on an unwanted surface. [15-17] For example, Mameli et al. [15] demonstrated area selective atomic layer deposition of ~1.5 nm thick SiO$_2$ on GeO$_2$ against Al$_2$O$_3$ by a three-step deposition (ABC-type cycle) using A: acetylacetone (Hacac), B: bis(diethylamino)silane and C: O$_2$ plasma. They reported that the gas phase Hacac inhibitor reacts only with the Al$_2$O$_3$ substrate and not with GeO$_2$ or
SiO$_2$; however, the inhibitor needed to be dosed in each ALD cycle since the O$_2$ plasma removed the Hacac inhibitor. Single step passivation has also been reported; for example, Hashemi et al.[16] demonstrated area selective ALD of ~30 nm ZnO on SiO$_2$ against Cu using diethylzinc and water as ALD precursors. This was accomplished with vapor phase passivation using dodecanethiol (DDT) self-assembled monolayer (SAM) followed by an ex-situ sonication to inhibit growth on Cu. The selectivity could be expanded to 100 nm by regenerating DDT SAM every 150 ALD cycles; however, regeneration of passivation layer may also necessitate another wet selective removal step for residual passivants after the deposition process is complete. [18]

To avoid using oxidants such as H$_2$O or O$_2$ plasma, there have been studies to deposit oxide thin films by employing metal alkoxides as a precursor that can supply both an oxygen and a metal atom. [13,14,19] Atanasov et al.[19] demonstrated inherent substrate-dependent growth of TiO$_2$ on hydroxyl terminated SiO$_2$ (Si-OH) against hydrogen terminated Si (Si-H) using titanium tetra-isopropoxide (TTIP) and TiCl$_4$. It is hypothesized that the oxidants hydroxylate H-Si surfaces and initiate nucleation on Si. This process did not use any passivant nor seeding layers; however, the nucleation delay on Si was only sufficient to deposit 2 nm TiO$_2$ on SiO$_2$.

Inherently selective ALD is a compelling process to achieve selective deposition on the nanoscale without using passivants, seeding layers, or additional plasma steps since this relies only on the reactivity of ALD precursors with different substrates. Previously, Choi et al demonstrated on selective MoSi$_x$ deposition on Si in preference to SiO$_2$, SiON and SiN, [20]; MoF$_6$ and Si$_2$H$_6$ did not react with OH-SiO$_2$ and NH$_3$-SiN due to the chemical inertness of the strong Si-O, Si-N, SiO-H and SiN-H bonds towards the ALD
precursors. In contrast, MoF$_6$ reacted with a H-Si surface by forming Si-MoF$_x$ bonds which enables a chain reaction with following Si$_2$H$_6$.

In this work, an insulating molybdenum silicon oxide (MoSiO$_x$) was deposited by ALD on silicon in preference to silicon oxide and silicon nitride using MoF$_6$ and Si$_2$H$_6$ and O$_2$ using substrate-dependent selectivity. A successful conformal MoSiO$_x$ deposition on a nanoscale three-dimensional Si sidewall with about 200:1 selectivity over SiO$_2$ and SiN were demonstrated which could be transferred to the multi-patterning process for 3-dimensional MOSFETs.

3.3 Experimental

Fig. 3.1 shows a schematic of the vacuum chamber. The selective deposition of MoSiO$_x$ was performed in a home-built reaction chamber (ALD chamber) pumped by a turbomolecular pump and a rotary pump connected in series. The chamber had an in-situ heating and sample transfer system using a pyrolytic boron nitride (PBN) heater mounted on a manipulator. The base pressure of the reaction chamber was $8.0 \times 10^{-8}$ Torr. The chamber wall was set to 80°C and dosing lines for MoF$_6$, Si$_2$H$_6$, N$_2$ and O$_2$ were kept at room temperature. Pneumatic valves (UHP diaphragm sealed valve, Swagelok) controlled by a computer program (Labview 8.0) were employed to precisely regulate the valve opening times in milliseconds. The processed samples were transferred into an ultra-high vacuum (UHV) chamber equipped with X-ray Photoelectron Spectroscopy (XPS) for characterization without air exposure.

P-type Si (001) (Waferworld), thermally grown SiO$_2$ (Waferworld), and SiON samples (Applied Materials) were used for the selective deposition of MoSiO$_x$. Note that
the SiON is actually a stoichiometric Si₃N₄ after a reactive ion etching (RIE) and O₂ plasma ashing process which mimics the surface condition of a lithographically patterned sample. The samples were rinsed sequentially with acetone, methanol and HPLC-grade water followed by a wet clean in a 0.5% HF solution for 30 seconds to remove native oxides. After the HF clean, the samples were rinsed again with HPLC-grade water for 10 seconds and blow-dried with high purity N₂. The HF cleaned samples were loaded into a sample loading chamber, and the chamber was pumped down to 5.0 × 10⁻⁶ Torr before transferring the samples to the UHV chamber. The chemical compositions of the samples were investigated using XPS in the UHV chamber before and after each experiment.

MoF₆ (Synquest Laboratories, 99%), Si₂H₆ (Air Liquide, 99.99%) and O₂ (Praxair, 10% balanced in He) were used as the ALD precursors at a temperature in the range of 120 – 200°C followed by an in-situ or ex-situ O₂ anneal at 300 – 350°C. As previously reported, [20] MoF₆ and Si₂H₆ selectively react with Si in preference to SiO₂ and SiNx to form MoSiₓ. Two approaches were employed to incorporate oxygen into the MoSiₓ using O₂ in a thermal process. The first method was to incorporate oxygen into the film during a three step ALD cycle: MoF₆ + Si₂H₆ + O₂ at 200°C. The dose sizes of MoF₆ and Si₂H₆ were 1.2 MegaL and 2.2 MegaL (1 Lanmuir (L) = 10⁻⁶ Torr × 1 second exposure of a gas). O₂ (10% balanced in He) was dosed using a leak valve at 120 mTorr for 6 mins which corresponds to 4.3 MegaL of O₂. Each precursor was separated by an N₂ purge at 90 mTorr for one minute. Additionally, an ex-situ post deposition anneal (PDA) under a constant flow of 100% O₂ at 1 SLM was performed at 350°C in an AllWin21 rapid thermal annealing system. The ex-situ O₂ anneal was performed at ~1 atm pressure for 10 mins which corresponds to 456 GigaL of O₂. The second method was to grow a MoSiₓ film selectively on a Si substrate
and convert the MoSi\textsubscript{x} film into MoSiO\textsubscript{x} at high temperature; the ALD of MoF\textsubscript{6} + Si\textsubscript{2}H\textsubscript{6} was performed at 120°C followed by an in-situ anneal in O\textsubscript{2} (10% balanced in He) at 15 Torr for 10 mins which corresponds to 900 MegaL of O\textsubscript{2} at 350°C.

A monochromatic Al Kα X-ray source and a hemispherical analyzer (XM 1000 MkII/SPHERA, Omicron Nanotechnology) were used for XPS. The anode voltage was set to 10 kV with a filament emission current of 25 mA. The focused beam size on the samples was 0.7 – 1 mm. For the XPS measurements, the samples were aligned to the detector to have a 30-degree take-off angle from the sample surface (i.e near glancing) for the surface sensitive detection. As the occasion demands, 60-degree take-off angle form the sample surface was also used for the bulk composition. The peak areas of XPS spectra were normalized to the sum of all elements after a sensitivity correction using the Casa XPS v2.3 program. The topology of the deposited film was studied using AFM (Agilent 5500) in tapping mode. The nanoscale patterned sample was supplied from Applied Materials and cross-sectional TEM was performed before and after the selective MoSiO\textsubscript{x} deposition at Applied Materials.

3.4 Results and Discussion

3.4.1 XPS of 3-step MoSiO\textsubscript{x} ALD at 200°C followed by in-situ and ex-situ PDA

The sequential three-step reaction of MoF\textsubscript{6}, Si\textsubscript{2}H\textsubscript{6} and O\textsubscript{2} on Si at 120°C and 200°C was investigated using an in-situ XPS. The chemical composition of the Si surface after each experiment step is shown in Fig. 3.2. Si and Mo are presented in two different bars in order to indicate the total amount (Si 2p and Mo 3d) together with the oxidized components
(Si (ox) and Mo (ox)) which correspond to Si$^{1+}$ through Si$^{4+}$ and Mo$^{1+}$ through Mo$^{6+}$. Note that MoSiO$_x$ should have both oxidized Si and oxidized Mo components.

Fig. 3.2(a) shows a cycle of MoSiO$_x$ deposition at 120°C on HF cleaned Si. (note: the raw XPS spectra are presented in Fig.S2). The Si sample had about 20% adventitious hydrocarbon (red and black) on the surface after the native oxide removal using an aqueous HF. 0.25 MegaL of MoF$_6$ were dosed at 120°C and 12% Mo and 28% F were deposited. All of the Mo was in oxidation states of +4 and +5 consistent with MoF$_x$ termination of the surface. MoF$_6$ has a self-limiting reaction on HF cleaned Si, and 0.25 MegaL of MoF$_6$ was the saturated dose of MoF$_6$ on Si at 120°C. [20] 26.4 MegaL of Si$_2$H$_6$ was dosed on MoF$_6$ saturated Si surface which reduced MoF$_x$ to Mo (0) by forming Mo-Si bonds consistent with MoSi$_x$ deposition. The 11% oxidized component of Si (grey bar) and 4% oxidized Mo component (purple bar) might be due to the O and F contamination at the surface. Subsequently, 3.5 MegaL of O$_2$ was dosed which increased O from 17% to 26%; however, the oxidized component of Mo remained 4% out of a total of 8%. After another 4.3 MegaL of O$_2$ was dosed at 120°C, O increased only by 2% and the oxidized component of Mo increased to 6% out of a total of 8%. At 120°C, reactivity of O$_2$ with a MoSiO$_x$ monolayer was insufficient to completely oxidize MoSi$_x$. In Fig. 3.2(b), the same sample was employed to investigate higher temperature (200°C) reaction with O$_2$. 4.3 MegaL O$_2$ at 200°C was able to fully oxidize Mo, the oxidized component of Si increased from 14% to 16%, and the O increased from 28% to 32% consistent with a complete conversion of MoSi$_x$ into MoSiO$_x$. After 3 additional ALD cycles at 200°C, the total thickness of the MoSiO$_x$ film on Si was ~ 2.2 nm calculated from the attenuation of the Si substrate. In contrast, during the same exposure of MoF$_6$, Si$_2$H$_6$, and O$_2$ at 120°C and 200°C, HF cleaned
SiO$_2$ remained non-reactive which is consistent with the inherent non-reactivity of the SiO$_2$ surface against these precursors. (Fig. 3.2(b))

After the MoSiO$_x$ ALD cycles at 120 – 200°C, in-situ and ex-situ post deposition anneals (PDA) in O$_2$ were performed to further oxidize the film. (note: the raw XPS spectra are presented in Fig. 3.13). Fig. 3.3(a) shows the XPS elemental compositions after each O$_2$ PDA step and Fig. 3.3(b-c) presents the corresponding oxidation states of Mo 3d and Si 2p. As deposited MoSiO$_x$ had oxidation states of Mo$^{1+}$ and Mo$^{3+}$. Si had Si$^{4+}$ and Si$^{0}$. Note that Si$^{0}$ component corresponds to the Si substrate peak. An in-situ O$_2$/He anneal was performed on MoSiO$_x$/HF-Si at 300°C for 6 mins at a constant flow of O$_2$/He at 80 – 150 mTorr. This corresponds to 432 MegaL of O$_2$. After the in-situ O$_2$/He anneal, F at the surface went down from 16% to 3% and O went up from 36% to 43% consistent with a substitution of surface F with O. However, the oxidation states of Mo still contained a large fraction of Mo$^{1+}$. Therefore, an ex-situ oxidation at ~ 1 atm was performed for 10 mins at 350°C using an AllWin21 rapid thermal annealing system with a constant 100% O$_2$ flow at 1 SLM at about 1 atm. This corresponds to 456 GigaL of O$_2$. After the ex-situ anneal, the sample was introduced back into the UHV chamber to analyze the compositions and oxidation states. The elemental composition showed a large amount of surface C and O which have resulted from the air exposure during transfer. However, the oxidation states of both Mo 3d and Si 2p were consistent with fully oxidized MoSiO$_x$. The could be due to either the higher temperature or ~10$^3 \times$ larger dose of O$_2$ compared to the in-situ O$_2$/He anneal at 300°C. Below, it is shown that the film can be fully oxidized (as quantified by XPS) by an in-situ anneal in O$_2$/He at at 15 Torr at 350°C.
3.4.2 Surface morphology of the MoSiO\textsubscript{x} film deposited via 3-step ALD

The surface morphologies of the deposited MoSiO\textsubscript{x} film from 3 step ALD were studied using atomic force microscopy (AFM) for as-deposited, after an in-situ O\textsubscript{2}/He anneal at 300°C, and after ex-situ O\textsubscript{2} anneal at 350°C. Fig. 3.4(a) shows the surface morphology of the as-deposited 3 step ALD MoSiO\textsubscript{x} on Si after the 4 ALD cycles at 120 - 200°C. The MoSiO\textsubscript{x} film was atomically flat with an RMS roughness of 5.3 Å. Fig. 3.4(b) depicts the 3 step ALD MoSiO\textsubscript{x} surface after an in-situ O\textsubscript{2}/He anneal at 15 torr at 300°C to further oxidize the unsaturated MoSiO\textsubscript{x} film. The film was smoother after the anneal with an RMS roughness of 3.8 Å. Fig. 3.4(c) shows an AFM image of the 3 step ALD MoSiO\textsubscript{x} surface after the ex-situ O\textsubscript{2} anneal at ~1 atm at 350°C for 10 mins. The surface after the ex-situ anneal was roughened and had ~12 nm tall agglomerations which might be due to the large insertion of oxygen. The RMS roughness was 1.7 nm. To check the selectivity of MoSiO\textsubscript{x} on SiO\textsubscript{2}, AFM was performed on HF cleaned SiO\textsubscript{2} after 4 ALD cycles of 3 step ALD MoSiO\textsubscript{x} followed by an in-situ O\textsubscript{2}/He anneal at 300°C (see Fig. 3.4(d)). The SiO\textsubscript{2} surface was very clean with an RMS roughness of 5.3 Å. There was no MoSiO\textsubscript{x} nucleation or particle formation observed on the surface which shows the absolute inherent selectivity of the MoSiO\textsubscript{x} ALD on SiO\textsubscript{2}.

3.4.3 Growth limit and selectivity of MoSiO\textsubscript{x} film deposited via 3-step ALD

To study the selectivity and growth rate of 3 step ALD MoSiO\textsubscript{x} with XPS, thicker films were deposited on Si and SiO\textsubscript{2}. A total of 20 ALD cycles of 3 step ALD MoSiO\textsubscript{x} at 200°C were performed and the film thickness was calculated by the attenuation of the substrate after each 5 ALD cycles. (note: the raw XPS spectra are presented in Fig. 3.14).
Fig. 5(a) presents the elemental percentage of Si and Mo from the Si and SiO$_2$ substrates for up to 20 ALD cycles at 200°C. As the number of cycles increases, the Si(0) percentage from the Si substrate decreases which is consistent with the attenuation of Si due to the MoSiO$_x$ growth. The Mo percentage on the Si substrate was saturated at ~20% after 5 ALD cycles consistent with the composition of the MoSiO$_x$ film being conformal throughout the film. In contrast, Si(ox) of SiO$_2$ which corresponded to the SiO$_2$ substrate remained at ~40% throughout the 20 ALD cycles which is consistent with no MoSiO$_x$ deposition. A negligible amount of Mo was detected on the SiO$_2$ substrate.

Fig. 3.5(b) shows the MoSiO$_x$ film thickness on Si and SiO$_2$ as a function of the number of ALD cycles. After the first 5 ALD cycles, the thickness of MoSiO$_x$ on Si was 3.30±0.35 nm which corresponds to a growth rate of 6.6 Å/cycle. The second set of 5 ALD cycles (up to 10$^{th}$ cycle) and the third set (up to 15$^{th}$ cycle) shows slower growth rates of 2.8 and 1.1 Å/cycle. After the 15$^{th}$ ALD cycle, there was no additional growth of MoSiO$_x$ on Si. Overall, MoSiO$_x$ on Si showed a logarithmic growth and saturated at 5.25±0.5 nm. The larger growth rate of MoSiO$_x$ during the first 5 ALD cycles might be due to MoF$_6$ reacting more than a monolayer of the Si substrate. As the film grew, the substrate effect became smaller and the growth rate decreased. After 15 ALD cycles, the MoSiO$_x$ film became inert to both MoF$_6$ and Si$_2$H$_6$ due to the strong bonds of Mo-O and Si-O which terminate the reaction. Conversely, there was no growth observed on SiO$_2$ for up to 20 ALD cycles.

Selectivity of MoSiO$_x$ ALD on SiO$_2$ was calculated from XPS sensitivity. After a total of 20 ALD cycles, there were 1.9% Mo and 6.4% F detected on SiO$_2$ by XPS. Assuming all of Mo and F were conformally covering the topmost surface of SiO$_2$, this
corresponds to less than 0.5Å thick film calculated using the inelastic mean free path (IMFP) of electron and electron attenuation length (AL) as follows:

\[
\lambda = \frac{143}{E^2} + 0.054\sqrt{E}
\]

\[
I = I_0 \exp(-t/\lambda \sin \theta)
\]

where \(\lambda\) is an IMFP of electron, \(E\) is a kinetic energy of electron, \(I\) is an attenuation length (AL), \(I_0\) is a constant, \(t\) is a thickness (layer depth) and \(\theta\) is an angle of emitted electron from the surface. Assuming a monolayer of the MoSiOₓ film is \(~3\) Å, MoSiOₓ on SiO₂ after 20 ALD cycles was calculated to 0.167 monolayer. As the MoSiOₓ film on Si after 20 ALD cycles was estimated to 5.25 nm, which corresponds to 17.5 monolayers, the selectivity of MoSiOₓ between Si and SiO₂ is at least 100:1 consistent with the more sensitive AFM determination of selectivity.

3.4.4 2-step ALD of MoSiₓ + in-situ O₂/He anneal

To overcome the growth limit, a second technique of selective MoSiOₓ deposition was investigated which was to selectively deposit MoSiₓ using MoF₆ and Si₂H₆ at 120°C and then convert the MoSiₓ film into MoSiOₓ via an in-situ O₂/He anneal at 350°C at 15 Torr. Fig. 3.6 shows the XPS composition of a new batch of HF cleaned Si and HF cleaned SiO₂ samples for the second technique denoted as “2 Step ALD”. HF cleaned Si had ~20% hydrocarbon on the surface. After 5 ALD cycles of MoF₆ and Si₂H₆ to deposit MoSiₓ at 120°C, the composition of the film was 31% Mo, 16% Si, 23% O and 29% F consistent with previous experiments. [20] Note that Mo(ox) was only 7% out of 31% consistent with metallic Mo-Si bond formation of MoSiₓ. After an in-situ O₂/He (10% balanced in He) anneal at 15 Torr for 10 mins at 350°C, All of Mo was oxidized, and the film surface was
mostly MoOx with only 4% Si. The data is consistent with the 350°C O2 anneal inducing loss of fluorine from the surface via SiFx desorption and formation of additional Mo-O bonds. To study the bulk composition of the film, near normal XPS (60° take-off angle from the sample surface) was performed. (see Fig. 3.6(a)) The bulk of the film had a Mo:Si:O ratio of 1: 0.8: 1.9 which is consistent with the in-situ O2/He anneal segregating MoOx on the surface of the film. This is consistent with the lower surface free energy of MoO3 compared to SiO2 (MoO3: 70 ergs/cm2 versus SiO2: 307 ergs/cm2)

HF cleaned SiO2 has a negligible amount of C at the surface as presented in Fig. 3.6(b). (note: the raw XPS spectra are presented in Fig. 3.15). After 5 cycles of MoSiX ALD at 120°C, there was 1.5% Mo and 8% F detected on the surface. After an in-situ O2/He anneal at 350°C, there was no change but a small decrease in F which is consistent with the inherently non-reactivity of MoSiOx on HF-SiO2. The selectivity estimation using XPS sensitivity was also performed for 2 step ALD. There were 1.5% Mo and 5% F observed on SiO2 after 5 ALD cycles of MoSiX followed by the in-situ O2/He anneal at 350°C. This corresponds to a 0.5-thick conformal film which is 0.167 monolayer assuming 1 monolayer is 3 Å. The thickness of MoSiOx on Si after the same deposition deposited was about 6 nm MoSiOx (~20 monolayers of MoSiOx) so that the selectivity of 2 step ALD was estimated to about 120:1. Fig. 3.6(c) presents the Mo 3d XPS spectra showing the oxidation states before and after the in-situ O2/He anneal. After 5 ALD cycles of MoF6 and Si2H6 at 120°C, Mo was mostly Mo0 consistent with metallic MoSiX being deposited. After the in-situ O2/He anneal at 350°C, Mo 3d peaks were shifted to Mo4+ and Mo5+ which corresponded to oxidized MoSiOx. Fig. 3.6(d) shows the Si 2p XPS spectra before and after the in-situ O2/He anneal. Before the in-situ O2/He anneal, Si had two oxidation states of Si(0) and
Si(4). Si(0) corresponds to Mo-Si bonds from MoSi\textsubscript{x} and Si(4) component is due to the surface F and O contamination. After the in-situ O\textsubscript{2}/He anneal at 350°C, all of Si at the surface was at an oxidation state of 3 consistent with a full conversion to MoSiO\textsubscript{x}.

### 3.4.5 Surface morphology and electrical property of the MoSiO\textsubscript{x} film

In Fig. 3.7, the surface morphology of MoSiO\textsubscript{x} before and after the in-situ O\textsubscript{2}/He anneal at 350°C are shown. The surface morphology of MoSi\textsubscript{x} was smooth with an RMS roughness of 6.9Å (Fig. 3.7(a)). After an in-situ O\textsubscript{2}/He anneal at 350°C, the MoSiO\textsubscript{x} surface remained smooth with an RMS roughness of 1.0 nm (Fig. 3.7(b)). The slight increase of the RMS roughness can be attributed to the O\textsubscript{2} incorporation. To investigate the electrical properties of the MoSiO\textsubscript{x} film, a Ni gate on top of MoSiO\textsubscript{x} with an Al back contact were deposited via thermal evaporation. Fig. 3.7(c-d) depicts the current density-voltage (I-V) and conductance density-voltage (G-V) curves. The current density through the MoSiO\textsubscript{x} film in the gate bias range was smaller than \(~1\times10^{-7}\)A and the conductance density was constant across the gate bias which are both consistent with an insulating MoSiO\textsubscript{x} film.

### 3.4.6 Improvement of the selectivity window of 2-step MoSiO\textsubscript{x}

Since the 2 Step ALD method relies on the selectivity of MoSi\textsubscript{x} before oxidizing the film using O\textsubscript{2}/He, the selectivity limit of MoSi\textsubscript{x} ALD was studied using AFM. After 5 and 10 ALD cycles of MoSi\textsubscript{x} were dosed on SiO\textsubscript{2}, the number of unwanted MoSi\textsubscript{x} particles on SiO\textsubscript{2} that were taller than 2.5 nm was detected using a SPIP v2.12 program. The threshold particle size of 2.5 nm was set to distinguish particles in proximity. Fig. 3.8(a) shows elemental compositions of SiO\textsubscript{2} after 5 and 10 MoSi\textsubscript{x} ALD cycles and corresponding
AFM images. There were 1% Mo detected on SiO$_2$ after 5 ALD cycles and 5.6% Mo after 10 ALD cycles. The AFM images show 16 particles/$\mu$m$^2$ after 5 ALD cycles and 268 particles/$\mu$m$^2$ after 10 cycles. The inherent selectivity of the MoSi$_x$ film on SiO$_2$ was preserved until 5 ALD cycles before having a critical amount of nucleation on SiO$_2$. The selectivity loss can be attributed to the decomposition of the precursors by the PBN heater that was placed in vacuum. To see the effect of the heater on the MoSi$_x$ selectivity, a cartridge heater, a different heater design, was installed and the number of MoSi$_x$ nuclei on SiO$_2$ were compared. The cartridge heater was placed on the air-side of the chamber conductively heating a Cu block on which the sample sits in vacuum, so that the precursors did not directly dose the heater. Using the cartridge heater, the MoSi$_x$ selectivity was greatly improved showing no nuclei on SiO$_2$ after 10 ALD cycles as shown in Fig. 3.8(b). XPS elemental composition only showed 0.5% Mo on SiO$_2$ after 10 ALD cycles which is an improvement of selectivity by a factor of 10 compared to the results using a PBN heater. There was no particle observed from AFM. This corresponds to ~10 nm thick MoSi$_x$ on Si which can be converted to MoSiO$_x$ by incorporating O$_2$. Using the cartridge heater, the selectivity could be extended to 200:1 calculated using the same XPS sensitivity method as described earlier.

3.4.7 TEM of 2-step MoSiO$_x$, demonstrated on a nanoscale patterned sample

Using inherently selective processes, a selective and conformal deposition of MoSiO$_x$ was demonstrated on a three-dimensional nano-trench structure with a high-aspect ratio. The structure of the patterned sample is described in Fig. 3.9(c). The Si fins are 225 nm tall and 50 nm wide with SiN mask on top of each Si fin separated by SiO$_2$. 

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Fig. 3.9(a) shows the elemental composition of the HF cleaned patterned sample. (note: the raw XPS spectra are presented in Fig. 3.16). The patterned sample had mostly SiN on the top-most surfaces. Note that there is 18% Si (0) which corresponds to the target area for MoSiOₓ deposition since the oxidized Si peak corresponds to the exposed SiN and SiO₂ surfaces. Fig. 3.9(b) shows the elemental composition after a selective MoSiOₓ deposition process. There was 8% fully oxidized Mo with 21% O. Note that all of the Si was oxidized consistent with a selective attenuation of the Si substrate (Si(0) component, the target area). The patterned sample shown in Fig. 3.9(c) is a top view SEM image of the HF cleaned patterned sample. The SiN mask was 50 nm wide and the gap between the SiN mask was 30 nm which is also shown in the insert on the left bottom corner. Fig. 3.9(d) shows the same region as Fig. 3.9(c) after the selective MoSiOₓ deposition. The gap between the features decreased to 20 nm and the SiN mask rows were enlarged to ~ 60 nm which is consistent with ~ 5 nm thick MoSiOₓ deposition on each sidewall of the Si fins.

Fig. 3.10 shows the cross sectional TEM images of the patterned sample before and after the selective MoSiOₓ deposition process. Fig. 3.10(a) shows the structure of the patterned sample. The patterned sample was cleaned using 5% HF solution for 30 seconds and selective MoSiOₓ deposition was performed. SiN mask and SiO₂ were etched by a 5% HF clean but MoSiOₓ was still very conformal and selective on Si. The deposited MoSiOₓ film was ~6 nm thick. The gap between each fin was ~20 nm which is consistent with the SEM image in Fig. 3.9(d). The TEM image demonstrates that the highly selective MoSiOₓ can be achieved on a patterned sample and be integrated into three-dimensional nanoscale multi-patterning processes.
3.5 Conclusions

A new approach to selectively deposit oxides on Si in preference to SiO$_2$ and SiN was demonstrated by two different inherently selective MoSiO$_x$ ALD processes using MoF$_6$, Si$_2$H$_6$ and O$_2$. Alternatingly dosed MoF$_6$, Si$_2$H$_6$ and O$_2$ at 200°C (3 Step ALD) deposited an oxygen-deficient MoSiO$_x$ film on Si with perfect selectivity over SiO$_2$ quantified by AFM. The selectivity estimated by XPS presented at least 100:1 between Si and SiO$_2$. An ex-situ anneal in 100% O$_2$ at 350°C could fully oxidized the film. The growth of MoSiO$_x$ on Si was limited up to 5 nm due to the inherent non-reactivity of the precursors towards the grown MoSiO$_x$ which demonstrates the strong substrate-dependent nature of MoSiO$_x$ ALD. For the thicker films, selective 2 step MoSi$_x$ ALD was employed before a conversion of the MoSi$_x$ film into MoSiO$_x$ by an in-situ O$_2$/He anneal. Loss of selectivity was not observed on SiO$_2$ until 10 nm of MoSi$_x$ was grown on Si which could expand the selectivity to 200:1. The selectivity of the process relies on the inherent selectivity of MoSi$_x$ ALD using MoF$_6$ and Si$_2$H$_6$ which deposits on Si but not on SiO$_2$ or SiON. It has been shown that this process is selective because of the weak Si-Si and H-Si bonds on Si and the ease of formation of SiF$_4$ on a Si substrate but the stronger Si-O, Si-N, SiO-H and SiN-H bonds in SiO$_2$ and SiN make this process less favorable. The conversion of metal or metal silicide into an oxide film is advantageous in terms of selectivity in that the process does not require any use of strong oxidants such as H$_2$O, H$_2$O$_2$ and O$_2$ plasma during the deposition which often leads to selectivity loss. For the selective ALD of metal or metal silicides such as MoSi$_x$, W, Mo, Co and CoSi$_2$, reductants are employed which utilize an inherent surface-dependent selectivity and subsequently convert them into oxides by an O$_2$.
PDA. Selective MoSiO$_x$ deposition on the sidewalls of Si fins in nanoscale demonstrated a great potential application in three-dimensional nanoscale multi-patterning processes.

3.6 Acknowledgements

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3.7 Figures

Figure 3.1. A schematic of vacuum chamber. The chamber was composed of a reaction chamber (ALD chamber), sample loading chamber, and UHV chamber equipped with X-ray photoelectron spectroscopy.
Figure 3.2. Elemental compositions at each deposition step of 3 step MoSiO$_x$ ALD. (a) At 120°C, MoF$_6$, Si$_2$H$_6$ and O$_2$ were sequentially dosed on HF cleaned Si. Mo was not fully oxidized after an ALD cycle at 120°C. Additional dosing with 4.3 MegaL of O$_2$ increase the fraction of oxidized Mo. The ALD process was continued on the sample at 200°C. The additional 4.3 MegaL of O$_2$ at 200°C fully oxidized the Mo. Additional cycles of MoF$_6$, Si$_2$H$_6$ and O$_2$ at 200°C deposited ~ 2.2 nm thick MoSiO$_x$ film with fully oxidized Mo. (b) During the same doses, HF cleaned SiO$_2$ shows negligible amount of Mo detected on the surface.
Figure 3.3. Elemental compositions and oxidation states of MoSiO$_x$ on HF cleaned Si from 3 Step ALD followed by in-situ and ex-situ O$_2$ post deposition anneals (PDA). (a) XPS compositions show fully oxidized Mo before and after the in-situ and ex-situ O$_2$ PDA. (b) Mo 3d peaks show complete oxidation of Mo after the ex-situ PDA at 350°C. (c) Si 2p peak also shows full conversion of Si into MoSiO$_x$. 
Figure 3.4. Surface morphologies of HF cleaned Si and SiO$_2$ after 3 step ALD MoSiO$_x$ deposition. (a) AFM image of the as-deposited MoSiO$_x$ film on HF-Si was atomically flat. (b) AFM after an in-situ O$_2$/He anneal at 300°C / MoSiO$_x$ / HF-Si showed a conformal film. (c) After an ex-situ O$_2$ anneal at 350°C, the MoSiO$_x$ surface on HF-Si was roughened with ~12 nm tall agglomerations. (d) SiO$_2$ after the MoSiO$_x$ ALD cycles followed by an in-situ O$_2$/He anneal at 300°C shows a flat SiO$_2$ surface without any MoSiO$_x$ nuclei.
Figure 3.5. XPS elemental percentage of Si and Mo and the MoSiO$_x$ film thickness on Si and SiO$_2$ for 3 step ALD MoSiO$_x$. (a) The Si substrate peak (Si(0)) was attenuated as the number of cycles increased while the SiO$_2$ substrate peak (Si(ox)) remained the constant which is consistent with the selective growth of MoSiO$_x$ deposition. (b) The growth of MoSiO$_x$ on Si was limited up to 5.25±0.5 nm. There was no growth of MoSiO$_x$ on SiO$_2$. The film thicknesses were calculated using the attenuation of the substrates.
Figure 3.6. Elemental compositions at each deposition step of 2 Step MoSi\textsubscript{x} + in-situ O\textsubscript{2}/He anneal on Si and SiO\textsubscript{2}. (a) 5 ALD cycles of MoF\textsubscript{6} and Si\textsubscript{2}H\textsubscript{6} at 120°C followed by an in-situ O\textsubscript{2}/He anneal at 350°C were performed on HF cleaned Si. (b) 5 ALD cycles of MoSi\textsubscript{x} ALD at 120°C and an in-situ O\textsubscript{2}/He anneal at 350°C on HF cleaned SiO\textsubscript{2}. (c) The raw Mo 3d XPS spectra after MoSi\textsubscript{x} deposition at 120°C followed by the in-situ O\textsubscript{2}/He anneal at 15 Torr at 350°C. (d) The raw Si 2p XPS spectra after MoSix deposition at 120°C followed by the in-situ O\textsubscript{2}/He anneal at 15 Torr at 350°C.
Figure 3.7. Surface morphologies of 2 Step ALD MoSiO\textsubscript{x} before and after the in-situ O\textsubscript{2}/He anneal at 350°C and its electrical properties. (a) The surface morphology of an as-deposited MoSi\textsubscript{x} film on Si. (b) The surface morphology of MoSiO\textsubscript{x} after the in-situ O\textsubscript{2}/He anneal at 350°C. (c) I-V curve of the MoSiO\textsubscript{x} film. (d) G-V curve of the MoSiO\textsubscript{x} film. Sweeping mode from 10kHz to 1 MHz frequency was used at -2 ~ 2 V gate bias.
Figure 3.8. Improvement of selectivity of 2 Step ALD MoSi\textsubscript{x} on SiO\textsubscript{2} using a cartridge heater compared to a PBN heater. (a) XPS chemical composition and AFM images of SiO\textsubscript{2} after 5 and 10 ALD cycles of MoSi\textsubscript{x} at 120°C using a PBN heater. (b) the XPS chemical composition and AFM images of SiO\textsubscript{2} after 5 and 10 ALD cycles of MoSi\textsubscript{x} at 120°C using a cartridge heater.
Figure 3.9. XPS elemental composition and SEM images of a patterned sample before and after selective 2 Step ALD MoSiO\textsubscript{x} + PDA deposition. (a) HF cleaned patterned sample mostly has SiN and Si(0) components. (b) After the selective MoSiO\textsubscript{x} deposition, there was MoSiO\textsubscript{x} together with SiN. (c) A top view SEM image of the HF cleaned patterned sample shows that the patterned sample had ~50 nm and ~30 nm trough structure. The insert is a schematic of the cross sectional patterned sample. (d) SEM image of the patterned sample after the MoSiO\textsubscript{x} deposition. The insert is a schematic of the cross-sectional patterned sample with MoSiO\textsubscript{x} deposition. After ALD, the patterned sample had ~60 nm and ~20 nm trough structure consistent with 5nm of ALD on the side walls.
Figure 3.10. Cross-sectional TEM image of the patterned sample before and after the selective 2 Step ALD MoSiO$_x$ + PDA deposition. (a) The patterned sample had Si fins covered with a SiN mask. There was a SiO$_2$ interlayer in between. (b) After the 5% HF clean followed by the MoSiO$_x$ deposition, MoSiO$_x$ was selectively deposited on the sidewalls of the Si fins. Note that a wet etch in 5% HF solution before the MoSiO$_x$ deposition etched the SiN and SiO$_2$ features.
Figure 3.11. A diagram of a self-aligned double patterning (SADP) process. (a) SADP using a conformal spacer ALD requires another etching step to leave the spacer only on the sidewalls of the mandrels. (b) Selective deposition can initially deposit an oxide film only on the sidewall of mandrels (red box).
Figure 3.12. XPS spectra of Si and SiO$_2$ at each deposition step of 3 step MoSiO$_x$ ALD.
Figure 3.13. XPS spectra of MoSiO$_x$ on HF cleaned Si from 3 Step ALD followed by in-situ and ex-situ O$_2$ post deposition anneals (PDA).
Figure 3.14. XPS spectra of Si and SiO₂ after 5, 10, 15 and 20 cycles of 3 step ALD MoSiOₓ at 200°C.
Figure 3.15. XPS spectra of Si and SiO₂ at each deposition step of 2 Step MoSiₓ + in-situ O₂/He anneal.
Figure 3.16. XPS spectra of a patterned sample before and after selective 2 Step ALD MoSiO_x + O_2 PDA deposition.
3.8 References

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Chapter 4

Selective Pulsed Chemical Vapor Deposition of Water-free HfO$_x$ on Si in Preference to SiO$_2$ and SiCOH

4.1 Abstract

Water-free HfO$_x$ was selectively deposited on Si in preference to SiCOH using Hf(O'Bu)$_4$ via a pulsed chemical vapor deposition process. The conformal HfO$_x$ film was deposited on Si by the thermal decomposition of the precursor, and the inherent selectivity of HfO$_x$ was retained over SiCOH until ~2 nm of HfO$_x$ was deposited on Si at 250$^\circ$C. Additional selectivity enhancement was demonstrated by employing molecular surface passivation and reversible desorption of the precursor via control of the purge time. 1,1,3,3-tetramethyldisilazane (TMDS) and Bis(dimethylamino)dimethylsilane (DMADMS) were used to passivate reactive -OH sites on SiO$_2$ and SiCOH to increase the selectivity to ~7 nm HfO$_x$ deposition on Si before any significant nucleation occurred on TMDS passivated SiCOH. It is expected that the selective water-free HfO$_x$ deposition can be used for patterning three-dimensional nanoscale structures in MOSFET devices.

4.2 Introduction

In Metal-Oxide-Semiconductor Field Effect Transistors (MOSFETs), high-k dielectric materials for gate oxide such as hafnium oxide (HfO$_x$) has been intensively studied for several decades. HfO$_x$ exhibits a high dielectric constant with moisture resistance and thermal stability so that it has been employed as a gate dielectric in conventional MOSFETs as a replacement for SiO$_x$. [1-3] As MOSFETs are scaled down
to 14 nm nodes or less, precise control of oxide thickness while maintaining good physical, electrical qualities is required. [4,5] Therefore, atomic layer deposition (ALD) of HfO$_x$ was employed because it provides angstrom scale thickness control with great conformality, and many successful HfO$_x$ ALD techniques using various precursors such as HfCl$_4$, tetrakis(dimethylamido)hafnium (TDMAHf), hafnium-t-butoxide (HTBO) with H$_2$O, H$_2$O$_2$ and Ozone have been reported. [6-9] However, patterning of the gate dielectric with three-dimensional features such as FinFETs and Gate-all-around (GAA) transistors common in the sub 10 nm nodes is challenging. Patterning sub-10 nm 3D features require multiple steps of lithography which might lead to an unsatisfactory resolution due to an imperfect alignment of masks or limited focal plane of the EUV source.

Area-selective atomic layer deposition (AS-ALD) is an alternative method to pattern sub-10 nm features. AS-ALD selectivity relies on the differential chemical reactivity the precursors and different substrates so that spontaneous patterning is possible. Therefore, a choice of reactants for a selective oxide deposition is critical since strongly oxidizing reactants such as H$_2$O and H$_2$O$_2$ easily provide nucleation sites on any surface. For example, previously reported HfO$_x$ ALD has been using water (H$_2$O), ozone (O$_3$), ammonium hydroxide (NH$_4$OH), hydrogen peroxide (H$_2$O$_2$) or oxygen (O$_2$) plasma as oxygen sources [6-12]. These oxidants are effective in forming a high quality HfO$_x$ film due to energetically favorable reactions of -OH groups or reactive oxygen species with Hf precursors; however, they can initiate nucleation on most of the surfaces which should be avoided for selective deposition.

Anderson et al. [13] have demonstrated waterless TiO$_2$ ALD using TiCl$_4$ and Ti(OiPr)$_4$, and Atanasov et al. [14] reported an inherent substrate-dependency of the
“water-free” TiO$_2$ process between hydrogen terminated Si (H-Si) and hydroxylated Si (OH-Si). The authors showed that eliminating strong oxidants such as water was critical to obtain selectivity by preventing oxidation of the Si-H terminated surface.

S. Sayan et al. [15] and T. S. Yang et al. [16] previously demonstrated a water-free HfO$_2$ deposition on Si via a single-source chemical vapor deposition (CVD) process. The authors employed a thermal decomposition of hafnium alkoxides by continuously exposing Si to the precursors; however, to the best of our knowledge, the selectivity of water-free HfO$_2$ deposition has never been reported.

In this study, water-free HfO$_x$ was selectively deposited on Si in preference to SiCOH and passivated SiO$_2$ by employing hafnium tetra-tert-butoxide (Hf(O$^t$Bu)$_4$) which is a source of both metal and oxygen. The HfO$_x$ deposition was performed via a pulsed CVD process which involved the decomposition of Hf(O$^t$Bu)$_4$. In case of CVD, a thermally pyrolyzed precursor is generally less sensitive to the initial surface condition which is not desirable for selectivity. However, unlike a conventional CVD process which continuously flows a precursor, Hf(O$^t$Bu)$_4$ was pulsed with a purge. Pulsed CVD provides a capability of investigating the mechanism of selectivity and of expanding selectivity by allowing reversibly physisorbed adsorbants to leave from the unwanted surface without reacting. The key of this work is to demonstrate the inherently selective CVD of water-free HfO$_x$ and its enhancement using small molecules passivants and a purge control.

### 4.3 Experimental

Fig. 4.1 shows a chamber schematic. A home-built reaction chamber was pumped by a turbopump (Pfeiffer TPU 062) and a backing rotary pump (Edwards RV3). The base
pressure of the reaction chamber was $8.0 \times 10^{-7}$ Torr. The reaction chamber had a manipulator rod with a sample mounting platform made of Cu. A cartridge heater was used to heat the Cu platform and the samples. The precursors and N$_2$ purge gas had dosing lines pointing at the samples with a 3-inch separation. The dosing was performed using pneumatic valves and leak valves. The chamber wall and dosing lines for precursors were kept at 150°C. After the deposition was performed, the processed samples were transferred in-situ into a UHV chamber to characterize the chemical compositions and oxidation states of the films using X-ray photoelectron spectroscopy (XPS). The UHV chamber was pumped by an ion pump (Agilent Varian VacIon 300 StarCell) and had a base pressed of $8.0 \times 10^{-10}$ Torr. The in-situ transfer was performed using the manipulators and transfer arm so that the samples were not exposed to the ambient air between the depositions and chemical analyses. For the XPS measurements, a monochromatic Al Kα X-ray source ($E = 1487$ eV) and a hemispherical analyzer (XM 1000 MkII/SPHERA, Omicron Nanotechnology) were employed. The anode voltage and filament emission current were set to 10 kV and 25 mA respectively with a hemisphere analyzer pass energy of 50 eV. The focused X-ray beam size on the sample was 0.7 – 1 mm in diameter. For the surface sensitive measurements, the XPS detector was aligned to 60° from the sample surface normal (i.e. near glancing), but for the detection of the bulk compositions of deposited films, 30° from the surface normal was employed. After the XPS data collection, the areas of the XPS peaks were calculated and corrected using their relative sensitivity factors reported in the Casa XPS v2.3 program. The chemical compositions were normalized to the sum of all elements. The morphology of the deposited films were analyzed using ex-situ atomic force microscopy (AFM) (Agilent 5500) in tapping mode.
Passivation of SiO$_2$ and SiCOH was performed in a separate vacuum chamber where the base pressure was 200 mTorr pumped by a mechanical pump (Edwards RV3). The chamber consisted of a sample stage which had a cartridge heater to heat the samples to a reaction temperature of 70°C. The chamber walls were kept at 25°C. SiO$_2$ samples were loaded in the passivation chamber after degreasing using acetone, methanol and HPLC grade water for 30 seconds each followed by a 30 second dip in a 0.5% HF(aq) solution. SiCOH samples were degreased using the same process but without the HF clean. 1,1,3,3-tetramethyldisilazane (TMDS) (97%, Sigma Aldrich) and Bis(dimethylamino)dimethylsilane (DMADMS) (>95%, Sigma Aldrich) were used as passivation agents. The precursor bottles were kept at room temperature. The passivants were continuously flowed into the chamber at a constant pressure of 10 Torr for 10 mins using a manual bellows valve. After the passivation process, the passivated SiO$_2$ and passivated SiCOH samples were removed from vacuum and quickly loaded into a sample loading chamber that was connected to the reaction chamber and UHV chamber to minimize the contamination from the air transfer.

B-doped Si (001), SiO$_2$ and SiCOH were degreased using acetone, methanol and HPLC water sequentially for 30 seconds. After the degrease, Si and SiO$_2$ were cleaned in a 0.5% HF(aq) solution for 30 seconds followed by a HPLC water rinse to remove a native oxide. A combination of two or three samples (i.e. HF cleaned Si and degreased SiCOH or HF cleaned Si, passivated SiO$_2$ and passivated SiCOH) were loaded together in the sample loading chamber and pumped down to the base pressure of $2.0 \times 10^{-7}$ Torr. By loading two or three different substrates at the same time, direct comparison of HfO$_x$ selectivity with
identical reaction conditions was ensured. Before the deposition, the samples were pre-
annealed in the UHV chamber at the corresponding deposition temperatures.

Selective CVD of HfO\textsubscript{x} was performed using Hafnium tert-butoxide (Hf(O\textsubscript{t}Bu\textsubscript{4}, 99.99%, Sigma Aldrich) at sample temperatures of 150-250°C. Hf(O\textsubscript{t}Bu\textsubscript{4} was contained in a glass tube that was vacuum-sealed to a stainless steel flange and dosing line. The container was kept at 80°C to increase the vapor pressure of Hf(O\textsubscript{t}Bu\textsubscript{4}. The exposure of Hf(O\textsubscript{t}Bu\textsubscript{4} per pulse was ~6,000 Langmuir calculated using a pressure spike detected by a convectron gauge in the reaction chamber. (1 Lanmuir (L) = 1×10\textsuperscript{-6} Torr × 1 second exposure of a gas). Each pulse of Hf(O\textsubscript{t}Bu\textsubscript{4 was separated by a N\textsubscript{2} purge for 15 seconds. The effect of the purge time on selectivity was determined by varying the purge time between 5 – 60 seconds at 250°C. The N\textsubscript{2} purge gas was continuously flowed into the reaction chamber at 130 mTorr during the deposition.

4.4 Results and Discussion

4.4.1 Temperature study of HfO\textsubscript{x} CVD on Si using XPS

HfO\textsubscript{x} single precursor CVD using Hf(O\textsubscript{t}Bu\textsubscript{4} was performed on HF cleaned Si at three different temperatures, 250°C, 200°C and 150°C. Removal of the native SiO\textsubscript{x} on Si using aqueous HF is known to leave the surface Si-H terminated. [17] The HfO\textsubscript{x} thickness was calculated using the inelastic mean free path (IMFP) and attenuation length of an electron from the Si substrate as shown below.

\[
\lambda = \frac{143}{E^2} + 0.054\sqrt{E}
\]

\[
I = I_0 \exp(-t/\lambda \sin \theta)
\]
where $E$ is a kinetic energy of electron, $I$ is the intensity of the substrate signal, $I_0$ is the intensity of the unattenuated substrate signal, $t$ is the thickness of the film on top of the substrate (layer depth), $\lambda$ is the IMFP of the electrons coming from the substrate and $\theta$ is the angle of emitted electron from the surface.

Fig. 4.2(a) shows the XPS chemical composition of Si after sequential Hf(O\textsuperscript{t}Bu\textsubscript{4} doses at 250°C, 200°C and 150°C. As loaded HF cleaned Si had 74% Si (depicted in yellow) and all the Si was in an oxidation state of 0 (depicted in grey). There was a total of 26% adventitious hydrocarbon and oxygen on the surface. After 10 pulses of Hf(O\textsuperscript{t}Bu\textsubscript{4} at 250°C, 19% Hf and 45% O were deposited, and the Si substrate peak was attenuated to 21%. After a total of 15 pulses at 250°C, Hf and O increased to 26% and 59% and the Si substrate was attenuated to 4% which is consistent with continuous growth of HfO\textsubscript{x}. There was 5% C on the surface consistent with the presence of butoxide ligands.

At 200°C, a HfO\textsubscript{x} film also continuously grew as the Hf(O\textsuperscript{t}Bu\textsubscript{4} doses increased. After a total of 150 pulses, the Si substrate was completely buried and HfO\textsubscript{x} was deposited with 13% C on the surface. Lastly, at 150°C only 4% Hf, 17% O and 23% C was deposited on Si after 125 pulses dose which indicates poor nucleation at 150°C on Si.

Fig. 4.2(b) shows the HfO\textsubscript{x} thickness on Si as a function of Hf(O\textsuperscript{t}Bu\textsubscript{4} doses at 250°C, 200°C and 150°C. At 250°C and 200°C, HfO\textsubscript{x} continuously grows with a growth rate of 1.48±0.12 Å/pulse and 0.47±0.02 Å/pulse, respectively. At 150°C the growth per pulse was only 0.04±0.01 Å/pulse which is consistent with poor nucleation of Hf(O\textsuperscript{t}Bu\textsubscript{4} on H-terminated Si at 150°C.
4.4.2 Selective HfOₓ deposition on Si in preference to SiCOH at 200°C

At 200°C, the selective pulsed HfOₓ CVD was observed on Si in preference to SiCOH as shown in Fig. 4.3. SiCOH is a highly porous silicon oxide doped with carbon with Si-CH₃ termination on the surface. [18] SiCOH is a common low-k material in nearly all logic and memory devices due to its electrical, thermal and chemical compatibility with the fabrication processes. [18-20] Fig. 4.3(a) shows the chemical compositions of Si and SiCOH after sequential doses of Hf(O'Bu)₄ at 200°C. After 20 pulses of Hf(O'Bu)₄ on HF cleaned Si, 12% Hf was deposited and O increased from 11% to 31%. The Si substrate was attenuated from 77% to 42%. After another 40 pulses, 8% of Si was present which is consistent with HfOₓ deposition. In contrast, on SiCOH, 20 pulses of Hf(O'Bu)₄ only deposited a trace amount of Hf on the surface. An additional 40 pulses of Hf(O'Bu)₄ deposited 12% Hf and O increased from 38% to 46%. Si was attenuated from 31% to 17%. This indicates that HfOₓ deposition at 200°C showed a nucleation delay on SiCOH which consistent with inherent selectivity. Fig. 4.3(b) shows the HfOₓ thicknesses on Si and SiCOH calculated using the substrate attenuation from XPS. For the thickness calculation, it was assumed that the HfOₓ film on SiCOH was conformal across the surface. The HfOₓ thickness after 20 pulses of Hf(O'Bu)₄ on Si and SiCOH was 0.7 nm and 0.1 nm, respectively. Another 40 pulses deposited 2.4 nm of HfOₓ on Si and 0.7 nm of HfOₓ on SiCOH. The inherent selectivity was retained up to ~ 0.7 nm growth on Si before the HfOₓ film started to grow on SiCOH.

Fig. 4.3(c) shows the raw XPS spectra of the Si 2p, O 1s and Hf 4d orbitals after HfOₓ deposition at 200°C. The Si 2p peak was at an oxidation state of 0 (99.7 eV) after the HF clean. The Si peak intensity decreased as HfOₓ was deposited and the Si oxidation state
mostly remained at the initial binding energy consistent with Si(0) with a trace amount of an oxidized Si component at 102.6 eV. The absence of the oxidized Si component indicates that the HfO$_x$ CVD at 200°C occurs without oxidizing more than a monolayer of the Si surface. The O peak of Hf cleaned Si was at 532.4 eV which corresponds to the H-C-O bonding from the adventitious hydrocarbon and the O peak shifted to 531.6 eV consistent with Hf-O bonds. The Hf 4d (214.2 eV and 225.2 eV) peaks became larger in intensity as the number of pulses increased showing the continuous growth of HfO$_x$.

### 4.4.3 Surface morphology of HfO$_x$ deposited at 200°C

The surface morphology of the deposited HfO$_x$ film on Si and SiCOH was evaluated using AFM depicted in Fig. 4.4. Fig. 4.4(a-b) shows the surface morphologies of HF cleaned Si before and after the HfO$_x$ deposition at 200°C. The HF cleaned Si surface was flat with a root mean square (RMS) roughness of 8.3 Å. After a total of 60 Hf(OtBu)$_4$ pulses at 200°C, the HfO$_x$ film was conformal with an RMS roughness of 2.1 Å. An AFM image of degreased SiCOH had < 2 nm tall chain-like features on the surface which might be due to the porous structure of the film and cross-linking of O-Si-C$_x$H$_y$ surface termination groups (Fig. 4.4(c)). [21,22] Fig. 4.4(d) shows the SiCOH surface after 60 pulses of Hf(OtBu)$_4$ at 200°C. The surface was smooth with a chain-like feature with an RMS roughness of 4.2 Å.

### 4.4.4 Strategies for improving selectivity

The inherent selectivity of HfO$_x$ on Si was less than 1 nm before growth took place on SiCOH at 200°C. The selectivity loss could be due to: (1) defect sites (reactive -OH
sites) on SiCOH and/or (2) lack of thermal energy or time for Hf(O\textsuperscript{t}Bu)\textsubscript{4} to desorb from SiCOH which can initiate nucleation. To test the first hypothesis that the defect sites initiated nucleation of HfO\textsubscript{x}, TMDS and DMADMS were employed to passivate the active -OH sites on SiCOH. The possible chemical reactions are:

$$(\text{Si-OH})_4^* + [(\text{CH}_3)_2\text{SiH}]_2\text{NH}(g) \rightarrow [(\text{Si-O})_2\text{-Si(\text{CH}_3}_2)_2]^* + 2\text{H}_2(g) + \text{NH}_3(g)$$ for TMDS and

$$(\text{Si-OH})_2^* + [(\text{CH}_3)_2\text{N}]_2\text{Si(\text{CH}_3}_2)_2(g) \rightarrow (\text{Si-O})_2\text{-Si(\text{CH}_3}_2)^* + 2(\text{CH}_3)_2\text{NH}(g)$$ for DMADMS

, where the asterisk indicates surface species.

$$S = \frac{T_G}{T_{NG}}$$ was used as a metric of the selectivity, where $T_G$ is the HfO\textsubscript{x} thickness on the growth area and $T_{NG}$ is the HfO\textsubscript{x} thickness on the non-growth area. The growth area was Si and the non-growth areas were SiCOH and passivated SiO\textsubscript{2}. The HfO\textsubscript{x} thicknesses were calculated using the XPS attenuation method and ellipsometry. As a control, HfO\textsubscript{x} deposition was also performed on OH-terminated SiO\textsubscript{2} (HF cleaned SiO\textsubscript{2}) at 200\textdegree C. A control sample of OH-terminated SiO\textsubscript{2} showed the same growth rate of HfO\textsubscript{x} as on Si which had a selectivity metric of $S=1.1\pm0.1$.

Fig. 4.5(a) shows the selective HfO\textsubscript{x} deposition on Si in preference to TMDS passivated SiO\textsubscript{2} (TMDS-SiO\textsubscript{2}) and DMADMS passivated SiO\textsubscript{2} (DMADMS-SiO\textsubscript{2}) using XPS at 200\textdegree C. After 20 pulses of Hf(O\textsuperscript{t}Bu)\textsubscript{4} pulses at 200\textdegree C, 2.9\pm0.6 nm HfO\textsubscript{x} was deposited on Si ($T_G$) and the selectivities were $S=2.2\pm0.7$ for DMADMS-SiO\textsubscript{2}, and $S=14.5\pm3.3$ for TMDS-SiO\textsubscript{2}. This significant improvement in selectivity compared to OH-terminated SiO\textsubscript{2} indicates that TMDS is highly effective for passivating -OH groups on the surface. For greater oxide thickness on Si ($T_G=10.7\pm0.1$ nm), the selectivity for TMDS decreased while the selectivity for DMADMS increased from $S=2.2\pm0.7$ at $T_G =2.9\pm0.6$
nm to 4.1±1.5 at T⁰₉=10.7±0.1 nm. In Fig. 4.5(b), the selectivity of different combinations of passivants and substrates were compared as a function of HfOₓ thickness on Si. (D+T) denotes a sequential passivation using DMADMS followed by TMDS and (T+D) denotes a sequential passivation using TMDS followed by DMADMS. (D+T) SiO₂ showed similar selectivity to TMDS while (T+D) SiO₂ exhibited a similar selectivity as DMADMS-SiO₂ consistent with the final passivant dominating the chemistry due to reversible bonding during the passivation process.

To study the hypothesis that reversible adsorption of the Hf precursor on SiCOH initiates the nucleation, selective HfOₓ deposition at 250°C was performed with different purge times between the Hf(OtBu)₄ pulses. The purge time between the doses was varied from 5 to 60 sec. Fig. 4.6(a) shows the timing scheme of the Hf(OtBu)₄ dosing process with example purge times of 5 s and 60 s. N₂ purge gas was continuously flowed at 130 mTorr. The HfOₓ thicknesses on SiCOH were plotted with respect to the HfOₓ thickness on Si in Fig. 4.6(b). At 250°C, with 5 second and 15 second purge times, there was 1 nm HfOₓ deposition on Si before a monolayer of HfOₓ (~0.25 nm) was deposited on SiCOH which was similar to the selectivity at 200°C. The selectivity was greatly improved by increasing the purge time to 30 s as shown by the selectivity loss on SiCOH being delayed until ~2.3 nm of HfOₓ deposited on Si. 60 s purge time further increased the selectivity, giving S = 13.6±0.5 at 3.4±0.1 nm of HfOₓ on Si. This corresponds to a monolayer of HfOₓ deposition on SiCOH. The data is consistent with reversible molecular chemisorption of the Hf precursor on the SiCOH surface.
4.4.5 Surface morphology of HfO$_x$ deposited at 250°C

The surface morphologies of Si and SiCOH were investigated using AFM after the selective HfO$_x$ deposition at 250°C with 60 s purge time. Fig. 4.7(a) shows the Si surface after deposition of a 5.2 nm thick HfO$_x$ film. The HfO$_x$ film was conformal with an RMS roughness of 3.8 Å but there were a few ~3 nm tall particles. Fig. 4.7(b) shows the SiCOH surface after ~ 0.6 nm of HfO$_x$ was deposited. HfO$_x$ on SiCOH was also conformal and there were also ~ 6 nm tall particles observed. The particle formation may be due to gas phase or walls reactions since they occur on all surfaces and might be suppressed by better reactor design to avoid wall reaction product from impinging on the wafer.

4.4.6 Optimized selectivity of HfO$_x$ on TMDS passivated SiCOH

Since TMDS was most effective at passivating -OH groups on SiO$_2$ and 60 s purge time could delay the nucleation on SiCOH, HfO$_x$ deposition with 60 s purge time was performed on TMDS passivated SiO$_2$ and TMDS passivated SiCOH as shown in Fig. 4.8. A total of 20 pulses of Hf(OtBu)$_4$ deposited 7.5±0.1 nm thick HfO$_x$ on Si (Fig. 4.8(a) as measured by ellipsometry). In contrast, there were only 7% Hf and 3% Hf detected on TMDS-SiO$_2$ and TMDS-SiCOH, corresponding to 0.27±0.03 nm and 0.12±0.02 nm thick HfO$_x$ respectively as calculated by the attenuation of the substrates in XPS. The selectivity metrics were S=28±1.9 for TMDS-SiO$_2$ and S=62±4.6 for TMDS-SiCOH both at 7.5±0.1 nm HfO$_x$ on Si.
4.4.7 The mechanism of selectivity

The proposed mechanism of the selective HfO\textsubscript{x} deposition is shown in Fig. 4.9. Fig. 4.9(a) shows a growth mechanism of HfO\textsubscript{x} on Si using Hf(O\textsuperscript{t}Bu)\textsubscript{4}. Hf(O\textsuperscript{t}Bu)\textsubscript{4} first molecularly adsorbs on the H-terminated Si surface and decomposes. The decomposition temperature of Hf(O\textsuperscript{t}Bu)\textsubscript{4} is ~200°C. [15] Once the precursor decomposes, the butoxide ligands leave as isobutylene (C\textsubscript{2}H\textsubscript{2}(CH\textsubscript{3})\textsubscript{2}) and Hf(O\textsuperscript{t}Bu)\textsubscript{4} transforms to Hf(O\textsuperscript{t}Bu)\textsubscript{x}OH\textsubscript{4-x}. Subsequently, OH groups can react with H-Si bonds to form Si-O-Hf(O\textsuperscript{t}Bu)\textsubscript{x}. This decomposition of Hf(O\textsuperscript{t}Bu)\textsubscript{4} is necessary to deposit HfO\textsubscript{x} on Si since the nucleation of HfO\textsubscript{x} does not readily occur on H-Si at 150°C which is below the decomposition temperature as shown in Fig. 4.2. As the Hf(O\textsuperscript{t}Bu)\textsubscript{4} decomposes, the HfO\textsubscript{x} film can continuously grow via a reaction of surface-bound Hf(OH)\textsubscript{x} and Hf(O\textsuperscript{t}Bu)\textsubscript{4}. Fig. 4.9(b) shows a model for the degreased SiCOH surface after Hf(O\textsuperscript{t}Bu)\textsubscript{4} dosing. Hf(O\textsuperscript{t}Bu)\textsubscript{4} first reversibly and molecularly adsorbs on the surface and decomposes at >200°C. However, since the surface is terminated with O-Si-CH\textsubscript{3} groups, Hf(O\textsuperscript{t}Bu)\textsubscript{x}(OH)\textsubscript{4-x} readily desorbs from the surface without reacting with O-Si-CH\textsubscript{3} bonds. This is consistent with top-most Si atoms being bonded to O (Si-O: 798 kJ/mol) and C (Si-C: 435 kJ/mol) which are harder to break compared to Si-H bonds (298 kJ/mol). [23] In addition, the Hf atom in Hf(O\textsuperscript{t}Bu)\textsubscript{4} is already bonded to four oxygens with strong bond energy of 791 kJ/mol. [23] The energetical stability of both the SiCOH surface and the Hf metal atoms of the precursor impede HfO\textsubscript{x} nucleation on the SiCOH surface while the CH\textsubscript{3} termination reduces the physisorption energy promoting desorption. However, the surface passivation of SiCOH is not perfect so the adsorbed precursor may diffuse and react with the defect -OH sites. This is consistent with better selectivity after passivation by TMDS.
Fig. 4.9(c) depicts the Hf(O\textsuperscript{t}Bu\textsubscript{4} reaction on passivated SiO\textsubscript{2} using TMDS or DMADMS. Both TMDS and DMADMS react with OH-terminated SiO\textsubscript{2} and ideally form O-Si-CH\textsubscript{3} surface terminations. This is the same surface condition as SiCOH in terms of the topmost Si atoms on the surface bonded to O and CH\textsubscript{3}. The subsequent Hf(O\textsuperscript{t}Bu\textsubscript{4} adsorption followed by the decomposition and desorption from the passivated surface is analogous to those on SiCOH in Fig. 4.9(b).

**4.5 Conclusions**

Hafnium oxide (HfO\textsubscript{x}) was selectively deposited on Si in preference to SiCOH and passivated SiO\textsubscript{2} using Hf(O\textsuperscript{t}Bu\textsubscript{4}. The inherent selectivity has benefited from the water-free process since commonly used oxygen sources such as H\textsubscript{2}O or H\textsubscript{2}O\textsubscript{2} can readily physisorb or chemisorb on any surface to initiate nucleation which is undesirable for selectivity. It was demonstrated that pulsed CVD allows for the Hf(O\textsuperscript{t}Bu\textsubscript{4} precursor to reversibly molecularly physisorb on SiCOH and the use of passivation molecules together with careful control of purge time is critical to improve the selectivity of the water-free oxide CVD.

HfO\textsubscript{x} deposition using a pulsed single precursor CVD of Hf(O\textsuperscript{t}Bu\textsubscript{4} showed excellent selectivity (S=62, 7.5 nm HfO\textsubscript{x} deposition on Si as opposed to 0.1 nm deposition on TMDS passivated SiCOH) and avoided substrate oxidation since it does not require H\textsubscript{2}O as an O source. The methods to control the reversible adsorption of the precursor to improve selectivity could be integrated into the patterning process for sub-10 nm MOSFETs with three-dimensional structures.
4.6 Acknowledgements

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4.7 Figures

Figure 4.1. A schematic of the vacuum system. The chamber consisted of a reaction chamber, sample loading chamber and UHV chamber equipped with X-ray photoelectron spectroscopy.
Figure 4.2. XPS elemental compositions and the growth rates of HfO$_x$ on H-terminated Si at 250°C, 200°C and 150°C. (a) Elemental composition of HF cleaned Si after sequential doses of Hf(O"Bu)$_4$ at 250°C, 200°C and 150°C. The elemental composition is normalized to the sum of all elements. (b) The growth rate of HfO$_x$ on H-terminated Si using Hf(O"Bu)$_4$ at 250°C, 200°C and 150°C.
Figure 4.3. Selective HfO$_x$ deposition on Si in preference to SiCOH at 200°C. (a) XPS elemental compositions showed that HfO$_x$ was selectively deposited on Si at 200°C. (b) HfO$_x$ thicknesses on Si and SiCOH were plotted as a function of Hf(O$^t$Bu)$_4$ doses at 200°C. ~0.7 nm HfO$_x$ was deposited on Si before nucleation occurred on SiCOH. (c) Raw XPS data of Si 2p, O 1s and Hf 4d show that HfO$_x$ was deposited without forming significant SiO$_x$ at the interface.
Figure 4.4. Surface morphologies of HF cleaned Si and degreased SiCOH before and after HfO\(_x\) deposition. (a) AFM image of HF cleaned Si. (b) The surface morphology of HF-Si after the HfO\(_x\) deposition at 200\(^\circ\)C. (c) AFM image of degreased SiCOH. (d) AFM image of degreased SiCOH after the HfO\(_x\) deposition at 200\(^\circ\)C.
Figure 4.5. Selectivity metric $(S)$ of passivated SiO$_2$ and SiCOH as a function of HfO$_x$ thickness on Si. (a) Chemical compositions of HF cleaned Si, TMDS passivated SiO$_2$ and DMADMS passivated SiO$_2$ after selective HfO$_x$ deposition at 200°C. TMDS was the most effective passivant on OH-terminated SiO$_2$. The HfO$_x$ on Si was 2.9 nm before less than a monolayer deposition occurred on TMDS-SiO$_2$. The DMADMS and TMDS molecular structures are shown on the right.
Figure 4.6. Selectivity enhancement of HfO$_x$ on Si versus SiCOH by increasing the purge time between the Hf(O$i^t$Bu)$_4$ pulses at 250°C. (a) A schematic timing diagram of Hf(O$i^t$Bu)$_4$ doses with a continuous N$_2$ purge. (b) HfO$_x$ thickness on SiCOH with the respect to HfO$_x$ thickness on Si with different purge times. The selectivity was improved by increasing the purge time between the Hf(O$i^t$Bu)$_4$ pulses. 60 s purge time showed 2 nm HfO$_x$ deposition on Si before any nucleation occurred on SiCOH.
Figure 4.7. Surface morphology of the HfO$_x$ films deposited at 250°C on Si and SiCOH. (a) HfO$_x$ on H-terminated Si showed a conformal film with an RMS roughness of 3.8 Å. (b) On degreased SiCOH, HfO$_x$ was conformal with ~6 nm tall particles.
Figure 4.8. Selectivity enhancement of HfO<sub>x</sub> on Si versus TMDS passivated SiO<sub>2</sub> and TMDS passivated SiCOH. (a) 20 pulses of Hf(O'Bu)<sub>4</sub> with 60 s purge on HF-Si at 250°C deposited 7.5 nm thick HfO<sub>x</sub>. (b) On TMDS-SiO<sub>2</sub>, 0.3 nm thick HfO<sub>x</sub> was deposited which gives a selectivity metric of S = 28±1.9. (c) On TMDS-SiCOH, 0.1 nm thick HfO<sub>x</sub> was deposited which gives a selectivity metric of S = 62±4.6.
Figure 4.9. Mechanism of selective HfO$_x$ pulsed CVD on Si versus SiCOH and passivated SiO$_2$. (a) On H-terminated Si, Hf(OtBu)$_4$ adsorbs on the surface and decomposes into Hf(OtBu)$_{4-x}$OH$_x$. Then OH reacts with H-Si and HfO$_x$ continuously grows. (b) Adsorbed and decomposed Hf(OtBu)$_4$ leaves from the O-Si-CH$_3$ terminated SiCOH surface. (c) TMDS and DMADMS reacts with OH-terminated SiO$_2$ and leaves a O-Si-CH$_3$ terminated surface which prevents the decomposed Hf(OtBu)$_4$ from reacting.
4.8 References


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