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InGaAs(001) and SiGe(001)/(110) Surface Passivation by Self-Limiting Deposition of Silicon Containing Control Layers

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

in

Materials Science and Engineering

by

Mary Ellen Edmonds

Committee in Charge:

Professor Andrew C. Kummel, Chair
Professor Yeshaiahu Fainman
Professor Yu-Hwa Lo
Professor Vlado Lubarda
Professor William C. Trogler

2016
The Dissertation of Mary Ellen Edmonds 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

2016
DEDICATION

To my Father for always believing in me and telling me I can do whatever I set my mind to, and to my Mother for always being there for me through all of life’s challenges.
EPIGRAPH

Nothing in life is to be feared, it is only to be understood. Now is the time to understand more, so that we may fear less.

Marie Curie
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<tr>
<td>Å</td>
<td>angstrom</td>
</tr>
<tr>
<td>AC</td>
<td>alternating current</td>
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<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
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<tr>
<td>ALD</td>
<td>atomic layer deposition</td>
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<tr>
<td>AMU</td>
<td>atomic mass units</td>
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<tr>
<td>BE</td>
<td>binding energy</td>
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<tr>
<td>BOE</td>
<td>buffered oxide etch</td>
</tr>
<tr>
<td>CB</td>
<td>conduction band</td>
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<tr>
<td>$C_{\text{max}}$</td>
<td>maximum capacitance</td>
</tr>
<tr>
<td>CV</td>
<td>capacitance voltage</td>
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<tr>
<td>CVD</td>
<td>chemical vapor deposition</td>
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<tr>
<td>DC</td>
<td>direct current</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>$D_{\text{it}}$</td>
<td>density of interface traps</td>
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<tr>
<td>DOS</td>
<td>density of states</td>
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<tr>
<td>$E_f$</td>
<td>Fermi level</td>
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<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>
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<tr>
<td>FGA</td>
<td>forming gas anneal</td>
</tr>
<tr>
<td>GGA</td>
<td>general gradient approximation</td>
</tr>
<tr>
<td>GV</td>
<td>conductance voltage</td>
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<tr>
<td>Symbol</td>
<td>Definition</td>
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<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>h</td>
<td>Planck’s constant</td>
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<tr>
<td>HV</td>
<td>high vacuum</td>
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<tr>
<td>I</td>
<td>electric current</td>
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<td>Langmuir</td>
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<tr>
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<td>MBE</td>
<td>molecular beam epitaxy</td>
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<td>MOSCAP</td>
<td>metal oxide semiconductor capacitor</td>
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<tr>
<td>MOSFET</td>
<td>metal oxide semiconductor field effect transistor</td>
</tr>
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<td>nm</td>
<td>nanometer</td>
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<td>PBE</td>
<td>Perdew-Burke-Emzerhof</td>
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<td>PBN</td>
<td>pyrolitic boron nitride</td>
</tr>
<tr>
<td>PP</td>
<td>pseudo potentials</td>
</tr>
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<td>PECVD</td>
<td>plasma enhanced chemical vapor deposition</td>
</tr>
<tr>
<td>PVD</td>
<td>physical vapor deposition</td>
</tr>
<tr>
<td>RDF</td>
<td>radial-distribution function</td>
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<tr>
<td>SPM</td>
<td>scanning probe microscopy</td>
</tr>
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<td>SRC</td>
<td>Semiconductor Research Corporation</td>
</tr>
<tr>
<td>STM</td>
<td>scanning tunneling microscopy</td>
</tr>
<tr>
<td>TMA</td>
<td>trimethylaluminum</td>
</tr>
<tr>
<td>UHV</td>
<td>ultra high vacuum</td>
</tr>
<tr>
<td>V</td>
<td>volts</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>VASP</td>
<td>Vienna ab-initio simulation package</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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VITA

EDUCATION

2011  Bachelor of Science in Materials Science and Engineering, Arizona State University

2012  Master of Science in Materials Science and Engineering, University of California, San Diego

2016  Doctor of Philosophy in Materials Science and Engineering, University of California, San Diego

PUBLICATIONS

M. Edmonds, S. Wolf, E. Chagarov, T. Kent, J. H. Park, R. Holmes, D. Alvarez, and A. C. Kummel, ”Self-limiting CVD of a passivating SiOx control layer on InGaAs(001)-(2x4) with the prevention of III-V oxidation,” (manuscript submitted to Surface Science).


“Surface Preparation and In/Ga Alloying Effects on InGaAs (001)-(2x4) Surfaces for ALD Gate Oxide Deposition,” M. Edmonds, T. Kent, E. Chagarov, A.C. Kummel. ECS Transactions, 50 (4), pp 129-140 (2012).

M. Edmonds, T. Kent, S. Wolf, K. Sardashti, M. Chang, J. Kachian, R. Droopad, E. Chagarov, and A. C. Kummel, ”In_{0.53}Ga_{0.47}As(001)-(2x4) and Si_{0.5}Ge_{0.5}(110) surface passivation by self-limiting deposition of silicon containing control layers,” VLSI Technology, Systems and Application (VLSI-TSA), 2016 International Symposium (April 2016).

“Rapid In-Situ Carbon and Oxygen Cleaning of In0.53Ga0.47As(001) and Si0.5Ge0.5(110) Surfaces via a H2 RF Downstream Plasma,” S. Wolf, M. Edmonds, X. Jiang, R. Droopad, B. Sahu, S. S. Siddiqui and A. Kummel. ECS Transactions, 72 (4), pp 291-302 (2016).


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Major Field: Materials Science and Engineering

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

InGaAs(001) and SiGe(001)/(110) Surface Passivation by Self-Limiting Deposition of Silicon Containing Control Layers

by

Mary Ellen Edmonds

Doctor of Philosophy in Materials Science and Engineering

University of California, San Diego, 2016

Professor Andrew C. Kummel, Chair

Metal oxide semiconductor field effect transistors (MOSFETs) are transitioning away from exclusive use of silicon and germanium into the employment of compound semiconductors such as SiGe and InGaAs to further increase transistor performance. A broader range of channel materials with higher electron or hole mobilities may be employed if a universal control interfacial layer, which bonds more ideally to high-k gate oxide materials, could be ALD or self-limiting CVD deposited on many different materials and crystallographic faces. Silicon bonds strongly to all crystallographic faces
of InGa$_{1-x}$As, In$_x$Ga$_{1-x}$Sb, In$_x$Ga$_{1-x}$N, SiGe, and Ge enabling transfer of substrate dangling bonds to silicon, which may then be passivated with atomic hydrogen, or functionalized with an oxidant such as HOOH(g) in order to create an Si-OH layer, or a nitriding agent such as N$_2$H$_4$(g) in order to create an SiO$_x$N$_y$ diffusion barrier and surface protection layer. This dissertation focuses on depositing saturated Si-H$_x$, and Si-OH thin films via three separate self-limiting CVD processes on InGaAs(001)-(2x4), and depositing a SiO$_x$N$_y$ thin film on Si$_{0.5}$Ge$_{0.5}$(110), Si$_{0.5}$Ge$_{0.5}$(001), and Si$_{0.7}$Ge$_{0.3}$(001) surfaces via an ALD process. XPS in combination with STS/STM were employed to characterize the electrical and surface properties of these silicon containing thin films on InGaAs(001)-(2x4) and Si$_x$Ge$_{1-x}$(110)/(001) surfaces. MOSCAP device fabrication was performed on n-type InGaAs(001), Si$_{0.5}$Ge$_{0.5}$(001), and Si$_{0.7}$Ge$_{0.3}$(001) substrates with and without the insertion of these silicon containing interfacial control layers deposited by novel self-limiting growth processes in order to determine the effects on $C_{\text{max}}$, frequency dispersion, and midgap trap states.
Chapter 1

Introduction

1.1 Scaling of Metal Oxide Semiconductor Field Effect Transistors

Metal oxide semiconductor field effect transistors (MOSFETs) are diverging from the exclusive use of silicon and germanium and into the employment of compound semiconductor materials such as InGaAs and SiGe in order to further reduce the transistor size while increasing transistor performance.\(^1\)\(^4\) Utilization of high mobility compound semiconductors along with high-K gate oxides provide the ability to maintain low MOSFET power operations through the application of low gate voltages with high drive currents. These power improvements require the control of many parameters, such as decreasing the equivalent oxide thickness (EOT) below 1 nm, which depends greatly upon the oxide nucleation growth occurring at every unit cell, and reducing the semiconductor interface/oxide defect density. This dissertation focuses on implementing InGaAs(001) and SiGe(001)/(110) surfaces for use as the channel, and high-k dielectrics, specifically, Al\(_2\)O\(_3\) and HfO\(_2\) for use as the gate oxide.

The semiconductor/oxide interface can degrade device performance through interfacial roughness or formation of surface defects.\(^5\) While the interface between silicon and SiO\(_2\) is of high quality, deposition of high-K gate oxides on compound semiconductor surfaces can lead to formation of strained atomic bonds, dangling surface bonds, and net surface charge formation which can result in Fermi level pinning and electronic trapping states.\(^6\)\(^9\) The goal of this dissertation is to clean and passivate defects on InGaAs(001) and SiGe (001)/(110) surfaces, and to improve the interfacial
bonding and nucleation between InGaAs/SiGe and high-K gate oxide materials in order to improve MOS device performance necessary for device implementation and scaling.

1.2 Ultra High Vacuum Chamber

InGaAs and SiGe surfaces are characterized before and after surface cleaning, passivation and deposition by placing samples into an Omicron variable temperature ultra-high vacuum (UHV) chamber equipped with an Omicron monochromatic X-ray photoelectron spectroscopy (XPS) system, and an Omicron Scanning Tunneling Microscopy /Spectroscopy (STM/STS) system. The UHV chamber is connected by a separation gate valve to the high vacuum (HV) chamber differentially pumped by two turbo molecular pumps backed by either rotary vane mechanical pumps or dry pumps. The HV chamber is divided into three main parts separated by gate valves: the load lock where samples are introduced into high vacuum, and two dosing chambers allowing for separation of reducing and oxidizing precursors. Both dosing chambers contain a manipulator for sample transfer and positioning which is equipped with a pyrolitic boron nitride (PBN) heater for resistive heating of samples to various temperatures as measured by a k-type thermocouple located directly adjacent to the sample. After dosing samples with precursor gas exposures at various temperatures, the samples may be transferred in-situ back into the UHV chamber for characterization with XPS and STM/STS. This multi-chamber HV/UHV system allows for sample processing and characterization all in-situ to avoid contamination by air exposure. The HV chambers, after bake out, can achieve base pressures as low as 1x10^{-7} Torr. Oxidizing precursors include H_{2}O(g), anhydrous N_{2}H_{4} (Sigma Aldrich and Rasirc, Inc.), and anhydrous HOOH(g) provided in
a proprietary solvent by Rasirc, Inc.. Reducing precursors include Si$_3$H$_8$ (Nova-kem), Si$_2$Cl$_6$ (Nova-kem), and Trimethylaluminum (TMA) (Strem Chemicals). The UHV chamber is comprised of two parts: the preparation chamber, and the Scanning Probe Microscopy (SPM) chamber, separated by a gate valve and both pumped by ionization and titanium sublimation getter pumps to achieve UHV base pressures of 2x10$^{-10}$ Torr and 1x10$^{-11}$ Torr. The preparation chamber contains a manipulator equipped with a PBN heater for resistive annealing and heating, an Omicron monochromatic XPS system, a Stanford research mass spectrometer, an Oxford Research TC-50 thermal gas cracker, and a tungsten wire for STM tip cracking. The SPM chamber contains the Omicron variable temperature STM/STS system with AFM capabilities, and a carousel for sample and STM tip storage. A schematic of the UHV/HV multi-chamber system is shown in Figure 1.1.

1.3 Scanning Tunneling Microscopy

STM has been employed at length throughout this dissertation to study surface morphology, atomic ordering, and surface coverage of chemisorbed species on InGaAs and SiGe with atomic scale resolution. The technique of STM was developed in 1981 by Gerd Binning and Heinrich Rohrer in order to probe surfaces of metals and semiconductors, and in 1983 the inventors scanned the silicon (111) surface at atomic resolution and resolved the 7x7 surface reconstruction.$^{11-13}$ The method works by having an atomically sharp conducting tip, such as a tungsten tip, positioned within a few angstroms above the sample surface in order to induce the quantum mechanical effect of electron tunneling between the tip and the sample surface by applying a bias between the
sample and tip, and controlling the positioning of the tip with fine piezoelectric crystals in the x, y, and z directions. A basic circuit diagram of the STM is shown in Figure 1.2. Electron tunneling is exponentially proportional to distance between the tip and sample, and by maintaining a constant tunneling current with a feedback loop, the surface topography, and local surface density of states (LDOS) is mapped at high resolution (angstroms). STM allows for the probing of filled and empty electrical states across a sample surface by biasing the sample at positive (empty state imaging) or negative (filled state imaging) voltage relative to the tip. On an InGaAs surface, when a positive bias is applied to the sample relative to the tip, electrons tunnel from the filled orbitals of the tip into the empty unoccupied orbitals of surface In/Ga atoms. Conversely, when a negative bias is applied to the sample relative to the tip, electrons tunnel from filled arsenic As atom orbitals into unoccupied orbitals of the tip. A schematic of filled states and empty state imaging is shown in Figure 1.3. The LDOS at specific points across a sample surface can be measured by a technique known as scanning tunneling spectroscopy (STS), where the tip is placed above a point on the surface and the voltage is swept while measuring the current.

1.4 Scanning Tunneling Spectroscopy

In order to probe the LDOS of the sample surface, the feedback loop is interrupted and STS measurements are made using a lock-in amplifier employing the variable height mode measurement technique, where the bias is swept from negative to positive voltages and simultaneously the tip-sample spacing is decreased incrementally for a decrease in magnitude of applied bias. The lock-in amplifier superimposes an
alternating current (AC) signal over the direct current (DC) applied for the sample-tip bias, and the in-phase AC component with modulation voltage is recorded. The variable height mode method allows for amplification of tunneling current over several orders of magnitude in order to probe a sample’s band gap and band edges for presence of surface electrical states. By taking the dI/dV measured from the lock-in amplifier and normalizing by $\frac{I}{V}$, the effect of variation of the tip-sample distance is mostly removed, and the result is directly proportional to the LDOS. The obtained $(dI/dV)/(I/V)$ curves are fitted using a linear function described in previous STM/STS studies in order to extract the measured band edge energies of the plotted $(dI/dV)/(I/V)$ spectra, as band offsets contain linear dependence on sample bias. The linear function fitting method contains slight rounding at the band gap onset due to temperature and AC modulation. Standard errors are obtained by the fitting process and reported for averaged STS curves. The uncertainties provided by the fitting method are statistical uncertainties using the least squares fitting and these reported uncertainties are much less than thermal broadening in STS measurements. This STS measurement technique has been shown to accurately reflect the LDOS of a sample within 4 eV of the surface Fermi level ($E_F$), where beyond 4 eV the obtained spectrum becomes dominated by electron tunneling barrier resonances. STS measurements provide lots of insight into the local electrical structure of a sample surface including local measurement of the surface band gap size, location of band gap edge or mid-gap trap states, and the position of the surface Fermi level (0 Volt position). For a p-type doped semiconductor, the Fermi level is located closer to or inside the valence band, while for an n-type doped semiconductor, the Fermi level is located closer to or inside the conduction band. When the Fermi level position
will not modulate for n-type versus p-type samples, the surface Fermi level is said to be pinned in position by surface states present throughout the band gap. By taking STS measurements on both InGaAs and SiGe samples before and after gaseous chemical precursor exposures, the surface Fermi level position is measured to determine any presence of surface Fermi level pinning.

1.5 X-Ray Photoelectron Spectroscopy

XPS has been the main surface characterization technique employed throughout this dissertation to study surface chemical composition, and surface saturation and coverage of chemisorbates for the top most 1-3 nm. The technique, based upon the photoelectric effect, includes a monochromatic X-Ray beam irradiating a sample surface of interest, and core or valence electrons are ejected from the solid with discrete characteristic kinetic energies. The ejected electrons are collected in a hemispherical multichannel analyzer detector where a series of lenses are used to specify the analysis area spot size, and the electron pass energy where voltages are applied to retard or accelerate the collected electrons. After passing through the series of lenses, the electrons enter a 5 channel electron multiplier (Omicron Channeltrons) where the current received from a single electron is amplified by a factor of $10^8$. The current from the Channeltrons is fed into a preamplifier where the electron counts are recorded in the form of a spectrum. The collected electron kinetic energy is measured by the detector, and the electron binding energy may be calculated by the following equation:

$$\text{KE}_{\text{electron}} = E_{\text{hv}} - \text{BE}_{\text{electron}} - \Phi_{\text{spec}}$$  \hspace{1cm} (1.5.)
where $KE_{\text{electron}}$ is the kinetic energy of the electron, $E_{\text{in}}$ is the incoming monochromatic X-Ray energy (1486.7 eV for Al K$_\alpha$), $BE_{\text{electron}}$ is the binding energy of the electron, and $\Phi_{\text{spec}}$ is the work function of the spectrometer detector. XPS detects the presence of any surface elemental chemical shifts, where a chemical shift is a binding energy shift due to chemical oxidation or reduction from bonding with atoms of relatively greater or lesser electronegativity. This measurement capability can help in determining the chemical species present on the surface, and chemical stoichiometry.

1.6 Capacitance Voltage Measurements

Metal oxide semiconductor field effect capacitors (MOSCAPs) have been fabricated throughout this dissertation to examine the capacitance-voltage (C-V) characteristics of high-K gate oxide deposition on InGaAs and SiGe semiconductor substrates, and defects associated with the high-K/semiconductor interface. The MOSCAP structure begins with the InGaAs or SiGe substrate undergoing a surface cleaning or passivation technique, followed by high-K gate oxide deposition, and lastly metal gate front and back contact deposition (nickel or aluminum used in this work), as shown in Figure 1.4. C-V measurements are performed by applying a DC bias across the gate metal front and back contacts, and using an LCR meter to apply a small AC signal (1 kHz to 1 MHz), and measure the capacitive current.

The C-V measurements associated with the MOSCAP device include positive and negative applied gate biases. The flatband voltage ($V_{\text{fb}}$) is defined as the bias which leaves no charge in the body and gate of the capacitor, and therefore no electric field across the gate oxide. The threshold voltage ($V_{\text{th}}$) is defined as the minimum applied
bias required for inversion to occur, where majority carriers have been completely repelled near the surface and minority carriers congregate at the surface. For an n-type doped semiconductor, applying a gate bias more positive than $V_{fb}$ leads to a positive charge at the gate metal, and a negative charge in the semiconductor, leading to an accumulation of electrons at the semiconductor surface when larger positive gate biases are applied (accumulation regime). When a negative bias, less than $V_{fb}$, is applied to the metal gate, the majority carriers (electrons) are repelled from the semiconductor surface, leading to the depletion regime where a positive space charge forms. When the gate bias is increased even more negative than $V_{th}$, the minority carriers (holes) are attracted to the negative charge at the semiconductor surface, leading to the formation of the inversion regime. The main C-V characteristics studied in this work include: the frequency dispersion in the accumulation regime indicative of border traps, the false-inversion bump ($D_{it}$ bump) location and magnitude indicative of gate-oxide/semiconductor interfacial trap states, and the $C_{max}$ value found in the accumulation regime which provides information on the thickness of the gate oxide and interfacial layer, and the quality of the deposited gate-oxide material.

### 1.7 Density Functional Theory

Density functional theory (DFT) is the quantum mechanical modeling method chosen throughout this dissertation to successfully and accurately model the electronic structure of many-body atomic and molecular systems, such as the high-K gate oxide and semiconductor interface. In order to support experimental results and offer more detailed information on the atomic and electronic structure of semiconductor/gate-oxide
interfaces, DFT molecular dynamics (DFT-MD) simulations are performed.\textsuperscript{23} DFT-MD simulations begin with a prepared bulk oxide sample which is relaxed and checked for amorphous quality prior to bonding with the semiconductor surface. This method allows for a computationally affordable and realistic modeling of amorphous gate-oxide/semiconductor interfaces which has been used by many groups to model high-K/III-V and high-K/Si(Ge) structures.\textsuperscript{23} STS and XPS experimental results are considered in order to construct DFT models which represent the InGaAs or SiGe surface bonding with the deposited silicon containing interfacial layers, and then the subsequent deposition of the high-k gate oxide material. This dissertation focuses on depositing thin electrically passivating silicon based interfacial films followed by the high-K gate oxide on the InGaAs/SiGe surface with the surface $E_f$ remaining unpinned, as experimentally confirmed with STS measurements and MOSCAPs. When constructing DFT models of the surface, the electron counting model, as described by M.D. Pashley is employed to ensure no net surface charge is accumulated in interfacial bonds, a condition necessary to ensure an unpinned surface $E_f$.\textsuperscript{8} By employing the electron counting model, and also the charge neutrality modeling described by L. Lin and J. Robertson to ensure each successive layer of growth on the surface contains no net charge, DFT models are created.\textsuperscript{24} These DFT simulations, and visualized band decomposed charge densities provide further information about the atomic bonding structures and LDOS of the InGaAs and SiGe interfaces.
Figure 1.1 Schematic diagram of the multi-chamber UHV system.
Figure 1.2 Schematic diagram of the basic STM circuit.
Figure 1.3 Schematic diagram of filled state and empty state STM imaging. In filled state imaging (a), the sample is biased negative with respect to the tip, and electrons tunnel from filled orbitals of the sample surface into empty state orbitals of the tip. In empty state imaging (b), the sample is biased positive with respect to the tip, and electrons tunnel from filled states of the tip into empty unfilled states of the sample surface.
Figure 1.4 Schematic diagram of MOSCAP device structure. The device includes front and backside metal contacts, deposited high-k gate oxide material, and the InGaAs or SiGe substrate. A DC bias is applied between the front and back metal contacts (Ni and Al metal), and an LCR meter is used to apply a small AC signal (1 kHz to 1 MHz) and the corresponding capacitive current is measured.
1.8 References


(22) Pierret, R. F. *Semiconductor device fundamentals*; Pearson Education India, 1996.


Chapter 2

Passivation of InGaAs(001)-(2x4) by Self-limiting CVD of a Silicon Hydride Control Layer

2.1 Abstract

A saturated Si-Hₙ seed layer for gate oxide or contact conductor ALD has been deposited via two separate self-limiting and saturating CVD processes on InGaAs(001)-(2x4) at substrate temperatures of 250°C and 350°C. For the first self-limiting process, a single silicon precursor, Si₃H₈, was dosed at a substrate temperature of 250°C and XPS results show the deposited silicon hydride layer saturated at about 4 monolayers of silicon coverage with hydrogen termination. STS results show the surface Fermi level remains unpinned following the deposition of the saturated silicon hydride layer, indicating the InGaAs surface dangling bonds are electrically passivated by Si-Hₙ. For the second self-limiting process, Si₂Cl₆ was dosed at a substrate temperature of 350°C and XPS results show the deposited silicon chloride layer saturated at about 2.5 monolayers of silicon coverage with chlorine termination. Atomic hydrogen produced by a thermal gas cracker was subsequently dosed at 350°C to remove the Si-Cl termination by replacing with Si-H termination as confirmed by XPS, and STS results confirm the saturated Si-Hₙ bilayer leaves the InGaAs(001)-(2x4) surface Fermi level unpinned. Density function theory modeling of silicon hydride surface passivation shows an Si-Hₙ monolayer can remove all the dangling bonds and leave a charge balanced surface on InGaAs.
2.2 Introduction

InGaAs intrinsically has very high electron mobility, making it a leading material for replacement of silicon as the n-type channel of metal oxide semiconductor field effect transistors (MOSFETs).\textsuperscript{1-3} Subnanometer FET devices have lower threshold voltages thereby making trap and fixed charge elimination critical.\textsuperscript{4-7} The III-V(001) surfaces are dominated by relatively unreactive filled and empty dangling bonds while the group IV dangling bonds are half filled and, therefore, highly reactive. The high reactivity of the group IV dangling bonds facilitates their elimination during deposition of gates oxides. Therefore, it is proposed that a thin layer (2–4 monolayers) of epitaxial crystalline silicon on InGaAs or related materials (GaAs or InAs) could facilitate dangling bond elimination and formation of a passive interface.

Previous work has shown the deposition of a thin molecular beam epitaxy (MBE) silicon interfacial control layer on the clean In\textsubscript{0.53}Ga\textsubscript{0.47}As(100) surface prior to SiO\textsubscript{2} deposition serves to reduce surface Fermi level pinning.\textsuperscript{7,8} Deposition of a thin MBE silicon layer on In\textsubscript{0.53}Ga\textsubscript{0.47}As(100) prior to Al\textsubscript{2}O\textsubscript{3} deposition lead to improved MOSFET device performance by decreasing frequency dispersion, reducing hysteresis, and lowering D\textsubscript{it}.\textsuperscript{8} Similarly, previous reports also show the physical vapor deposition (PVD) of an a-silicon passivation layer prior to deposition of a bilayer gate insulator stack (1 nm Al\textsubscript{2}O\textsubscript{3}/5 nm HfO\textsubscript{2}) passivates In\textsubscript{0.53}Ga\textsubscript{0.47}As, as C-V characteristics showed inversion and low D\textsubscript{it}, and XPS results show no III-V oxide formation.\textsuperscript{9} Ex-situ deposition of a thin ~1.2 nm a-silicon layer by PECVD on In\textsubscript{0.53}Ga\textsubscript{0.47}As prior to Al\textsubscript{2}O\textsubscript{3} gate oxide ALD has been shown to suppress gallium suboxide formation and MOSFET devices exhibit higher
drive current and higher effective electron mobility values.\textsuperscript{10,11} Detailed XPS studies have shown the presence of Ga\textsubscript{2}O\textsubscript{3} at the interface of both GaAs and In\textsubscript{0.53}Ga\textsubscript{0.47}As based MOSFET devices leads to high frequency dispersion and consequently high $D_{it}$, while an ex-situ deposition (PECVD) of an a-silicon layer on GaAs/In\textsubscript{0.53}Ga\textsubscript{0.47}As surfaces eliminates Ga +3 oxide formation and significantly lowers frequency dispersion while increasing device drive current in MOSFET C-V measurements.\textsuperscript{12}

Si based interface control layers have also been investigated on GaAs(100) based MOSFET devices by PVD and PECVD techniques. Physical vapor deposition (PVD) of multilayer silicon has been used to passivate GaAs(100), but this method has been shown to require a minimum thickness of 1.5 nm in order to effectively passivate the III-V surface and protect against oxygen diffusion to the III-V surface and the concomitant formation of high $D_{it}$ during high temperature annealing.\textsuperscript{13,14} GaAs(100) based MOSFET devices with a 1.2 nm a-silicon passivation layer deposited by ex-situ plasma enhanced chemical vapor deposition (PECVD) prior to Al\textsubscript{2}O\textsubscript{3} gate oxide ALD have been fabricated and show low frequency dispersion, negligible false inversion, and high drive current as the silicon layer getters oxygen, protecting from higher III-V oxidation states.\textsuperscript{15,16}

The silicon MBE and PVD processes leave the surface terminated with unpassivated silicon atoms which have half-filled dangling bonds which pin the Fermi level and readily react with trace gasses such as H\textsubscript{2}O. Chemical vapor deposition (CVD) processes expose the substrate to one or more gaseous precursors in order to grow conformal thin films at a given temperature. CVD growth is usually not limited to a single atomic layer, as heterogeneous and homogeneous surface reactions may occur. In an atomic layer deposition (ALD) process, precursors and growth temperature are chosen
to inhibit gas phase reactions and to limit chemical reactivity to heterogeneous surface species. An ALD reaction always employs two precursors, one an oxidant and one a reductant, which are dosed in separate “half reactions” to avoid homogeneous reactions. Surface dangling bonds are terminated at each ALD half-cycle reaction; since one reactant is an oxidant while the other is a reductant, each heterogeneous half-cycle is self-limiting. At the end of the ALD process, the surface is terminated with one of the ALD precursors and usually no dangling bonds. Consequently, ALD allows deposition of silicon with dangling bonds already passivated by ALD precursor ligands thereby providing chemical passivation.

Commercial ALD flow-type reactors operate at 0.75 - 7.5 torr where one ALD cycle consists of a pulse of the first ALD precursor, followed by an inert gas purge to remove traces of unreacted precursor and gaseous byproducts, followed by a pulse of the second ALD precursor and a subsequent inert gas purge. Many surface science reports include self-limiting and saturating atomic layer deposition half-cycle reactions in a high vacuum (base pressure <10^-3 torr), or ultra-high vacuum environment (base pressure <~10^-9 torr) and will be referred to here as HV-ALD or UHV-ALD. The high/ultra-high vacuum environment aides in protecting the substrate and deposited thin films from unwanted contaminants which may be more prevalent in higher base pressure systems. In HV-ALD or UHV-ALD, the inert gas purge steps are usually replaced by simple vacuum purge steps. Previously, a silicon HV-ALD growth process was reported on SiO2 using alternate pulses of Si2H6 and SiCl4 at substrate temperatures of 355-385°C, and each ALD cycle required several minutes as formation of the HCl(g) byproduct is slow below 400°C. Silicon UHV-ALD was reported on Ge substrates by alternating
pulses of Si₂Cl₆ and atomic hydrogen or by alternating pulses of SiH₂Cl₂ and SiH₄ at substrate temperatures of 400° - 560°C.¹⁹,²⁰ Silicon UHV-ALD processes on Si substrates have been reported with alternating pulses of SiH₂Cl₂ and atomic hydrogen or by alternating pulses Si₂H₆ and Si₂Cl₆, at substrate temperatures (400° - 560°C).²¹,²² These HV/UHV-ALD processes employ high substrate temperatures which probably desorb the passivating ligand and may cause changes in substrate reconstruction or composition for InGaAs and related materials.²³

In this report, a self-limiting and saturating HV-CVD process using a single silicon ALD precursor (Si₃H₈) at a low substrate temperature of 250°C is compared with a second self-limiting and saturating HV-CVD growth process employing the silicon precursor, Si₂Cl₆, at a substrate temperature of 350°C. The Si₃H₈ process results in depositing a saturated thin silicon hydride capping layer (approximately 4 monolayers) on the InGaAs(001)-(2x4) surface and leaving the surface Fermi level unpinned and ready for subsequent atomic layer deposition (ALD) deposition of the gate oxide. Once the Si-H groups passivate substrate dangling bonds, saturation occurs because H₂ desorption from silicon dihydride is slow at 250°C and H₂ desorption from silicon monohydride species does not occur below 445°C.²⁴ The Si₂Cl₆ self limiting CVD process results in a thin saturated silicon bilayer deposited on the InGaAs(001)-(2x4) surface and the InGaAs surface is left terminated with Si-Cl groups. Atomic hydrogen produced by a thermal gas cracker is subsequently dosed at 350°C to quickly remove the Si-Cl termination by replacing with Si-H termination through a ligand exchange reaction resulting in the HCl(g) desorption byproduct. This process also leaves the surface Fermi level unpinned and ready for subsequent surface functionalization with an oxidant or
further silicon multilayer growth by ALD. As far as we know, this is the first report of epitaxial deposition of 2-4 layers of silicon with hydrogen termination by self-limiting CVD; the process is inherently self-limiting because it takes advantage of the low desorption temperature of hydrogen and chlorine from InGaAs relative to silicon.

2.3 Experimental

This study employs n-type (Si dopant) and p-type (Be dopant) samples consisting of 0.2 μm of 1-2x10^{18} doped In_{0.53}Ga_{0.47}As layers grown by MBE on commercially available InP substrates. The samples were capped with a 50 nm As^2 layer and shipped/stored under vacuum prior to being loaded into the Omicron ultrahigh vacuum (UHV) preparation chamber with a base pressure of 1x10^{-10} Torr. In the preparation chamber, the samples were degassed at 250°C for 30 minutes and, subsequently, decapped and annealed for one hour by radiatively heating at 360-370°C to obtain the InGaAs(001)-(2x4) surface reconstruction.

Following annealing, the samples were characterized by an Omicron in situ monochromatic XPS using the aluminum Kα excitation source (hv=1486.7 eV) with spectra taken at a glancing angle of 30° to obtain enhanced surface sensitivity. XPS raw counts were collected using the XPS constant analyzer energy mode with a pass energy of 50eV and line width of 0.1 eV. XPS peak shape analysis was conducted using CASA XPS v.2.3 by employing a Shirley background subtraction. All XPS raw core level peaks were corrected by Schofield photoionization cross sectional relative sensitivity factors. Oxygen contamination was monitored over the course of the experiments by XPS and percentages were calculated by dividing the O 1s corrected peak area by the sum of the
As 2p, Ga 2p, and In 3d, and Si 2p corrected peak areas. For the Si$_3$H$_8$ process, the percent O was below the XPS detection limit and for the Si$_2$Cl$_6$ process, the percent O was <5% [see supplemental material]. Carbon contamination for both processes was below the XPS detection limit. Following XPS elemental analysis of the surface, the samples were transferred to the SPM analysis chamber which has a base pressure of 2x10$^{-11}$ Torr. In the SPM chamber, scanning tunneling microscopy (STM) was performed at 300 K to determine the atomic order of the surface by using constant current mode with the tunneling current set point at 0.1 nA and the sample bias set to -3 V for filled state imaging. Scanning tunneling spectroscopy (STS) was performed to determine the electrical quality of the surface and probe the local surface density of states using variable-z mode with the sample bias swept from -1.5 to +1.5 V and the tip simultaneously moving towards and then away from the surface. An applied $\Delta z$ initial offset ranging from -0.2 to -0.8 nm was used in order to maximize $I(V)$ signal without crashing the STM tip. The $dI/dV$ spectra were recorded using a lock-in amplifier and STS curves are reported by averaging 10-12 single curves taken across the sample surface.

After initial characterization, the samples were transferred back to the preparation chamber and radiatively heated to 250°C or 350°C for 15 minutes while simultaneously the high vacuum ALD chamber manipulator was also heated to 250°C or 350°C for 15 minutes to facilitate a faster sample transfer. Prior to sample transfer to the HV-ALD chamber, Si$_3$H$_8$ or Si$_2$Cl$_6$ were prepulsed in the ALD dosing chamber to coat the chamber walls with precursor prior to sample transfer. This preheating and prepulsing procedure was done before every dose of Si$_3$H$_8$ or Si$_2$Cl$_6$. 
Both processes are referred to as CVD processes because the InGaAs substrate undergoes some surface induced etching by hydrogen or chlorine dissociated ligands from Si$_3$H$_8$ or Si$_2$Cl$_6$, keeping these processes from classification as true ALD.$^{26,27}$ The HV-CVD processes include the substrate in the HV-ALD chamber (base pressure <2x10$^{-7}$ Torr) undergoing exposure to Si$_3$H$_8$ or Si$_2$Cl$_6$ at 250°C or 350°C with the exposure measured in Langmuirs (1x10$^{-6}$ Torr/1 second) by a convectron gauge located adjacent to the HV-ALD chamber. The HV-CVD process transfers well into a commercial ALD tool as demonstrated in the Beneq TFS-200 continuous flow reactor where MOSCAP fabrication employing the Si$_2$Cl$_6$ based passivation process was demonstrated [see supplemental material]. For the saturating Si$_3$H$_8$ based process, the sample was transferred into the HV-ALD dosing chamber and 13 MegaLangmuir Si$_3$H$_8$ was dosed at 250°C. Following Si$_3$H$_8$ dosing, the sample was transferred back to the preparation chamber where XPS was performed. Following an initial 13 MegaLangmuir Si$_3$H$_8$ dose, the sample was exposed to a series of additional doses at 250°C to increase the integrated dose to 50, 100, and 300 MegaLangmuir of Si$_3$H$_8$. The 13, 50, and 100 MegaLangmuir total Si$_3$H$_8$ doses consisted of 10 second pulses of 7.5 x 10$^{-2}$ Torr and the 300 MegaLangmuir total dose (additional 200 MegaLangmuir) consisting of 10 second pulses of 1x10$^{-1}$ Torr. After each dose, the sample was transferred to the preparation chamber for XPS studies. After the 300 MegaLangmuir dose, the sample was transferred to the SPM chamber for STM and STS. Following STM and STS of the complete 300 MegaLangmuir dosed surface, the sample was subsequently annealed to 450°C for 30 minutes at a heating rate of 2 K/s. During annealing, a mass spectroscopy measurement was taken with a quadropole mass spectrometer equipped with an RGA detector located
in the preparation chamber (SRS RGA 100). The RGA detector was operated in histogram mode to examine the partial pressure versus mass of detected gas species by sweeping across 0-70 amu. STS was performed to determine any effect on the surface Fermi level position following high temperature annealing. Mass Spectroscopy shows 2x higher presence of H2 species (m=2 amu) seen during the 30 minute 450°C anneal [see supplemental material].

For the self-limiting and saturating CVD growth process with Si2Cl6, the sample was transferred into the ALD dosing chamber and 3 MegaLangmuir Si2Cl6 was dosed at 350°C. Following the initial 3 MegaLangmuir Si2Cl6 dose, the sample was exposed to a series of additional doses at 350°C to increase the integrated dose to 12, and 21 MegaLangmuir of Si2Cl6. After each Si2Cl6 dose, the sample was transferred back to the preparation chamber where XPS was performed. The 3, 12, and 21 MegaLangmuir total Si2Cl6 doses consist of 10 second pulses of 2.5 x 10^{-2} Torr. After the complete 21 MegaLangmuir dose, the sample was dosed with 500 Langmuirs of atomic hydrogen in order to remove the surface chlorine termination by replacing with hydrogen termination through a ligand exchange reaction creating an HCl(g) byproduct. An Oxford Applied Research TC-50 thermal gas cracker was employed to produce atomic hydrogen and was operated at 65 Watts, producing atomic hydrogen at 50% efficiency. The 500 Langmuir dose consists of H2(g) flowed for 8 minutes and 20 seconds at an H2 pressure of 1x10^{-6} Torr; note the calculated Langmuirs does not include the H cracking fraction since this could not be experimentally verified so the reported atomic H Langmuirs are an upper limit.
The Density-Functional Theory (DFT) simulations were performed using VASP plane-wave DFT simulation package with projector augmented-wave (PAW) pseudopotentials\textsuperscript{28-33} and PBE exchange-correlation functional.\textsuperscript{34} The InGaAs was a regular polymorph with 50% Ga and 50% In. Initially, the InGaAs unitcell was optimized at variable volume to avoid internal compression/strain. The optimized unitcell was later used to build the InGaAs supercell and initial slabs with desired surfaces. All slab relaxations were performed using conjugate-gradient relaxation algorithm with a force tolerance level of 0.05 eV/Å and Gamma-centered 5x7x1 K-point grid. During relaxations the 3 bottom layers of InGaAs slabs were permanently fixed in their bulk-like positions and saturated with pseudo-H atoms with 1.25 |e| charge to simulate continuous bulk. The Si atoms at upper surfaces were passivated by normal 1.0 |e| H atoms. To avoid possible dipoles, dipole correction in vertical Z direction was applied.

\textbf{2.4 Results and Discussion}

\textbf{2.4.1 XPS of Si}_3\text{H}_8 \text{ saturation on InGaAs(001)-(2x4)}

Figure 2.1(a) shows the raw XPS peak areas for Ga 3p and Si 2p peaks on the clean (2x4) surface, and following 13, 50, 100, and 300 MegaLangmuir Si\textsubscript{3}H\textsubscript{8} doses. The Ga 3p spin orbit split peaks are located at binding energies 104.4 eV and 107.9 eV, and the Si 2p peak is located at a binding energy of 99.5 eV. With each additional dose, the Si 2p peak area increases and the substrate Ga 3p peak decreases, indicative of increasingly higher surface coverage of SiH\textsubscript{x} groups. Figure 2.1(b) shows the corrected XPS peak areas for the clean n-type InGaAs(001)-(2x4) surface, and following 13, 50,
100, and 300 MegaLangmuir Si$_3$H$_8$ doses. In 3d, Ga 2p, and As 2p higher binding energy peaks were chosen in order to analyze the top most monolayers of the surface. The corrected peak area of In 3d is about three times higher than Ga 2p and As 2p corrected peak areas on the clean decapped surface consistent with the In 3d having a binding energy less than half the binding energy of Ga 2p and As 2p (therefore a greater probe depth), as well as the reported phenomenon that indium segregates to the top most surface layers of InGaAs(001) alloys.$^{35-37}$ The decrease in the In 3d, Ga 2p, and As 2p substrate peaks with an increase in silicon coverage is consistent with a uniform surface coverage of silicon. The Si 2p corrected peak area following the 13 MegaLangmuir Si$_3$H$_8$ dose is half that of the total In, Ga, and As combined substrate peak areas. The total 300 MegaLangmuir Si$_3$H$_8$ dose is 23 times the initial 13 MegaLangmuir dose yet the increase in silicon coverage is only 2.7. The XPS data is consistent with a self-limiting CVD growth process.

To further quantify the saturation, Fig. 2.1 (c) shows change in silicon coverage versus Si$_3$H$_8$ dose for 13, 50, 100, and 300 MegaLangmuir total doses on n-type InGaAs(001)-(2x4) at 250°C. The change in silicon coverage was calculated for each Si$_3$H$_8$ dose by dividing the increase in corrected Si 2p peak area by the increase in dose. The thickness of the deposited silicon capping layer can be calculated from the equation $\ln(I/I_o) = -t/\lambda$, where I is the sum of the intensity of the In 3d, Ga 2p, and As 2p peaks following each Si$_3$H$_8$ dose, $I_o$ is the sum of the intensity of the In 3d, Ga 2p, and As 2p peaks on the clean InGaAs(001)-(2x4) surface, t is the thickness of the deposited silicon layer, and $\lambda$ is the inelastic mean free path of the collected electrons of the InGaAs substrate (1 nm). Using this equation, the total 300 MegaLangmuir Si$_3$H$_8$ dose saturates
at about 4.5 monolayers of silicon coverage with hydrogen termination. The calculated silicon thickness closely corresponds with the ratios shown in Fig. 2.1 (d).

2.4.2 STM/STS of Si$_3$H$_8$ saturation on InGaAs(001)-(2x4)

Figure 2.2 (a) shows a filled state STM image of the clean InGaAs(001)-(2x4) surface and 2.2 (b) shows 300 MegaLangmuir Si$_3$H$_8$ dosed on the p-type InGaAs(001)-(2x4) surface at 250°C with no further annealing. Vertical ordering along the same direction as the underlying substrate arsenic dimer (2x4) rows is observed in regions across the STM image. Five line traces are taken across these ordered regions (Fig. 2.2 (c)). Spacing between ordered rows is nearly identical to the clean (2x4) surface with average spacing at 1.5±0.26 nm consistent with III-V dangling bond elimination through silicon bonding in a commensurate structure with the substrate in regions across the surface. Line traces were measured across the surface as shown in fig. 2.2 (d); surface features vary in height by one atomic step (~2.3±0.2 Å standard error) showing high surface uniformity. Previous STM studies of MBE silicon growth on the GaAs(001)-(2x4) surface show silicon absorbs in localized heteroepitaxial ordered structures across the (2x4) surface with several surface reconstructions present, consistent with our finding of local surface epitaxy. As shown in previous work, epitaxial growth of silicon on the In$_{0.53}$Ga$_{0.47}$As surface is not required for surface passivation and improving MOSFET device performance. This self-limiting CVD process using Si$_3$H$_8$ results in local surface epitaxy as shown with both STM and XPS measurements, as the Si 2p peak shows resolved spin-orbit splitting [see supplemental].
Figure 2.2 (e) shows the STS measurements probing the local surface density of states of the n-type decapped InGaAs(001)-(2x4) surface before and after a saturated 300 MegaLangmuir Si$_3$H$_8$ dose at 250°C. It has previously been shown that InGaAs(001)-(2x4) based MOSFETs exhibit good Fermi level modulation characteristics, indicating the InGaAs(001)-(2x4) surface Fermi level is unpinned. The conduction and valence band edges align with that of the clean surface showing a saturation Si$_3$H$_8$ dose at 250°C leaves the surface Fermi level unpinned. Figure 2.2 (e) also shows subsequently annealing the saturated 300 MegaLangmuir Si$_3$H$_8$ on n-type InGaAs(001)-(2x4) surface to 450°C for 30 minutes causes the surface Fermi level to shift towards mid-gap, indicative of surface dangling bonds created by desorption of H$_2$ (g) from silicon due to the high temperature annealing. Similar results are seen on the p-type InGaAs(001)-(2x4) surface showing the surface Fermi level also remains unpinned and p-type following a saturation 300 MegaLangmuir Si$_3$H$_8$ dose at 250°C [Figure 2.2 (f)]. Desorption limited CVD growth occurs at 250°C, where the presence of any available clean InGaAs surface sites provide a path for H$_2$ recombinative desorption to occur and further silicon multilayer growth to continue slowly until saturation is found at about 4.5 monolayers of silicon with hydrogen termination. Si-H$_3$ is the least stable hydride species with desorption on a silicon terminated surface occurring at 225°C, leaving Si-H$_2$ and Si-H groups deposited on the surface which are stable up to 330°C. H$_2$ desorption is close to zero at 250°C on a silicon terminated surface consistent with the surface being saturated with Si-H$_2$ and Si-H species after all clean InGaAs surface sites have reacted with silicon. The H$_2$ desorption peak from arsenic-rich surface reconstructions of GaAs(001) starts at 225°C. The 300 MegaLangmuir total Si$_3$H$_8$ dose (additional 200
MegaLangmuir $\text{Si}_2\text{H}_8$ following the total 100 MegaLangmuir $\text{Si}_2\text{H}_8$ dose) takes over half an hour to complete at the indicated dosing pressure. This lengthy dose time assists in the slow $\text{H}_2$ desorption from remaining clean InGaAs surface sites, and from neighboring Si-H$_2$ sites, where H$_2$ recombinatively desorbs at low temperatures until nearly complete surface saturation with Si-H and Si-H$_2$ species is reached.$^{24}$

### 2.4.3 XPS of $\text{Si}_2\text{Cl}_6$ saturation on InGaAs(001)-(2x4)

Figure 2.3 (a) shows the raw XPS peak areas for Ga 3p and Si 2p peaks on the clean (2x4) surface, and following 3, 12, and 21 MegaLangmuir $\text{Si}_2\text{Cl}_6$ doses. The Ga 3p spin orbit split peaks are located at binding energies 104.4 eV and 108.2 eV, the Si 2p spin orbit split peaks is located at binding energy 99.8 eV. The Si 2p spin orbit split peaks are well resolved for 12 and 21 MegaLangmuir $\text{Si}_2\text{Cl}_6$ total doses and a new Si 2p chemical state is seen at a higher binding energy (100.5-101 eV) indicative of Si-Cl$_x$ bonding or Si-O$_x$ bonding from the small amount of oxygen contamination seen over the course of the experiment [see supplemental material].$^{42,43}$ With each additional dose, the Si 2p peak area increases and the substrate Ga 3p peak decreases, indicative of increasingly higher surface coverage of silicon until the surface reaches saturation and is left terminated by chlorine. Figure 2.3 (b) shows the surface composition from XPS for the clean n-type InGaAs(001)-(2x4) surface, and following 3, 12, and 21 MegaLangmuir $\text{Si}_2\text{Cl}_6$ doses. In 3d, Ga 2p, and As 2p higher binding energy peaks are chosen in order to analyze the top most monolayers of the surface. Note the decrease in the In 3d, Ga 2p, and As 2p substrate peaks with a concurrent increase in silicon coverage consistent with a uniform surface coverage of silicon. The Si 2p peak area following the 3 MegaLangmuir
Si$_2$Cl$_6$ dose is about 5/6 that of the total In, Ga, and As combined substrate peak areas.

The total 21 MegaLangmuir Si$_2$Cl$_6$ dose is 7 times the initial 3 MegaLangmuir dose yet the increase in silicon coverage is only 1.87. The XPS data is consistent with a self-limiting CVD growth process. The XPS data in Figure 2.3 (b) shows that the chlorine signal is negligible following the initial Si$_2$Cl$_6$ dose but is more prominent following the 12 and 21 MegaLangmuir doses consistent with excess surface gallium and indium being preferentially etched by chlorine following the initial 3 MegaLangmuir Si$_2$Cl$_6$ dose. It is hypothesized that once excess surface gallium and indium has been etched and all clean In, Ga, and As surface sites have reacted with Si-Cl$_x$ groups, the surface becomes saturated by chlorine termination as shown following the total 21 MegaLangmuir Si$_2$Cl$_6$ dose. Chlorine desorption from silicon is close to zero at 350°C.

Fig. 2.3 (c) shows change in silicon coverage versus Si$_2$Cl$_6$ dose for 3, 12, and 21 MegaLangmuir total doses on n-type InGaAs(001)-(2x4) at 350°C as well as an additional 500 Langmuir atomic hydrogen dosed at 350°C following the total 21 MegaLangmuir Si$_2$Cl$_6$ dose at 350°C. The change in silicon coverage is calculated for each Si$_2$Cl$_6$ dose by dividing the increase in corrected Si 2p peak area by the increase in dose. Self-limiting and saturating coverage of silicon on the InGaAs(001)-(2x4) surface is seen following the saturated 21 MegaLangmuir Si$_2$Cl$_6$ dose as no further increase in the rate of silicon coverage is observed. Similar results are seen on the p-type InGaAs(001)-(2x4) surface. Figure 2.3(d) shows the Si/(In+Ga+As) XPS peak area ratios for clean n-type (2x4), 3 MegaLangmuir, 12 MegaLangmuir, and 21 MegaLangmuir total Si$_2$Cl$_6$ doses at 350°C before and after an additional 500 Langmuir atomic hydrogen dose at 350°C. The ratios shown in Fig. 2.3 (d) correspond with the thickness of the deposited
silicon capping layer, which was calculated from the equation \( \ln(I/I_o) = -t/\lambda \), where \( I \) is the sum of the intensity of the In 3d, Ga 2p, and As 2p peaks following each \( \text{Si}_2\text{Cl}_6 \) dose, \( I_o \) is the sum of the intensity of the In 3d, Ga 2p, and As 2p peaks on the clean InGaAs(001)-(2x4) surface, \( t \) is the thickness of the deposited silicon layer, and \( \lambda \) is the inelastic mean free path of the collected electrons of the InGaAs substrate (1 nm). Using this equation, the total 21 MegaLangmuir \( \text{Si}_2\text{Cl}_6 \) dose saturates at about 2.5 monolayers of silicon coverage.

### 2.4.4 STM/STS of \( \text{Si}_2\text{Cl}_6 \) saturation on InGaAs(001)-(2x4)

Figure 2.4 (a) and (b) shows filled state STM images of 21 MegaLangmuir \( \text{Si}_2\text{Cl}_6 \) dosed on the n-type InGaAs(001)-(2x4) surface at 350°C followed by 500 Langmuir atomic hydrogen dosed at 350°C with no further annealing. Vertical ordering along the same direction as the underlying substrate arsenic dimer (2x4) rows is observed on regions of the surface and four line traces are taken across these ordered regions (Fig. 2.4 (c)). The spacing between rows is nearly identical to the clean (2x4) surface with average spacing at 1.6±0.1 nm consistent with III-V dangling bond elimination through silicon bonding locally in a commensurate structure. Line traces were measured across the surface as shown in Fig. 2.4 (d); surface features vary in height by one atomic step (~2.4 ± 0.1 Å), showing high surface uniformity.

Figure 2.4 (e) shows the STS measurements of the n-type decapped InGaAs(001)-(2x4) surface before and after saturation \( \text{Si}_2\text{Cl}_6 \) dosing followed by 500 Langmuir atomic hydrogen, and 4 additional 9 MegaLangmuir \( \text{Si}_2\text{Cl}_6 \) + 500 Langmuir of atomic H ALD cycles all dosed at 350°C. The conduction and valence band edges align with that of the
clean surface showing a saturation Si$_2$Cl$_6$ dose followed by atomic hydrogen dose at 350°C leaves the surface Fermi level unpinned. Similar results are seen on the p-type InGaAs(001)-(2x4) surface showing the surface Fermi level also remains unpinned and p-type following saturation Si$_2$Cl$_6$ dosing, 500 Langmuir atomic hydrogen, and following an additional 4 Si$_2$Cl$_6$ + atomic H ALD cycles all dosed at 350°C [Figure 2.4 (f)].

2.4.5 DFT Simulations

DFT simulations of the initial stages of silicon hydride passivation of the InGaAs(001)-(2x4) surface are shown in Fig. 2.5. Fig. 2.5 (a) and (b) shows partial coverage (less than 1 monolayer) of Si-H$_2$ groups bonding to surface arsenics. Fig. 2.5 (c) and (d) shows full monolayer coverage of Si-H and Si-H$_2$ groups on the InGaAs surface containing As bulk-like termination with surface arsenics bonding to a mixture of Si-H and Si-H$_2$ groups. As seen in XPS results for the Si$_2$Cl$_6$ based process, the InGaAs surface is increasingly arsenic rich with each increasing dose of Si$_2$Cl$_6$. Following the initial 3 MegaLangmuir Si$_2$Cl$_6$ dose, the As 2p peak becomes asymmetric due to the formation of As-Si bonds, leading to a chemical shift of As 2p to a higher binding energy [see supplemental material]. The passivation model shown in Fig. 2.5 (e) and (f) contains a topmost InGaAs surface layer comprised of ½ arsenic and ½ indium/gallium atoms bonding to Si-H, consistent with the XPS data from the Si$_3$H$_8$ based process showing nearly equivalent amounts of gallium and arsenic on the surface. Following the initial 13 MegaLangmuir Si$_3$H$_8$ dose, the As 2p and Ga 2p peaks become asymmetric due to the formation of As-Si and Ga-Si bonds, leading to a chemical shift of As 2p to a higher binding energy and a chemical shift of Ga 2p to a slightly lower binding energy [see
supplemental material]. All initial DFT calculations of the silicon hydride passivation of the InGaAs(001)-(2x4) surface shown in Fig. 2.5 are in agreement with the STS results showing the surface Fermi level remaining unpinned.

M.D. Pashley described the electron counting model applied to the (In)GaAs(001)-(2x4) reconstructed surface which stated surface bonding conditions necessary to maintain no net surface charge, a condition essential to creating an unpinned surface Fermi level.45 L. Lin and J. Robertson employ this electron counting rule model to create surface interfacial passivating layers on reconstructed semiconductor surfaces by maintaining no net charge for each successive layer of growth.5 The electron counting rule model has been applied to all DFT models shown in Fig. 2.5 with number of valence electrons for indium/gallium, arsenic, silicon, and hydrogen are 3, 5, 4, and 1. For the partial coverage model shown in Fig. 2.5 (a), the sp² hybridized indium/gallium surface atoms accommodate the charge deficiency found on each of the sp³ hybridized arsenic surface atoms. The full monolayer coverage model shown in Fig. 2.5 (c) is comprised of all sp³ hybridized atoms. Here each surface arsenic bonds to 1 Si-H group (containing 1 filled dangling bond) and 1 Si-H₂ group, leaving the overall unit cell charge balanced. The full coverage model shown in Fig. 2.5 (e) contains 4 sp² hybridized Si-H groups which contain excess electrons to balance the charge deficiency on the sp³ hybridized surface indium/gallium and arsenic atoms leaving the unit cell charge neutral.

2.5 Conclusions
Deposition of a thin silicon hydride capping layer on InGaAs(001)-(2x4) has been achieved via two separate self-limiting CVD processes as shown by XPS. The 250°C
Si$_3$H$_8$ process only requires the use of a single ALD precursor, Si$_3$H$_8$, with self-limiting growth of 4.5 monolayers of Si-H coverage achieved at a very low temperature. The Si$_2$Cl$_6$ 350°C process produces a thinner Si-H capping layer (2.5 monolayers) and allows for multilayer silicon growth by ALD through cyclically dosing Si$_2$Cl$_6$ and atomic hydrogen. STM and STS measurements show both self-limiting CVD processes on InGaAs(001)-(2x4) produce an atomically locally ordered and electrically passivated surface, with the surface Fermi level ($E_F$) shifting from the valence to the conduction band for p-type vs. n-type samples consistent with an unpinned $E_F$. Initial DFT calculations show the InGaAs(001)-(2x4) surface is electronically passivated by Si-H$_x$ groups via the satisfaction of the electron counting rule for a charge neutral interface. The calculated local density of states are in agreement with the experimental STS measurements showing the surface Fermi level remains unpinned, and the passivating silicon hydride control capping layer is ready for ALD gate oxide nucleation. Initial MOSCAP fabrication results also show the insertion of a silicon passivation layer by dosing Si$_2$Cl$_6$ on the InGaAs(001) surface prior to the deposition of Al$_2$O$_3$ leads to lower frequency dispersion, higher $C_{\text{max}}$, and a smaller false inversion indicative of lower $D_{\text{it}}$ at midgap.$^{46}$ The initial device results show the deposited silicon layer with hydrogen termination seeds high-K gate oxide nucleation, and improves device performance.

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 Journal

### 2.7 Supplemental Materials

Figure 2.6 shows mass spectroscopy results taken (a) directly before and (b) during a 30 minute 450°C anneal of the saturated 300 MegaLangmuir Si$_3$H$_8$ dosed n-type InGaAs (001)-(2x4) surface. Note the 20x higher presence of H$_2$ species (m=2 amu) during the anneal indicative of H$_2$ desorption from the surface, creating dangling bonds on silicon. Figure 2.7 shows the raw XPS peaks for As 2p, Ga 2p, In 3d, Ga 3p and Si 2p on clean InGaAs(2x4), and following 13, 50, 100, and 300 MegaLangmuir total Si$_3$H$_8$ doses at 250°C. Silicon chemically shifts As 2p, Ga 2p, and In 3d to slightly higher binding energies. The Si 2p peak shows the deconvolution of Si 2p$^{1/2}$ and Si 2p$^{3/2}$ spin orbit split peaks. Figure 2.8 shows the raw XPS peak areas fitted for C 1s and O 1s (Figure 2.8 (a)), As 2p (Figure 2.8 (b)), and Ga 2p (Figure 2.8 (c)) peaks on clean InGaAs(2x4), and following 13, 50, 100, and 300 MegaLangmuir total Si$_3$H$_8$ doses at 250°C. The carbon and oxygen are below XPS detection limits. The As 2p peak is shown following 13 MegaLangmuir total Si$_3$H$_8$ doses at 250°C showing the bulk As-In/Ga chemical state and the As-Si chemical state shifted to slightly higher binding energy. The Ga 2p peak is shown following 13 MegaLangmuir total Si$_3$H$_8$ doses at
250°C showing the bulk Ga-As chemical state and the Ga-Si chemical state shifted to slightly lower binding energy.

Figure 2.9 contains the raw XPS peak areas for As 2p, Ga 2p, In 3d, Ga 3p, Si 2p, As 3s, and Cl 2p on clean InGaAs(2x4), and following 3, 12, and 21 MegaLangmuir total Si₂Cl₆ doses at 350°C, and following a 500 Langmuir atomic hydrogen dose at 350°C. Silicon chemically shifts As 2p, Ga 2p, In 3d, and As 3s to slightly higher binding energies. The atomic hydrogen pulse removes the chlorine termination on silicon and replaces with atomic hydrogen. The Si 2p peak shows the deconvolution of Si 2p⁴/² and Si 2p³/² spin orbit split peaks and a chemical state shifted to higher binding energy from silicon bonding to chlorine or some surface oxygen. Also note the Si 2p peak shifts to lower binding energy following the atomic hydrogen dose. Figure 2.10 shows the raw XPS peak areas fitted for C 1s and O 1s (Figure 2.10 (a)), As 2p (Figure 2.10 (b)), and Ga 2p (Figure 2.10 (c)) peaks on clean InGaAs(2x4), and following 3, 12, and 21 MegaLangmuir total Si₂Cl₆ doses at 350°C, and following a 500 Langmuir atomic hydrogen dose at 350°C. The carbon content is below the XPS detection limits while the oxygen content remains below 5%. Oxygen content is calculated by dividing the O 1s corrected peak area by the addition of the In 3d, Ga 2p, As 2p, and Si 2p corrected peak areas and multiplying by 100 to get a percentage. The As 2p peak is shown following 3 MegaLangmuir total Si₂Cl₆ doses at 350°C showing the bulk As-In/Ga chemical state and the As-Si chemical state shifted to slightly higher binding energy. The Ga 2p peak is shown following 3 MegaLangmuir total Si₂Cl₆ doses at 350°C showing the bulk Ga-As chemical state and no Ga-Si chemical state detected.
Figure 2.11 shows the results of MOSCAP fabrication on the wet cleaned InGaAs(001) surface with and without the insertion of an Si$_2$Cl$_6$ deposited interfacial control layer in the commercial Beneq TFS-200 Continuous Flow ALD reactor. Figure 2.11 (a) shows InGaAs(001) sample cleaned by 3 min dip in 6:1 buffered oxide etchant (BOE) followed by 10 seconds of water rinse. After drying the sample by N$_2$ gas, it was transferred to the ALD reactor with minimal air exposure. Afterwards, 20 cycles of 45 ms TMA pre-pulses and 60 cycles of 200 ms TMA and 50 ms H$_2$O were applied in order to deposit Al$_2$O$_3$ with approximately 6.0 nm physical thickness. After Al$_2$O$_3$ ALD, Ni gate metals and Al back contacts were deposited using thermal evaporation and DC sputtering, respectively. Figure 2.11 (b) shows an InGaAs(001) sample which underwent the 3 min dip in 6:1 buffered oxide etchant (BOE) followed by 10 seconds of water rinse. The sample was dried by N$_2$ gas and quickly loaded into the ALD reactor. Next 30 cycles of 100 ms long Si$_2$Cl$_6$ pulses were dosed at 350°C followed by 30 s of H$_2$ remote plasma at with 50 W forward power. This exposure is equivalent to 3 MegaLangmuir total exposure of Si$_2$Cl$_6$ at 350°C which is seen to deposit ~1 monolayer of silicon coverage on InGaAs(001). Afterwards, 20 cycles of 45 ms TMA pre-pulses and 60 cycles of 200 ms TMA and 50 ms H$_2$O were dosed to deposit Al$_2$O$_3$ with approximately 6.0 nm physical thickness. After each TMA and H$_2$O pulse, a 6 s argon purge was employed. After Al$_2$O$_3$ ALD, Ni gate metals and Ni back contacts were deposited using thermal evaporation. Figure 2.11 (c) shows the MOSCAP in (a) after a 15 minute forming gas anneal (FGA) (5% H$_2$/N$_2$) at 250°C. Figure 2.11 (d) shows the MOSCAP in (b) after a 15 minute FGA (5% H$_2$/N$_2$) at 250°C. As can be seen, the MOSCAP with the silicon passivating layer deposited by Si$_2$Cl$_6$ shown in (d) contains less frequency
dispersion, higher $C_{\text{max}}$, and a smaller false inversion bump compared with the MOSCAP shown in (c) without the silicon passivating layer. C-V measurements were performed using an Agilent-B1500 semiconductor analyzer.
Figure 2.1 XPS of Si$_3$H$_8$ dosed InGaAs(001)-(2x4). XPS raw counts are corrected by Schofield photoionization cross sectional relative sensitivity factors. (a) Raw XPS peak areas for Ga 3p and Si 2p on clean InGaAs(2x4), and following 13, 50, 100, and 300 MegaLangmuir total Si$_3$H$_8$ doses at 250°C. (b) XPS corrected peak areas for 13, 50, 100, and 300 MegaLangmuir total Si$_3$H$_8$ doses at 250°C on n-type InGaAs(001)-(2x4). (c) Rate of change of silicon coverage versus total Si$_3$H$_8$ dose as calculated from XPS corrected Si 2p peak areas for 13, 50, 100, and 300 MegaLangmuir total Si$_3$H$_8$ doses at 250°C on n-type InGaAs(001)-(2x4). (d) XPS corrected peak area ratio of Si/(In+Ga+As) for clean (2x4), 13 Mega Langmuir Si$_3$H$_8$, 50 Mega Langmuir Si$_3$H$_8$, 100 Mega Langmuir Si$_3$H$_8$, and 300 Mega Langmuir Si$_3$H$_8$ total doses at 250°C. Note error bars are standard errors.
Figure 2.2 STM/STS of Si$_3$H$_8$ dosed InGaAs(001)-(2x4). (a) Large area filled state STM image of the clean decapped InGaAs(001)-(2x4) surface (b) enlarged area filled state STM images following 300 MegaLangmuir Si$_3$H$_8$ dose at 250°C on p-type InGaAs(001)-(2x4) with no further annealing. Dotted lines in (b) indicate rows in which line trace are taken across. (c) Four line traces taken across ordered regions of the surface with average row spacing at 1.5 +/- 0.26 nm. Arrows point to the atomic positions in each line trace. (d) Line traces taken across the filled state STM image shown in (b). Surface features vary in height by a maximum of one atomic step (~2.3 +/- 0.2 Å). (e) STS results of the decapped n-type InGaAs(001)-(2x4) surface, the 300 MegaLangmuir total Si$_3$H$_8$ dose at 250°C, and the 300 MegaLangmuirSi$_3$H$_8$ dosed surface following a 30 minute anneal at 450°C (average of 11 STS curves). Note the surface Fermi level shifts towards mid-gap after annealing, indicative of surface dangling bonds created by increasing the rate of desorption of H$_2$ (g) from silicon. (f) STS results of the decapped p-type InGaAs(001)-(2x4) surface before and after the 300 MegaLangmuir total Si$_3$H$_8$ dose at 250°C. The alignment of both the valence and conduction bands and the Fermi level position remains the same on both n-type and p-type surfaces following the saturation dose, indicative of surface passivation.
Figure 2.3 XPS of Si$_2$Cl$_6$ dosed InGaAs(001)-(2x4). XPS raw counts are corrected by Schofield photoionization cross sectional relative sensitivity factors. (a) Raw XPS peak areas for Ga 3p and Si 2p on clean InGaAs(2x4), and following 3, 12, and 21 MegaLangmuir total Si$_2$Cl$_6$ doses at 350°C. (b) XPS corrected peak areas for 3 MegaLangmuir Si$_2$Cl$_6$, 12 MegaLangmuir Si$_2$Cl$_6$, 21 MegaLangmuir Si$_2$Cl$_6$, and 21 MegaLangmuir Si$_2$Cl$_6$ + 500 Langmuir atomic hydrogen on n-type InGaAs(001)-(2x4). All doses done at 350°C. (c) Rate of change of silicon coverage versus total Si$_2$Cl$_6$ dose as calculated from XPS corrected Si 2p peak areas for 3, 12, and 21 MegaLangmuir total Si$_2$Cl$_6$ doses at 350°C on n-type InGaAs(001)-(2x4). (d) XPS corrected peak area ratio of Si/(In+Ga+As) for clean (2x4), and 3, 12, and 21 MegaLangmuir total Si$_2$Cl$_6$ doses at 350°C on n-type InGaAs(001)-(2x4).
Figure 2.4 STM/STS of Si$_2$Cl$_6$ dosed InGaAs(001)-(2x4). (a) Large area and (b) enlarged area filled state STM images following 21 MegaLangmuir Si$_2$Cl$_6$ dose at 350°C and 500 Langmuir atomic hydrogen dosed at 350°C on n-type InGaAs(001)-(2x4) with no further annealing. Dotted lines indicate rows in which line trace are taken across. Arrows point to atomic positions in each line trace. (c) Four line traces taken across ordered regions of the surface with average row spacing at 1.6 +/- 0.1 nm. (d) Line traces taken across the filled state STM image shown in (a). Surface features vary in height by one atomic step (~2.4 +/- 0.1 Å) showing high surface uniformity. (e) STS on n-type InGaAs: clean n-type InGaAs (2x4), 3 MegaLangmuir dose of Si$_2$Cl$_6$ at 350°C, 21 MegaLangmuir Si$_2$Cl$_6$, 500 L atomic Hydrogen, and 4 ALD cycles at 350°C (an average of 9 STS curves are shown). Each Silicon ALD cycle = 9 MegaLangmuir Si$_2$Cl$_6$ at 350°C followed by 500 Langmuir atomic H at 350°C. (f) STS on p-type InGaAs: clean n-type InGaAs (2x4), 3 MegaLangmuir dose of Si$_2$Cl$_6$ at 350°C, 21 MegaLangmuir Si$_2$Cl$_6$ and 500 Langmuir of atomic hydrogen, and an additional 4 ALD cycles at 350°C (an average of 9-13 STS curves are shown). Note the alignment of both the valence and conduction bands following the saturation dose as well as the Fermi level position remaining the same on both n-type and p-type surfaces indicative of surface passivation.
Figure 2.5 DFT simulations of SiHₓ passivation of InGaAs(001)-(2x4). (a) DFT model of partial coverage of Si-H₂ groups passivating the InGaAs(001)-(2x4) surface. (b) Calculated local density of states for the partial coverage DFT model shown in (a). Note the Fermi level remains unpinned following partial coverage passivation. (c) DFT model of full coverage of Si-H₂/Si-H groups passivating the InGaAs(001)-(2x4) surface. Note the topmost InGaAs surface is arsenic rich with one Si-H group and one Si-H₂ group bonding to each surface arsenic atom. (d) Calculated local density of states for the full coverage DFT model shown in (c). The Fermi level remains unpinned following full coverage passivation. (e) DFT model of full coverage of Si-H₂/Si-H groups passivating the InGaAs(001)-(2x4) surface. Note the topmost InGaAs surface contains ½ arsenic and ½ indium/gallium atoms bonding to Si-Hₓ groups. (f) Calculated local density of states for the full coverage DFT model shown in (e). The Fermi level remains unpinned following the passivation.
Figure 2.6 Mass Spectroscopy of Si₃H₈ dosed InGaAs(001)-(2x4). Mass Spectroscopy results taken (a) directly before and (b) during a 30 minute 450°C anneal of the saturated 300 MegaLangmuir Si₃H₈ dosed n-type InGaAs (001)-(2x4) surface. Note the 20x higher presence of H₂ species (m=2 amu) during the anneal indicative of H₂ desorption from the surface, creating dangling bonds on silicon.
Figure 2.7 XPS spectra of Si$_3$H$_8$ dosed InGaAs(001)-(2x4). Raw XPS peak areas for As 2p, Ga 2p, In 3d, Ga 3p, and Si 2p on clean InGaAs(2x4), and following 13, 50, 100, and 300 MegaLangmuir total Si$_3$H$_8$ doses at 250°C. Silicon chemically shifts As 2p, Ga 2p, and In 3d to slightly higher binding energies. The Si 2p peak shows the deconvolution of Si 2p$^{1/2}$ and Si 2p$^{3/2}$ spin orbit split peaks.
Figure 2.8 XPS of C 1s and O 1s spectra and substrate peak chemical state deconvolution of Si$_3$H$_8$ dosed InGaAs(001)-(2x4). (a) Raw XPS counts across C 1s and O 1s binding energies on clean InGaAs(2x4), and following 13, 50, 100, and 300 MegaLangmuir total Si$_3$H$_8$ doses at 250°C showing the carbon and oxygen is below XPS detection limits. (b) As 2p peak is shown following 13 MegaLangmuir total Si$_3$H$_8$ doses at 250°C showing the bulk As-In/Ga chemical state and the As-Si chemical state shifted to slightly higher binding energy. (c) Ga 2p peak is shown following 13 MegaLangmuir total Si$_3$H$_8$ doses at 250°C showing the bulk Ga-As chemical state and the Ga-Si chemical state shifted to slightly lower binding energy.
Figure 2.9 XPS spectra of Si$_2$Cl$_6$ dosed InGaAs(001)-(2x4). Raw XPS peak areas for As 2p, Ga 2p, In 3d, Ga 3p, Si 2p, As 3s, and Cl 2p on clean InGaAs(2x4), and following 3, 12, and 21 MegaLangmuir total Si$_2$Cl$_6$ doses at 350°C and following a 500 Langmuir atomic hydrogen dose at 350°C. Silicon chemically shifts As 2p, Ga 2p, In 3d, and As 3s to slightly higher binding energies. The atomic hydrogen pulse removes the chlorine termination on silicon and replaces with atomic hydrogen. The Si 2p peak shows the deconvolution of Si 2p$^{1/2}$ and Si 2p$^{3/2}$ spin orbit split peaks and a chemical state shifted to higher binding energy from silicon bonding to chlorine or some surface oxygen. Also note the Si 2p peak shifts to lower binding energy following the atomic hydrogen dose.
Figure 2.10 XPS of C 1s and O 1s spectra and substrate peak chemical state deconvolution of Si<sub>2</sub>Cl<sub>6</sub> dosed InGaAs(001)-(2x4). (a) Raw XPS counts across C 1s and O 1s binding energies on clean InGaAs(2x4), and following 3, 12, and 21 MegaLangmuir total Si<sub>2</sub>Cl<sub>6</sub> doses at 350°C and following a 500 Langmuir atomic hydrogen dose at 350°C. The carbon content is below the XPS detection limits while the oxygen content remains below 5%. Oxygen content is calculated by dividing the O 1s corrected peak area by the addition of the In 3d, Ga 2p, As 2p, and Si 2p corrected peak areas and multiplying by 100 to get a percentage. (b) As 2p peak is shown following 3 MegaLangmuir total Si<sub>2</sub>Cl<sub>6</sub> doses at 350°C showing the bulk As-In/Ga chemical state and the As-Si chemical state shifted to slightly higher binding energy. (c) Ga 2p peak is shown following 3 MegaLangmuir total Si<sub>2</sub>Cl<sub>6</sub> doses at 350°C showing the bulk Ga-As chemical state and no Ga-Si chemical state detected.
Figure 2.11 MOSCAP fabrication employing the Si$_2$Cl$_6$ passivation process on InGaAs(001) in the Beneq TFS-200 Continuous Flow ALD reactor. (a) InGaAs(001) sample cleaned by 3 min dip in 6:1 buffered oxide etchant (BOE) followed by 10 s of water rinse. After drying the sample by N$_2$ gas, it was transferred to the ALD reactor with minimal air exposure. Afterwards, 20 cycles of 45 ms TMA pre-pulses and 60 cycles of 200 ms TMA and 50 ms H$_2$O were applied in order to deposit Al$_2$O$_3$ with approximately 6.0 nm thickness. After Al$_2$O$_3$ ALD, Ni gate metals and Al back contacts were deposited using thermal evaporation and DC sputtering, respectively. (b) InGaAs(001) sample underwent the 3 min dip in 6:1 buffered oxide etchant (BOE) followed by 10 s of water rinse. The sample was dried by N$_2$ gas and quickly loaded into the ALD reactor. Next 30 cycles of 100 ms long Si$_2$Cl$_6$ pulses were dosed at 350°C followed by 30 s of H$_2$ remote plasma at with 50 W forward power. This exposure is equivalent to 3 MegaLangmuir total exposure of Si$_2$Cl$_6$ at 350°C which is seen to deposit ~1 monolayer of silicon coverage on InGaAs(001). Afterwards, 20 cycles of 45 ms TMA pre-pulses and 60 cycles of 200 ms TMA and 50 ms H$_2$O were dosed to deposit Al$_2$O$_3$ with approximately 6.0 nm physical thickness. After each TMA and H$_2$O pulse, a 6 s Ar purge was employed. After Al$_2$O$_3$ ALD, Ni gate metals and Ni back contacts were deposited using thermal evaporation. (c) The MOSCAP shown in (a) underwent a 15 minute forming gas anneal (5% H$_2$/N$_2$) at 250°C. (d) The MOSCAP shown in (b) underwent a 15 minute forming gas anneal (5% H$_2$/N$_2$) at 250°C. As can be seen, the MOSCAP with the silicon passivating layer deposited by Si$_2$Cl$_6$ shown in (d) contains less frequency dispersion, higher C$_{max}$, and a smaller false inversion bump compared with the MOSCAP shown in (c) without the silicon passivating layer.
2.8 References


Chapter 3

Self-limiting CVD of a passivating SiOₓ control layer on InGaAs(001)-(2x4) with the prevention of III-V oxidation

3.1 Abstract

A thin passivating SiOₓ control layer has been deposited via self-limiting CVD on the InGaAs(001)-(2x4) surface by first depositing 2-3 monolayers of silicon with –Clₓ termination using Si₂Cl₆, and then subsequently oxidizing the silicon seed layer by employing anhydrous HOOH(g) at a substrate temperature of 350°C. After HOOH(g) dosing, XPS spectra show a higher binding energy shoulder peak on Si2p indicative of SiOₓ bonding, while an unshifted Si 2p component remains, and In 3d, Ga 2p, and As 2p peaks show no higher binding energy components consistent with the prevention of III-V oxidation. Scanning tunneling spectroscopy (STS) measurements show after SiOₓ deposition on the InGaAs(001)-(2x4) surface, the bandgap broadens towards that of SiO₂, and the surface Fermi level remains unpinned with the electronic structure free of states in the bandgap leaving the surface ready for subsequent gate oxide ALD. Density functional theory calculations support the experimental STS data showing TMA nucleation directly on SiOₓ/InGaAs(001) leaves an electrically passive interface with the bandgap free of defect states and the surface ready for high-K gate oxide nucleation.

3.2 Introduction

InGaAs contains intrinsically high electron mobility, making it a promising candidate for replacement of silicon in the n-type channel region of metal oxide...
One of the challenges of replacing silicon by III-V materials in the channel lies in the formation of a low defect, thermodynamically stable gate high-K dielectric which can match or exceed the capacitance and interfacial properties of HfO$_2$ on silicon. For process integration, it is critical that the high-K on III-V be amorphous and compatible with conventional back-end processing which makes integration of conventional amorphous high-k materials (such HfO$_2$ and ZrO$_2$) a priority. Previous reports show III-V suboxides and excess As$_2$O$_3$ and As$_2$O$_3$ pin the surface Fermi level, and InGaAs/GaAs native oxides serve as a poor dielectric gate as the oxides are unstable and leaky. Deposition of high-K gate oxide directly on the GaAs(001) surface has produced poor capacitance-voltage characteristics such as large frequency dispersion, hysteresis, and high leakage current all of which are attributed to the formation of interfacial III-V oxides. In this report, a thin saturating silicon oxide control layer is deposited by self limiting reaction chemistry on the InGaAs(001) surface in order to eliminate III-V dangling bonds by passivating with silicon, and to create a surface interfacial silicon layer terminated with –OH and –O groups which can nucleate high-K gate oxide ALD with virtually any metal precursor while protecting the III-V surface from oxidation.

Previous work has shown that deposition of a thin passivating MBE silicon control layer on In$_{0.53}$Ga$_{0.47}$As(100) prior to Al$_2$O$_3$ gate oxide deposition improved MOSFET performance by lowering frequency dispersion, reducing hysteresis, and lowering $D_{it}$. Similarly, physical vapor deposition (PVD) of a silicon control layer (1.5 nm) on GaAs(001) effectively passivated the III-V surface and protected against oxygen diffusion to the III-V surface as well as prevented formation of high $D_{it}$ during high
temperature annealing of MOS gate stacks. These MBE and PVD methods improve the interfacial properties between the high-K gate oxide and III-V surface with nanometer scale films, but in order to continue scaling MOSFET size in a 3D topology such as a finFET and maintain an EOT below 1 nm, ALD and self-limiting CVD methods must be implemented for more precise deposition at the subnanometer range.

Silicon ALD on SiO$_2$ was reported with alternate pulses of Si$_2$H$_6$ and SiCl$_4$ at substrate temperatures of 355-385°C, and each ALD cycle required several minutes as the HCl(g) desorption byproduct formation is slow below 400°C. Silicon ALD was reported on Ge substrates by alternating pulses of Si$_2$Cl$_6$ and atomic hydrogen, or SiH$_2$Cl$_2$ and SiH$_4$, at substrate temperatures of 400° - 560°C. Silicon ALD processes on Si substrates have been reported with alternating pulses of SiH$_2$Cl$_2$ and atomic hydrogen, or Si$_2$H$_6$ and Si$_2$Cl$_6$, at substrate temperatures (400° - 560°C). These ALD processes employ high substrate temperatures which may desorb the passivating ligand and may cause changes in substrate reconstruction or composition for InGaAs and related III-V materials. Previous work reported SiO$_2$ ALD by cyclically dosing ozone and tris(dimethylamino)silane at room temperature on Si(100), plasma assisted SiO$_2$ ALD by sequentially pulsing H$_2$Si[N(C$_2$H$_5$)$_2$]$_2$ and O$_2$ plasma at 50-400°C on Si(100), and room temperature SiO$_2$ CVD on Si(100) by SiCl$_4$ and H$_2$O in the presence of a NH$_3$ catalyst. SiO$_2$ ALD has been reported on GaAs(001) at room temperature by cyclically dosing SiCl$_4$ and H$_2$O in the presence of anhydrous pyridine. The study reported the SiO$_2$ films lead to formation of higher oxidation states of both Ga and As and concurrently higher D$_{it}$ which was only eliminated after high temperature post deposition annealing at 400-600°C. In this study, a plasma-less self-limiting CVD process is developed to deposit a
thin Si-Ox control layer (8-10 Å) on the InGaAs(001)-(2x4) surface through dosing Si2Cl6 followed by anhydrous HOOH(g) at 350°C with no post deposition annealing required; the process prevents III-V substrate oxidation as determined by XPS, while maintaining an unpinned surface Fermi level as shown by STS measurements, leaving the III-V surface passivated and ready for high-K gate oxide deposition.

3.3 Experimental

This work employs n-type (Si dopant) samples consisting of 0.2 μm of 1-2x10^{18} doped In_{0.53}Ga_{0.47}As(001) layers grown by MBE on commercially available InP(001) substrates. The samples are capped with an As2 layer (50 nm) and shipped/stored under vacuum prior to introduction into the Omicron ultrahigh vacuum (UHV) preparation chamber with a base pressure of 1x10^{-10} Torr. In the preparation chamber, the samples are degassed at 250°C for 30 minutes, then decapped and annealed for one hour by radiatively heating at 360-370°C to obtain the arsenic rich InGaAs(001)-(2x4) surface reconstruction.

Following annealing, the samples are characterized by an Omicron in situ monochromatic XPS using the aluminum Kα excitation source (hv=1486.7 eV) with spectra recorded at a glancing angle of 30° to enhance surface sensitivity. XPS raw counts are recorded using the XPS constant analyzer energy mode with a pass energy of 50eV and line width of 0.1 eV. XPS peak shape analysis is conducted using CASA XPS v.2.3 with Shirley background subtraction. All XPS raw core level peaks are corrected by Schofield photoionization cross sectional relative sensitivity factors. Following XPS elemental analysis, the samples are transferred to the SPM chamber (base pressure of
2x10^{-11} \text{Torr}, where scanning tunneling microscopy (STM) is performed at 300 K to determine the atomic order of the surface by using constant current mode with the tunneling current set point at 0.1 nA and the sample bias set to -3 V for filled state imaging. Scanning tunneling spectroscopy (STS) is performed to determine the electrical quality of the surface and probe the local surface density of states using variable-z mode with the sample bias swept from -1.5 to +1.5 V and the tip simultaneously moving towards and then away from the surface. An applied Δz initial offset ranging from -0.2 to -0.8 nm is used to maximize I(V) signal without crashing the STM tip. The dI/dV spectra are recorded using a lock-in amplifier and STS curves are reported by averaging 10-12 single curves taken across the sample surface. The curves are fitted (dashed red line in reported spectra) using a method described in previous STM/STS studies to extract the measured band edge energies of the collected (dI/dV) spectra. The fit employs a linear function with slight rounding at the band gap onset due to temperature and AC modulation. Standard errors are obtained by the fitting process and reported for the averaged STS curves. The uncertainties provided by the fitting method are statistical uncertainties using least squares fitting, and the reported uncertainties are much less than thermal broadening in STS measurements.

After the initial characterization, the samples are transferred back to the preparation chamber and radiatively heated to 350°C for 15 minutes while simultaneously heating the high vacuum ALD chamber manipulator to 350°C for 15 minutes to facilitate a faster sample transfer. All doses are performed in the high vacuum ALD chamber, and exposures are measured in Langmuirs (1x10^{-6} Torr/1 second) by a convectron gauge located in the HV-ALD chamber. The SiO_x deposition process is
described as a self-limiting CVD process due to the initial InGaAs substrate surface induced etching by chlorine dissociated ligands from Si$_2$Cl$_6$, keeping the process from classification as true ALD.$^{24,25}$ Previous work describes the self-limiting deposition of silicon on InGaAs(001)-(2x4),$^{26}$ which includes the InGaAs substrate exposed to a saturation dose of Si$_2$Cl$_6$ at 350°C. In this work, the SiO$_x$ self-limiting CVD process begins with an 87.6 MegaLangmuir total Si$_2$Cl$_6$ exposure at 350°C (25 second pulses of 2.5 x 10$^{-2}$ Torr) and post XPS analysis to confirm saturation of silicon with –Cl termination on the InGaAs(001) surface.

Following saturation of Si-Cl$_x$ on the InGaAs(001)-(2x4) surface, the sample is subsequently exposed to anhydrous HOOH(g) at 350°C to induce HOCl(g) and HCl(g) desorption and leave the silicon bonded to –OH and –O groups to create the self-limiting and saturating SiO$_x$ control layer. The anhydrous HOOH(g) is delivered by Teflon tubing to the stainless steel HV-ALD chamber in order to minimize HOOH(g) decomposition. The anhydrous HOOH(g) is produced from a teflon vessel which contained a membrane and a solvent based HOOH(g) solution (developed by Rasirc, Inc). The hydrogen peroxide diffuses across a largely gas-impermeable ionic exchange membrane within the vaporizer. The solvent cannot cross the membrane, which allows HOOH(g) to pass through to the HV-ALD chamber while preventing passage of the solvent, making the delivered dose anhydrous HOOH(g). The exposure are reported here in Langmuirs assuming a 0% dissociation rate of HOOH(g). The sample is introduced to three total anhydrous HOOH(g) exposures at 350°C: 90.5 MegaLangmuir HOOH(g), followed by two additional 60 MegaLangmuir HOOH(g) exposures, where each exposure consists of 45 second pulses of 5 x 10$^{-2}$ Torr. Following each HOOH dose, the sample is transferred
back to the preparation chamber where XPS is performed. Each HOOH(g) exposure consisted of 45 second pulses of $8 \times 10^{-2}$ Torr. Following HOOH(g) dosing, the sample is heated to 250°C and TMA is introduced by dosing 50,000 L and an additional 250,000 L; TMA is dosed with 5 milliTorr continuous pulses for 10 seconds and 50 seconds.

### 3.4 DFT Computational Details

The Density-Functional Theory (DFT) simulations are performed using the VASP plane-wave DFT simulation package with PBE exchange-correlation functional and projector augmented-wave (PAW) pseudopotentials. The InGaAs slab is simulated as a regular polymorph with equal number of Ga and In atoms. Initially, the InGaAs unit cell is optimized at a variable volume to avoid internal compression/strain. This DFT-optimized unit cell is subsequently employed to build the InGaAs supercell and initial slabs with the desired surface terminations. All slab relaxations are performed using a conjugate-gradient (CG) relaxation algorithm with a force tolerance level of 0.05 eV/Å and Gamma-centered 5x7x1 K-point grid. During the relaxations the 3 bottom layers of the InGaAs slabs are permanently fixed in their bulk-like positions and saturated with pseudo-H atoms with a 1.25 |e| charge to simulate a continuous bulk. The atoms at the upper surface layers are passivated by normal 1.0 |e| H atoms. To avoid a possible dipole effect, dipole correction in vertical Z direction was applied.

### 3.5 Results and Discussion

#### 3.5.1 XPS of Si$_2$Cl$_6$, HOOH, and TMA saturation on InGaAs(00)-(2x4)
Figure 3.1 (a) shows the raw XPS peak areas for Ga 3p and Si 2p peaks on the clean (2x4) surface, and following 3, 12, and 21 MegaLangmuir Si₂Cl₆ doses. The Ga 3p spin orbit split peaks are located at binding energies 104.4 eV and 108.2 eV, the Si 2p spin orbit split peaks are located at binding energy 99.8 eV. The Si 2p 1/2 and 3/2 spin orbit split peaks are resolved for 12 and 21 MegaLangmuir Si₂Cl₆ total doses and a new Si 2p chemical state is seen at higher binding energy 100.5-101 eV indicative of Si-Clₓ/Si-Oₓ bonding with oxygen presence seen from a small amount of oxygen contamination over the course of the experiment [see supplemental material]. Each additional dose increases the Si 2p peak area and decreases the substrate Ga 3p peak areas, indicative of increasingly higher silicon coverage until surface saturation is reached and the surface silicon left terminated by chlorine.

Figure 3.1 (b) shows the surface elemental composition from XPS for the clean n-type InGaAs(001)-(2x4) surface, and following 3, 12, and 21 MegaLangmuir Si₂Cl₆ doses. In 3d, Ga 2p, and As 2p higher binding energy peaks are chosen in order to analyze the top most monolayers of the surface. 21 MegaLangmuir Si₂Cl₆ is 7 times the initial 3 MegaLangmuir dose, yet the increase in Si 2p corrected peak area is only 1.87X. The XPS data is consistent with a self-limiting CVD growth process. The XPS data is consistent with a self-limiting CVD growth process. Figure 3.1 (b) shows the chlorine signal is negligible following the initial Si₂Cl₆ dose but is more prominent following the 12 and 21 MegaLangmuir doses consistent with excess surface gallium and indium being preferentially etched by chlorine initially. Once excess surface gallium and indium species have been etched and all clean In, Ga, and As surface sites have reacted with Si-Clₓ, the surface becomes saturated by chlorine termination as shown following the total
12, and 21 MegaLangmuir Si₂Cl₆ doses as chlorine desorption from silicon is close to zero at 350°C.²⁶,³⁶ Figure 3.1 (c) shows the deconvolution of Ga 3p 1/2 and 3/2 spin orbit split peaks, Si 2p 1/2 and 3/2 spin orbit split peaks, and the higher binding energy SiClₓOᵧ component following the saturation dose of 21 MegaLangmuir Si₂Cl₆. The SiClₓOᵧ component makes up ~11% of the total Si 2p signal, showing that the majority of silicon deposited on the surface is unshifted Si⁺⁰. The thickness of the deposited silicon capping layer is calculated from the equation ln(I/I₀) = -t/λ, where I is the sum of the intensity of the In 3d, Ga 2p, and As 2p peaks following each Si₂Cl₆ dose, I₀ is the sum of the intensity of the In 3d, Ga 2p, and As 2p peaks on the clean InGaAs(001)-(2x4) surface, t is the thickness of the deposited silicon layer, and λ is the inelastic mean free path of the collected electrons of the InGaAs substrate (1 nm). Using this equation, the total 21 MegaLangmuir Si₂Cl₆ dose saturates at about 2.5-3 monolayers of silicon coverage with chlorine termination.

For the HOOH(g), the InGaAs(001)-(2x4) surface is initially exposed to 87.6 MegaLangmuir Si₂Cl₆ at 350°C, and XPS results confirm 2.5 monolayers of silicon coverage with chlorine termination (Figure 3.2). Following the Si-Clₓ saturation, anhydrous HOOH(g) is dosed on the surface to induce desorption of HCl(g) and HOCl(g) by-products, and leave the surface terminated by –O and –OH groups. Figure 3.2 shows the XPS corrected peak areas of As 2p, Ga 2p, In 3d, Si 2p (total signal and higher binding energy shifted component), Cl 2p, O 1s, Al 2p, and C 1s of the decapped InGaAs(001)-(2x4) surface, and following 87.6 MegaLangmuir Si₂Cl₆, 90.5 MegaLangmuir HOOH(g), an additional 60 MegaLangmuir HOOH(g), and a final 60 MegaLangmuir HOOH(g) exposure with all doses at a substrate temperature of 350°C.
After a total of 150.5 MegaLangmuir HOOH(g), the –O coverage on the surface saturates as there is no further increase in the oxygen signal even after dosing an additional 60 MegaLangmuir (210.5 MegaLangmuir HOOH(g) total). It is hypothesized that some chlorine may be bound to silicon subsurface, and serves to block oxygen from fully oxidizing the silicon bilayer to SiO₂, as the ratio of oxygen to silicon is ~1.55, and there is still unshifted silicon, and residual chlorine following HOOH(g) dosing.

Following the saturation HOOH(g) dosing, the surface was exposed to TMA in order to see if a high-K metal ALD precursor would directly nucleate on the surface. TMA was dosed at a sample temperature of 250°C, with an initial 50,000 L exposure followed by an additional 250,000 L. Dimethylaluminum groups are present on the surface as both the aluminum and carbon signals are seen in XPS (Figure 3.2). The TMA coverage on the surface is found to saturate as 250,000 L is 5 times the initial TMA exposure, but the change in coverage of aluminum is only 1.2X and change in carbon is 1.5X.

Figure 3.3 shows the XPS raw peak areas for Si 2p, As 2p 3/2, Ga 2p 3/2, In 3d 5/2, O1s, and Cl 2p on the decapped InGaAs(001)-(2x4) surface, and following 87.6 MegaLangmuir Si₂Cl₆ at 350°C, and 210.5 MegaLangmuir total HOOH(g) at 350°C. The Si 2p peak (Figure 3.3 (a)) after the Si₂Cl₆ dose is found at binding energy 99.8 eV, and following the HOOH(g) exposure the peak shifts to 103.1 eV, which is within the binding energy range reported for substoichiometric SiOₓ films in literature.³⁰ A small unshifted Si 2p peak remains at 99.8 eV showing the HOOH(g) is unable to fully oxidize the Si-Clₓ control layer, and is unable to diffuse through and attack the InGaAs substrate.
Figure 3.3 (b) shows the As 2p 3/2 peak undergoes a chemical shift ~0.5 eV higher due to formation of As-Si bonds, but no higher binding energy shoulder components are observed on the In, Ga, or As substrate peaks (Figure 3.3 (b) – (d)), indicating no oxidation of the substrate has occurred. On the clean surface, there are As-As bonds and As dangling bonds. While substitution of As-As bonds for As-Si should have little effect on the As peak energy, substitution of As dangling bonds for As-Si covalent bonds should increase the As peak energy. Any etching of In or Ga which results in substitution of As-In or As-In bonds for As-Si will also contribute to the increase in As electron binding energy. Figure 3.3 (f) shows the presence of chlorine still remains on the surface following the HOOH(g) exposure.

### 3.5.2 STS/STM of Si2Cl6, HOOH, and TMA saturation on InGaAs(00)-(2x4)

Figure 3.4 (a) shows the STS measurements probing the local surface density of states of the n-type decapped InGaAs(001)-(2x4) surface before (teal curve) and after saturation Si2Cl6 dosing (purple curve) at 350°C. Following 87.6 MegaLangmuir Si2Cl6, the conduction and valence band edges align with the clean (2x4) surface, the Fermi level position lies near the conduction band edge, and there are no defect states found present inside the bandgap indicating the surface Fermi level remains unpinned. Figure 3.4 (b) shows an overlay of STS measurements following 87.6 MegaLangmuir Si2Cl6 (purple curve), and following 210.5 MegaLangmuir HOOH(g) at 350°C (green curve). After HOOH(g) dosing, the surface Fermi level is seen to shift to midgap (shown by blue arrows) consistent with surface dipole formation from –OH groups and oxygen bonding to the surface. The bandgap increases from ~0.78 ± 0.02 eV to ~1.37 ± 0.02 eV as the
surface is now terminated by 3-4 monolayers of SiO\textsubscript{x} and is increasing towards the bandgap of bulk SiO\textsubscript{2}.

Figure 3.4 (c) shows the STS measurements after 87.6 MegaLangmuir Si\textsubscript{2}Cl\textsubscript{6} and 210.5 MegaLangmuir HOOH(g) at 350°C (green curve), and an additional 300,000 L TMA dosed at 250°C (pink curve). After TMA dosing the bandgap (1.27 ± 0.02eV) is nearly the same size as that after HOOH(g) dosing, and the Fermi level position is found shifted slightly above midgap closer to the conduction band edge (shown by blue arrows), consistent with surface Fermi level unpinning and the –OH and -O induced surface dipole being lessened through surface bonding with dimethylaluminum groups.

Figure 3.5 (a) shows a filled state STM image of the clean n-type InGaAs(001)-(2x4) surface following 87.6 MegaLangmuir Si\textsubscript{2}Cl\textsubscript{6} dosed at 350°C with an inset in the lower left-hand corner showing the clean InGaAs(2x4) surface. Figure 3.5 (b) shows a typical line trace taken across the ordered row region of the STM image shown in (a) after saturation Si\textsubscript{2}Cl\textsubscript{6} dosing. The clean (2x4) surface contains surface terminating As-As dimer rows spaced at ~1.7 nm, and after Si\textsubscript{2}Cl\textsubscript{6} dosing the surface remains quasi-ordered with ordered rows seen along the same direction as the underlying (2x4) surface rows at an average row spacing of 1.6±0.1 nm indicative of Si-Cl\textsubscript{x} species absorbing in commensurate fashion with the underlying III-V substrate.

Figure 3.5 (c) shows the (2x4) surface following the saturated 87.6 MegaLangmuir Si\textsubscript{2}Cl\textsubscript{6} dose at 350°C, and 210.5 MegaLangmuir HOOH(g) at 350°C. The surface does not contain atomic ordering, but uniform SiO\textsubscript{x} coverage is seen across the surface, as shown in Figure 3.5 (d), where a typical line trace taken across the surface is shown. Surface features were found to vary in height by less than one atomic step (~1.9 ± 0.02 Å) on the
saturated SiO\textsubscript{x}/InGaAs(001)-(2x4) surface showing high uniform nucleation and growth of SiO\textsubscript{x} across the surface.

3.6 DFT Simulations

Initial DFT modeling of the SiO\textsubscript{x}/InGaAs(001) interface with and without TMA passivation is performed in order to examine various interfacial bonding configurations. In order to first model the InGaAs(001) surface bonding with silicon after dosing with Si\textsubscript{2}Cl\textsubscript{6}, the InGaAs surface is terminated by all sp\textsuperscript{3} hybridized arsenic atoms. This arsenic-rich surface termination is consistent with the self-limiting and saturating Si\textsubscript{2}Cl\textsubscript{6} deposition process, which XPS shows with higher coverage of Si\textsubscript{2}Cl\textsubscript{6}, the InGaAs surface becomes more arsenic-rich as surface In/Ga species are preferentially etched by chlorine. Figure 3.6 (a) shows a model of the silicon passivated InGaAs(001) surface after dosing with HOOH(g): the Si capped As-rich InGaAs(001) surface is terminated with 50% Si-OH groups (with one filled dangling bond on Si), and 50% Si bonded to two –OH groups since this is the maximum -OH coverage which is consistent with the electron counting rule developed by M.D. Pashley for an unpinned charge neutral interface.\textsuperscript{38} All DFT models shown in Figures 6 and 7 follow the electron counting rule. The calculated density of states (DOS) for the bonding configuration shown in Fig. 3.6 (a) shows a narrow bandgap with the Fermi level position located slightly above midgap (Fig. 3.6 (b)). The narrow bandgap is consistent with Fermi level pinning. Figure 3.6 (c) shows the arsenic-rich InGaAs(001) surface with each surface arsenic bonding to one Si-OH group (with one filled dangling bond on Si), and one Si bonded to an H atom, and an –OH group. This model contains \(\frac{1}{2}\) the amount of –OH groups on the surface in order to
alleviate any steric hindrance from bulky –OH groups, and also to be more consistent with experimental XPS results showing an Si:O ratio of 0.65, with this model containing a Si:O ratio of 0.7. The calculated DOS still shows a narrow bandgap with the Fermi level position is located slightly above midgap, consistent with pinning.

Figure 3.7 shows two different bonding configurations for monomethylaluminum (MMA) groups replacing hydrogen atoms bonding to all O atoms found in the Fig. 3.6 (c) model. The Figure 3.6 (c) model is chosen for TMA passivation because this –OH coverage more closely reflects the Si:O experimental values obtained from XPS measurements. Figure 3.7 (a) shows MMA groups bridge bonding between neighboring oxygen atoms. Figure 3.7 (b) contains the calculated DOS which shows a narrow bandgap with the Fermi level located slightly above midgap. Figure 3.7 (c) shows MMA groups bridge bonding between adjacent, closer neighboring oxygen atoms and the calculated DOS (Fig. 3.7 (d)) contains a larger bandgap more reflective of experimental STS measurements confirming TMA passivation of the SiO$_x$/InGaAs(001) surface can produce an electrically passive interface ready for high-K gate oxide deposition. The calculated total energies of the models in Figure 3.7 (a) and (c) are shown below each model in order to compare the relative thermodynamic stabilities of both passivation bonding configurations, as both models contain the same number of atoms. Figure 3.7 (c) contains ~0.9 eV lower total energy than the model shown in Figure 3.7 (a), indicating Fig. 3.7 (c) is both electrically passivated and also the more energetically favorable bonding configuration.

3.7 Conclusions
A thin SiO$_x$ control layer (8-10 Å) is deposited on the InGaAs(001)-(2x4) surface by a plasma-less self-limiting CVD process by dosing Si$_2$Cl$_6$ followed by anhydrous HOOH(g) at 350°C with no post deposition annealing required. High-k gate oxide, such as Al$_2$O$_3$, directly nucleates and saturates on the SiO$_x$ terminated surface as confirmed with XPS measurements after dosing TMA at 250°C. STM measurements show the self-limiting CVD process on InGaAs(001)-(2x4) produces uniform SiO$_x$ coverage as surface features are found to vary in height by less than one atomic step. STS measurements show TMA dosing on the SiO$_x$/InGaAs surface leaves a bandgap free of midgap defect states with the Fermi level position found slightly above midgap closer to the conduction band edge, consistent with surface Fermi level unpinning and the –OH and -O induced surface dipole being lessened through surface bonding with MMA or DMA groups. DFT simulations of SiO$_x$ passivation on InGaAs(001) show a narrow pinned bandgap consistent with experimental STS showing a surface induced dipole from –OH/O groups shifting the Fermi level midgap. DFT simulations indicate TMA passivation can lead to a bandgap free of defect states and surface Fermi level unpinning. XPS shows this SiO$_x$ growth process prevents III-V substrate oxidation, and maintains an unpinned surface Fermi level as shown by STS measurements and supported by DFT simulations, leaving the III-V surface passivated and ready for high-K gate oxide deposition.

3.8 Acknowledgements

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”Self-limiting CVD of a passivating SiOₓ control layer on InGaAs(001)-(2x4) with the prevention of III-V oxidation,” (manuscript submitted to Surface Science). The dissertation author was the primary investigator and author of this paper.

3.9 Supplemental Materials

The typical raw XPS peak areas for C 1s and O 1s on clean InGaAs(2x4), and following 3, 12, and 21 MegaLangmuir total Si₂Cl₆ doses at 350°C are shown in Figure 3.8 (a). The carbon content is below the XPS detection limits and oxygen remains below 5% during the course of the entire experiment. Oxygen content is calculated by dividing the O 1s corrected peak area by the addition of the In 3d, Ga 2p, As 2p, and Si 2p corrected peak areas and multiplying by 100 to get a percentage. The As 2p peak is shown (Fig. 3.8 (b)) following 3 MegaLangmuir total Si₂Cl₆ doses at 350°C showing the bulk As-In/Ga chemical state and the As-Si chemical state shifted to slightly higher binding energy. The Ga 2p peak is shown (Fig. 3.8 (c)) following 3 MegaLangmuir total Si₂Cl₆ doses at 350°C showing the bulk Ga-As chemical state and no Ga-Si chemical state detected.

The raw XPS peaks for C 1s and Al 2p on decapped InGaAs(2x4), and following 87.6 MegaLangmuir total Si₂Cl₆ dose at 350°C, 210.5 MegaLangmuir total HOOH(g) dose at 350°C, 50,000 L TMA at 250°C, and 300,000 L total TMA at 250°C are shown in Figure 3.9. The Al 2p signal is absent on the decapped, 87.6 MegaLangmuir Si₂Cl₆, and 210.5 MegaLangmuir HOOH(g) surfaces (Fig. 3.9 (a)), and the signal emerges and saturates after TMA dosing as the 300,000 L total dose is 5 times the initial 50,000 L dose but the change in aluminum coverage is only 1.2X (Fig. 3.9 (b)). Fig. 3.9 (c) shows
the carbon content throughout the course of the experiment, where on the decapped, 87.6 MegaLangmuir Si$_2$Cl$_6$, and 210.5 MegaLangmuir HOOH(g) surfaces there is no real C 1s signal detected over noise, and after TMA doses the C 1s signal emerges and saturates from chemisorption of monomethylaluminum or dimethylaluminum groups on the surface as the 300,000 L total dose is 5 times the initial 50,000 L dose but the change in carbon coverage is only 1.5X.
Figure 3.1 XPS of Si$_2$Cl$_6$ on InGaAs(001)-(2x4). XPS raw counts corrected by Schofield photoionization cross sectional relative sensitivity factors. (a) Raw XPS peak areas for Ga 3p and Si 2p on clean InGaAs(2x4), and following 3, 12, and 21 MegaLangmuir total Si$_2$Cl$_6$ doses at 350$^\circ$C. (b) XPS corrected peak areas for 3 MegaLangmuir Si$_2$Cl$_6$, 12 MegaLangmuir Si$_2$Cl$_6$, and 21 MegaLangmuir Si$_2$Cl$_6$ on n-type InGaAs(001)-(2x4). All doses at 350$^\circ$C. (c) XPS peak fitting of Si 2p and Ga 3p peaks following 21 MegaLangmuir Si$_2$Cl$_6$ dosed at 350$^\circ$C. Ga 3p 1/2 and 3/2 spin orbit split peaks are shown in green, SiCl$_x$O$_y$ component shown in purple, and Si 2p 1/2 and 3/2 spin orbit split peaks shown in orange.
**Figure 3.2** XPS of Si$_2$Cl$_6$, HOOH(g), and TMA on InGaAs(001)-(2x4). XPS raw counts corrected by Schofield photoionization cross sectional relative sensitivity factors. XPS corrected peak areas of As 2p, Ga 2p, In 3d, Si 2p (total signal and higher binding energy shifted component), Cl 2p, O 1s, Al 2p, and C 1s of the decapped InGaAs(001)-(2x4) surface, and following 87.6 MegaLangmuir Si$_2$Cl$_6$, 90.5 MegaLangmuir HOOH(g), an additional 60 MegaLangmuir HOOH(g), a final 60 MegaLangmuir HOOH(g) exposure, 50,000 L TMA, and an additional 250,000 L TMA. All Si$_2$Cl$_6$ and HOOH(g) exposures at a substrate temperature of 350°C, and TMA doses at a substrate temperature of 250°C.
Figure 3.3 XPS spectra after Si₂Cl₆, and HOOH(g) exposure on InGaAs(001)-(2x4). XPS raw peak areas of Si 2p (a), As 2p 3/2 (b), Ga 2p 3/2 (c), In 3d 5/2 (d), O 1s (e), and Cl 2p (f) on the decapped InGaAs(001)-(2x4) surface, and following 87.6 MegaLangmuir Si₂Cl₆, and 210.5 MegaLangmuir HOOH(g) total exposure. All doses performed at a substrate temperature of 350°C.
Figure 3.4 STS of Si$_2$Cl$_6$, HOOH(g), and TMA exposure on InGaAs(001)-(2x4). (a) STS measurements on clean n-type InGaAs (2x4) (teal curve), and following 87.6 MegaLangmuir Si$_2$Cl$_6$ at 350°C (purple curve). (b) STS of clean n-type InGaAs (2x4) dosed with 87.6 MegaLangmuir Si$_2$Cl$_6$ (purple curve), and an additional 210.5 MegaLangmuir HOOH(g) at 350°C (green curve). (c) STS of clean n-type InGaAs (2x4) dosed with 87.6 MegaLangmuir Si$_2$Cl$_6$ and 210.5 MegaLangmuir HOOH(g) at 350°C (green curve), and an additional 300,000 L TMA dosed at 250°C (pink curve). Blue arrows indicate the shifting direction of the conduction band and valence band edges after HOOH(g) and TMA doses.
**Figure 3.5** STM of Si$_2$Cl$_6$, and HOOH(g) saturation on InGaAs(001)-(2x4). (a) Filled state STM image of 87.6 MegaLangmuir Si$_2$Cl$_6$ dosed at 350°C on the InGaAs(001)-(2x4) surface. The left-hand lower corner contains an enlarged inset of the clean InGaAs(001)-(2x4) surface. (b) Typical line trace taken across the STM image shown in (a) along the ordered row regions seen across the surface following 87.6 MegaLangmuir Si$_2$Cl$_6$. Row spacing was measured at 1.6±0.1 nm. (c) Filled state STM image of 87.6 MegaLangmuir Si$_2$Cl$_6$ dosed at 350°C followed by an additional 210.5 MegaLangmuir HOOH(g) at 350°C on the InGaAs(001)-(2x4) surface. (d) Typical line trace taken across the STM image shown in (c) indicating the surface features vary in height by no more than ~1.9 ± 0.02 Å showing the surface contains high uniform coverage of SiO$_x$. 
Figure 3.6 DFT simulations of SiO\textsubscript{x} passivation on InGaAs(001). (a) As-rich InGaAs(001) unit cell with half the surface arsenic bonded to one Si-OH group (with one filled dangling bond on Si), and half the surface arsenic bonded to one Si bonded to two -OH groups. (b) calculated DOS for the model shown in (a) containing a narrow bandgap. (c) As-rich InGaAs(001) surface with each surface arsenic bonding to one Si-OH group (with one filled dangling bond on Si), and one Si bonded to an H atom, and an –OH group. (d) calculated DOS for the model presented in (c) containing a narrow bandgap. Valence band maximum and conduction band minimum values are marked by red and green lines.
Figure 3.7 DFT simulations of TMA on SiOₓ/InGaAs(001). (a) As rich InGaAs(001) unit cell with SiOₓ configuration shown in Fig. 6 (c) with monomethyl aluminum (MMA) groups bridge bonding between neighboring oxygen atoms. (b) calculated DOS for the model shown in (a) containing a narrow bandgap. (c) As rich InGaAs(001) unit cell with SiOₓ configuration shown in Fig. 6 (c) with MMA groups bridge bonding between adjacent, closer neighboring oxygen atoms. (d) calculated DOS for the models shown in (c) with a large bandgap free of midgap defect states. Valence band maximum and conduction band minimum values are marked by red and green lines. Total energies are shown below each model.
Figure 3.8 XPS carbon and oxygen spectra and substrate peak chemical state deconvolution of Si$_2$Cl$_6$ dosed InGaAs(001)-(2x4). (a) Raw XPS counts for C 1s and O 1s binding energies on clean InGaAs(2x4), and following 3, 12, and 21 MegaLangmuir total Si$_2$Cl$_6$ doses at 350°C. The carbon is below the XPS detection limits while the oxygen remains below 5%. Oxygen percentage is calculated by dividing the O 1s corrected peak area by the addition of the In 3d, Ga 2p, As 2p, and Si 2p corrected peak areas and multiplying by 100. (b) As 2p peak is shown following 3 MegaLangmuir Si$_2$Cl$_6$ dose at 350°C showing the bulk As-In/Ga chemical state and the As-Si chemical state shifted to slightly higher binding energy. (c) Ga 2p peak is shown following 3 MegaLangmuir Si$_2$Cl$_6$ doses at 350°C showing the bulk Ga-As chemical state and no Ga-Si chemical state detected.
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Figure 3.9 XPS aluminum and carbon spectra of Si$_2$Cl$_6$, HOOH(g), and TMA dosed InGaAs(001)-(2x4). (a) Raw XPS counts across the Al 2p peak on clean InGaAs(2x4), and following 87.6 MegaLangmuir total Si$_2$Cl$_6$ dose at 350°C, and 210.5 MegaLangmuir total HOOH(g) dose at 350°C. The Al 2p signal is absent from the surface during the course of Si$_2$Cl$_6$, and HOOH(g) exposures. (b) Al 2p peak emerges following 50,000 Langmuir TMA dose at 250°C, and saturates following 300,000 L total TMA dose at 250°C. (c) Raw XPS counts across the C 1s peak on clean InGaAs(2x4), and following 87.6 MegaLangmuir total Si$_2$Cl$_6$ dose at 350°C, 210.5 MegaLangmuir total HOOH(g) dose at 350°C, 50,000 L total TMA dose at 250°C, and 300,000 L total TMA dose at 250°C. The C 1s signal emerges and saturates after TMA doses due to the chemisorption of monomethylaluminum or dimethylaluminum groups on the surface.
3.10 References


Chapter 4

Low Temperature Thermal ALD of a SiN$_x$ Interfacial Diffusion Barrier and Interface Passivation Layer on Si$_x$Ge$_{1-x}$(001) and Si$_x$Ge$_{1-x}$(110)

4.1 Abstract

Atomic layer deposition of a silicon rich SiN$_x$ layer on Si$_{0.7}$Ge$_{0.3}$(001), Si$_{0.5}$Ge$_{0.5}$(001), and Si$_{0.5}$Ge$_{0.5}$(110) surfaces has been achieved by sequential pulsing of Si$_2$Cl$_6$ and N$_2$H$_4$ precursors at a substrate temperature of 285°C. XPS spectra show a higher binding energy shoulder peak on Si2p indicative of SiO$_x$N$_y$Cl$_z$ bonding while Ge2p and Ge3d peaks show a only a small amount of higher binding energy components consistent with only interfacial bonds, indicating the growth of SiO$_x$N$_y$ on the SiGe surface with negligible subsurface reactions. Scanning tunneling spectroscopy (STS) measurements confirm the SiN$_x$ interfacial layer forms an electrically passive surface on p-type Si$_{0.7}$Ge$_{0.3}$(001), Si$_{0.5}$Ge$_{0.5}$(110), and Si$_{0.5}$Ge$_{0.5}$(001) substrates as the surface Fermi level is unpinned and the electronic structure is free of states in the band gap. DFT calculations show that Si rich a-SiON$_x$ can produce a lower interfacial defect density than a stoichiometric a-Si$_3$N$_4$ film. The SiO$_x$N$_y$ layer serves to improve the Si$_x$Ge$_{1-x}$ surface by preventing formation of Ge-O bonds. MOSCAP devices were fabricated on p-type Si$_{0.7}$Ge$_{0.3}$(001) and Si$_{0.5}$Ge$_{0.5}$(001) substrates with and without the insertion of an ALD SiO$_x$N$_y$ interfacial layer, and the SiO$_x$N$_y$ layer resulted in a decrease in interface state density near midgap with a comparable $C_{\text{max}}$ value.

4.2 Introduction
Si$_x$Ge$_{1-x}$ intrinsically has high hole mobility which can be further enhanced by compressively straining the crystal lattice by growing Si$_x$Ge$_{1-x}$ on a substrate with a lower Ge content. As semiconductor device manufacturing continues the scaling of gate stacks to the subnanometer equivalent oxide thickness (EOT) regime, thin film deposition requires high conformality with nucleated growth in every unit cell to ensure low defect density and low gate leakage. Passivation and functionalization of the Si$_x$Ge$_{1-x}$ surface remains challenging as Ge surface dangling bonds act to pin the SiGe surface Fermi level, and Ge sub-oxide surface species degrade semiconductor mobility and create a higher density of interfacial trap states in the band gap. Plasma nitridation of pure Ge and low content Ge (x=0.5-1) Si$_x$Ge$_{1-x}$ surfaces has served as an effective passivating interfacial layer between the semiconductor and oxide by maintaining a low density of interfacial trap states; in addition, it prevents Ge out-diffusion into the oxide. However, it remains challenging to fully nitridate surface Ge atoms present at the SiGe surface because silicon is more reactive than germanium leading to formation of a non-uniform interfacial layer. However, plasma post-nitridation of Al$_2$O$_3$/Si$_{0.75}$Ge$_{0.25}$ gate stacks has been shown to decrease the density of interfacial trap states at the cost of increasing the EOT.

Low temperature CVD growth of silicon nitride films on Si(001) substrates by dosing Si$_2$Cl$_6$ followed by N$_2$H$_4$ at 350°C - 400°C substrate temperatures at extremely high pressure (160 Torr) has also been previously reported. The reported CVD silicon nitride films contained ~30 at% hydrogen, which may be due to the absence of purge steps between half cycle reactions or the high deposition pressure. Silicon nitride plasma assisted ALD has been previously reported on ZnSe substrates at 350°C-450°C by
alternating pulses of Si$_2$Cl$_6$ and NH$_3$ plasma. Si$_2$Cl$_6$ was pulsed for 30 seconds at a peak chamber pressure of 70 mTorr followed by a 30 second Ar purge at 80 mTorr. The NH$_3$ plasma was produced with an argon carrier gas at a total dose pressure of 100 mTorr. The report shows highly conformal SiN$_x$ deposited films of ~30 nm thickness with a reported growth per cycle of ~1.2 Å. Many similar plasma assisted silicon nitride ALD processes have been reported by employing alternating pulses of NH$_3$ plasma and a silane precursor (SiH$_4$, SiH$_2$Cl$_2$, SiCl$_4$, and Si$_3$Cl$_8$) at temperature ranges of 350°C - 623°C on silicon (001), germanium (001), and low Ge content SiGe (001) substrates. Lower temperature plasma assisted ALD has also been reported through the sequential pulsing of NH$_3$ or N$_2$ plasma and a silane precursor (SiH$_4$, SiH$_2$Cl$_2$, and N(SiH$_3$)$_3$) at temperatures of 250°C - 500°C on Si(001) substrates. Room temperature silicon nitride deposition on Si(001) substrates has been reported by jet-vapor deposition of SiH$_4$ in a He carrier gas or an N$_2$ plasma in a He carrier gas. The jet-vapor deposition process requires a specialized chamber set-up which may be difficult to scale to large area substrates with uniform coverage for subnanometer thickness on 3D structures (finFETs).

Thermal silicon nitride atomic layer deposition (ALD) has been previously reported by alternate pulses of Si$_2$Cl$_6$ (1 Torr pulses) and N$_2$H$_4$ (0.1 Torr pulses, 98% N$_2$H$_4$ and 2% H$_2$O) on an NH- terminated Si(001) surface. The experiments employed both very high temperatures (>525°C) and very long N$_2$H$_4$ half-cycle pulse time (12 min). The growth mechanism is in contrast to a report by K. Park et. al of thermal decomposition of Si$_2$Cl$_6$ at temperatures exceeding 500°C. For this high temperature Si$_2$Cl$_6$ and N$_2$H$_4$ reaction, Morishita et al. reported each precursor, Si$_2$Cl$_6$ and 98% N$_2$H$_4$
containing residual H₂O, was consecutively flowed into the reaction chamber (base pressure of 1x10⁻³ Torr) without carrier gas for a fixed time of 4 seconds; subsequently, all valves to precursor containers and pumping lines were shut so that the gas was left in the reaction chamber for the designated exposure time of 735 seconds. While the oxidant and reductant were dosed at separate times, this process may not be a true ALD process, as the stagnant Si₂Cl₆ gas in the reaction chamber may have a partial decomposition and introduce a CVD component; however, Morishita et al’s pioneering work did show that low temperature N₂H₄ reactions might be feasible. The present study employs anhydrous hydrazine to keep the Si-Nₓ surface free of unwanted oxygen or water contamination during film deposition; this was not part of the Morishita et al. process which produced 4% oxygen in film growth attributed to residual water in the hydrazine.

In this work, subnanometer passivating (~6-10 Å) silicon nitride films have been deposited on low and high Ge content SiₓGe₁₋ₓ(001)/(001) surfaces by a plasma-free ALD process using Si₂Cl₆ and N₂H₄ at a low substrate temperature (285°C) with low half-cycle pulse times and vacuum purges between precursor pulses. This study employs anhydrous hydrazine as the nitriding agent, both to keep the Si-Nₓ surface free of unwanted oxygen contamination, and to eliminate plasma induced surface damage by nitriding the surface through a thermal ALD process. MOSCAP device fabrication was performed on p-type Si₇₀Ge₃₀(001) and Si₀.₅Ge₀.₅(001) substrates with and without the insertion of a SiNₓ passivating interfacial layer deposited by ALD and a decrease in extracted interface state density, particularly near midgap, was observed for a comparable Cₓ value for the SiNₓ passivated surfaces compared to the non-passivated surface.
4.3 Experimental

This study employed p-type Si$_{70}$Ge$_{30}$(001) (Applied Materials, Inc.) and Si$_{50}$Ge$_{50}$(001) (GLOBALFOUNDRIES, Inc.) films epitaxially grown on p-type Si(001) substrates and p-type Si$_{50}$Ge$_{50}$(110) films epitaxially grown on p-type Si(110) substrates (GLOBALFOUNDRIES, Inc.). The Si$_x$Ge$_{1-x}$ surface underwent a degrease procedure by ultra-sonication with acetone for ten minutes, isopropyl alcohol for ten minutes, and deionized water for five minutes. Next, the sample was dipped into a beaker containing a 2% HF/water solution with a layer of toluene on top for 2 minutes. After 2 minutes, the sample was pulled out through the layer of toluene and quickly transferred into the ultrahigh vacuum (UHV) preparation chamber with a base pressure of 1x10$^{-10}$ Torr before the layer of toluene evaporated from the surface. This process was employed to prevent the sample from being air exposed following the 2% HF dip. The sample was subsequently characterized by an Omicron in situ monochromatic XPS using the aluminum Kα excitation source (hv=1486.7 eV) with spectra taken at a glancing angle of 30° to obtain enhanced surface sensitivity. XPS raw counts were collected using the XPS constant analyzer energy mode with a pass energy of 50 eV and line width of 0.1 eV. XPS peak shape analysis was conducted using CASA XPS v.2.3 by employing a Shirley background subtraction. All XPS raw core level peaks were corrected by Schofield photoionization cross sectional relative sensitivity factors. Following the initial sample XPS characterization, the sample was radiatively heated to 330°C for 15 minutes in the UHV preparation chamber and dosed with 1800 Langmuir of atomic hydrogen in order to remove surface carbon contamination; a Langmuir was defined at a flux of 10$^{-6}$ Torr/sec of gas for all gasses in this study. An Applied Research TC-50 thermal gas cracker was
employed to produce atomic hydrogen and was operated at 65 Watts, producing atomic hydrogen at an estimated 50% efficiency. The 1800 Langmuir dose consists of H₂(g) flowed for 30 minutes at an H₂ pressure of 1x10⁻⁶ Torr; note, the calculated Langmuirs do not include the H cracking fraction since this could not be experimentally determined so the reported atomic hydrogen Langmuirs are an upper limit. XPS was taken of the surface to determine the background carbon, oxygen, silicon, and germanium surface percentages prior to SiNₓ deposition.

The high vacuum ALD (HV-ALD) dosing chamber (base pressure of 3x10⁻⁶ Torr) with attached precursor dosing lines was pumped by a turbomolecular pump backed by a dry pump, and the entire chamber, precursor dosing lines, and connecting line to the dry pump were heated for 12 hours at 125°C. 12 hours of heating time was employed to ensure all stainless steel vacuum components reached the temperature of >100°C, to ensure both precursors would not stick to adsorbates (H₂O, hydrocarbon, etc) on the chamber walls and to eliminate the formation of the ammonium-chloride like powder byproduct. Subsequently, the sample was radiatively heated to 285°C for 15 minutes in the UHV preparation chamber while simultaneously the HV-ALD chamber manipulator was also heated to 250°C or 350°C for 15 minutes to facilitate a faster sample transfer. The sample was transferred to the HV-ALD dosing chamber, and 400 MegaLangmuir of N₂H₄ was dosed at a substrate temperature of 285°C to terminate the surface with NHₓ groups and prepare the surface for ALD. Next, 10-20 SiNₓ ALD cycles were performed at a substrate temperature of 285°C in order to deposit silicon nitride films of varying thickness on the SixGe₁₋ₓ surface. Each ALD cycle consisted of 13.5 MegaLangmuir Si₂Cl₆ (0.1 Torr dosed for 135 seconds) followed by 20 MegaLangmuir N₂H₄ (0.4 Torr
dosed for 50 seconds) at a substrate temperature of 285°C. Anhydrous N₂H₄ was employed (Rasirc, Inc.), and prior to every new sample deposition, the N₂H₄ source container was recharged with 750 Torr of ultra-high purity N₂ to act as a carrier gas for delivery of N₂H₄ (vapor pressure of 15 Torr at 25°C). In between half-cycle pulses, a HV purge of 85 seconds was employed to ensure any residual precursor was removed from the deposition chamber before introduction of the next half-cycle. Following deposition, the sample was transferred back to the UHV preparation chamber and radiatively heated to 285°C for 15 minutes and dosed with 1800 Langmuirs of atomic hydrogen in order to remove any residual chlorine left in the deposited SiNₓ film by inducing an HCl(g) desorption byproduct. The surface was subsequently characterized by XPS and transferred into the UHV SPM analysis chamber (base pressure of 2x10⁻¹¹ Torr).

In the SPM chamber, scanning tunneling spectroscopy (STS) was performed to determine the electrical quality of the surface and probe the local surface density of states. Variable-z mode measurements were taken using an external lock-in amplifier with modulation signal (0.1 Vac, 650 Hz) to directly obtain the dI/dV and I/V spectra by sweeping the sample bias from -2.5 to +2.5 V, and simultaneously moving the tip towards and then away from the surface. An applied Δz initial offset ranging from -0.2 to -0.8 nm was used in order to maximize the I(V) signal without crashing the STM tip. The raw I/V data are smoothed by a broadening function to create \( \frac{I}{V} \) using a low-pass filter with energy width of (3.0 eV)/2π (filter frequency parameter value of (3.0 eV)¹), as described in previous studies. The dI/dV spectra are normalized by dividing by . The STS curves are reported by averaging 10-12 individual (dI/dV)/(\( \frac{I}{V} \)) curves taken across the sample surface. These averaged curves are fitted (dashed red line in
reported spectra) using a linear function described in previous STM/STS studies in order to extract the measured band edge energies of the plotted \((dI/dV)/(I/V)\) spectra, as band offsets contain linear dependence on sample bias.\(^{29-31}\) The linear function fitting method contains slight rounding at the band gap onset due to temperature and AC modulation. Standard errors are obtained by the fitting process and reported for averaged STS curves. The uncertainties provided by the fitting method are statistical uncertainties using the least squares fitting,\(^{32}\) and these reported uncertainties are much less than thermal broadening in STS measurements.

After SiNx deposition, the samples were taken out of UHV and placed under 750 Torr ultra-high purity N\(_2\) until ready for MOSCAP fabrication. Capacitance-voltage (C-V) characterization of SiNx/SiGe interfaces was performed by fabrication of HfO\(_2\)/SiNx/SiGe metal-oxide-semiconductor capacitors (MOSCAPs). HfO\(_2\) ALD was performed at 300°C in the Beneq TFS-200 continuous flow reactor using Ar carrier gas, with 40 sequential pulses of HfCl\(_4\) (500 ms) and H\(_2\)O (500ms). After each precursor pulse, a 6s long Ar purge was employed. Following HfO\(_2\) ALD, Ni gate metal and Al back contacts were deposited by thermal evaporation and DC sputtering, respectively. C-V were measured at variable frequencies ranging from 2 kHz to 1 MHz with AC modulation amplitude of 30-50 mV and DC bias range of -2 to 2 V. By fitting the frequency dispersion of C-V and conductance- voltage (G-V) responses around the depletion region and inversion region, the density of interface traps at various energy levels relative to the edge of valence band was calculated using the full interface state model, which consists of a \(\Delta\) circuit of three complex elements to represent charge trapping by interface traps.\(^{33,34}\)
All DFT simulations were performed by VASP plane-wave DFT package using projector augmented-wave (PAW) pseudopotentials (PP), PBE-GGA exchange-correlation functional for DFT-MD and more accurate HSE06 hybrid-functional for the final electronic structure calculations. The first step in the density-functional theory (DFT) simulations was modeling a-SiO$_{0.8}$N$_{0.8}$ and a-Si$_3$N$_4$ interlayers on SiGe(001). The SiGe substrate was a 2x2x3 SiGe supercell using lattice constants which were DFT-relaxed at variable volume. The 3 bottom layers were permanently fixed in bulk-like positions and passivated by relaxed H atoms to simulate continuous bulk. The upper surface of SiGe slab was Si-terminated. The larger 2x2 surface area of the supercell provides more realistic amorphous interlayer/SiGe simulations than the 1x1 SiGe unitcell surface area. Due to high computational cost of DFT molecular dynamics (MD) simulations, the largest supercell was chosen which could provide a reasonable simulation time. The 2x2x3 SiGe supercell had 96 atoms, while the a-HfO$_2$ sample had 120 atoms. In addition, around 20 passivating H atoms and around 20 interlayer O/N atoms were included to the system resulting in roughly 250 atoms in total. Furthermore, the SiGe slab and a-HfO$_2$ sample should have a thickness around 10 Å or higher to have bulk-like properties. With these constraints, the 2x2 supercell surface area was the most computationally affordable. Switching to a greater 3x3 surface area would have made the whole a-HfO$_2$/interlayer/SiGe stack too large for computationally affordable DFT-MD simulations. The a-SiO$_{0.8}$N$_{0.8}$ and a-Si$_3$N$_4$ interlayers were formed by DFT molecular dynamics (DFT-MD) in 2 stages.

To form the a-SiO$_{0.8}$N$_{0.8}$ interlayer, initially 8 Si, 7 O and 7 N atoms were added randomly on the surface resulting together with 8 surface Si atoms in 16 Si, 7 O and 7 N
atoms. The stack was annealed at 800K for 1000 fs, cooled to 0 K for 200 fs and relaxed to the ground state with the conjugate-gradient relaxation algorithm. This formed the “Si-rich sub-stoichiometric” layer of a-SiO$_{0.8}$N$_{0.8}$ (or a-SiO$_{0.4}$N$_{0.4}$). Since DFT-MD is a computationally expensive technique, the simulated timescale for systems of 100-300 atoms is typically limited to picoseconds (~ 1fs time-step) to have a reasonable run time. Using a higher annealing temperature accelerates kinetic processes and effectively elongates simulated timescale. The 800K annealing temperature was chosen to be lower than the melting temperature of the SiGe stack. The melting temperature for Ge is 1210K, for Si is 1685K, and for Si$_{0.5}$Ge$_{0.5}$ it is estimated to be 1382K. The DFT-MD temperature 800K was chosen lower than 1382K because of two reasons: i) the DFT melting temperature can be lower than the experimental one; ii) having an annealing temperature above 800K often causes deposited O/N atoms to leave the surface. To form the stoichiometric interlayer, an additional 6 O and 6 N atoms were added in a random manner to the previous surface resulting in total 16 Si, 13 O and 13 N atoms. This stack was again annealed at 800K for 1000 fs, cooled to 0 K for 200 fs, and relaxed to the ground state with the conjugate-gradient relaxation algorithm giving the “stoichiometric” layer of a-SiO$_{0.8}$N$_{0.8}$.

The a-Si$_3$N$_2$ and a-Si$_3$N$_4$ interlayers on SiGe(001) were formed in similar manner. Originally 8 Si and 11 N atoms were added randomly on the surface resulting together with 8 surface Si atoms in 16 Si and 11 N atoms. The slab was DFT-MD annealed, cooled, and relaxed as described previously forming a Si-rich sub-stoichiometric layer of a-Si$_3$N$_2$. At the second stage, 10 more N atoms were added in random manner to the previous surface resulting in 16 Si, 21 N atoms and DFT-MD annealed, cooled, relaxed
as described previously forming fully stoichiometric layer of a-Si₃N₄. The high-quality model of a-HfO₂ was generated for the SiGe(001) substrate area using the “melt-and-quench” approach by using DFT-MD at finite temperature described in detail elsewhere. The amorphous a-HfO₂ sample was selected from a batch of 10 DFT-MD samples with different simulation parameters and compared against reference experimental and calculated properties such as coordination distribution, band gap, average coordination numbers, radial-distribution functions (RDF’s) and others to ensure high sample realism and absence of defects. The amorphous samples were generated to fit the SiGe(001) substrate cross-sectional area. The selected amorphous bulk sample was cut to create surfaces before stacking to the interlayer/SiGe substrate.

The selected a-HfO₂ sample was stacked on the previously simulated a-SiO₀.₄N₀.₄, a-SiO₀.₉N₀.₁,a-Si₃N₂, and a-Si₃N₄ interlayers on SiGe(001) resulting in stacks. The stacks were annealed at 800K for 1000 fs, cooled to 0 K for 200 fs and relaxed to the ground state with conjugate-gradient relaxation algorithm. Since standard PBE exchange-correlation functional underestimates semiconductor bandgaps, the simulated stacks were rescaled from PBE to HSE06 SiGe lattice constants (different by several %) and accurate electronic structure including density of states and band-decomposed charge density was calculated with the HSE06 functional.

4.4 Results and Discussion

4.4.1 XPS of SiNx on SiGe(001) and SiGe(110)

XPS was employed in order to determine the ALD saturation pulses of Si₂Cl₆ and N₂H₄ at 285°C on Si₀.₅Ge₀.₅(110) and Si₀.₇Ge₀.₃(001) surfaces. Figure 4.1 (a) shows the
Si$_{0.5}$Ge$_{0.5}$(110) corrected XPS peak areas of Si 2p (both the total Si 2p peak area and the higher binding energy shoulder of Si 2p are shown), Ge 3d, O 1s, C 1s, N 1s, and Cl 2p normalized to the sum of the total (shifted and unshifted) Si 2p and total Ge 3d signals for the as-loaded wet cleaned Si$_{0.5}$Ge$_{0.5}$(110) surface, and following an 1800 Langmuir atomic hydrogen dose at 330°C, 400 MegaLangmuir N$_2$H$_4$ dose at 285°C, 1X Si$_2$Cl$_6$ dose at 285°C (13.5 MegaLangmuir), 3X additional Si$_2$Cl$_6$ dose at 285°C (40.5 MegaLangmuir), 1X N$_2$H$_4$ dose at 285°C (20 MegaLangmuir), and 3X N$_2$H$_4$ dose at 285°C (60 MegaLangmuir). Both the SiCl$_x$ and NH$_x$ coverages reach near saturation coverage following a 1X dose indicating an ALD process occurs at 285°C as seen by a negligible increase in Si 2p or N 1s corrected peak areas with increased dosing times.

Figure 4.1 (b) shows the corrected XPS peak areas normalized to the sum of total Si 2p and total Ge 3d signal on the Si$_{0.7}$Ge$_{0.3}$(001) surface following an 1800 Langmuir atomic hydrogen dose at 330°C, 400 MegaLangmuir N$_2$H$_4$ dose at 285°C, 1X Si$_2$Cl$_6$ dose at 285°C (13.5 MegaLangmuir), 3X additional Si$_2$Cl$_6$ dose at 285°C (40.5 MegaLangmuir), 1X N$_2$H$_4$ dose at 285°C (20 MegaLangmuir), and 3X N$_2$H$_4$ dose at 285°C (60 MegaLangmuir). Similar to the Si$_{0.5}$Ge$_{0.5}$(110) case, both the SiCl$_x$ and NH$_x$ coverages saturate following a 1X dose, consistent with an ALD process. It is noted that for even the first 1-2 monolayers of SiN$_x$, the Si/N ratio is independent of crystal face.

These surface sensitive XPS spectra show the hydrogen cleaned Si$_{0.5}$Ge$_{0.5}$(110) surface contains ~63% germanium while the hydrogen cleaned Si$_{0.7}$Ge$_{0.3}$(001) surface contains ~38% germanium. Small amounts of carbon (<~5%) and oxygen (<~10%) detected on both the SiGe(001) and (110) surfaces remain following the initial wet cleaning procedure and the in-situ atomic H dry cleaning due to adsorption of oxygen
containing hydrocarbons onto surface silicon from the brief air exposure occurring during the sample transfer into high vacuum and the 330°C atomic hydrogen cleaning. Following a 1X dose of N\textsubscript{2}H\textsubscript{4}, the Si\textsubscript{0.5}Ge\textsubscript{0.5}(110) surface contains less than half the amount of residual chlorine on the surface as compared with the Si\textsubscript{0.7}Ge\textsubscript{0.3}(001) surface, consistent with Si-Cl surface species being more thermodynamically stable than Ge-Cl species, and a germanium rich SiGe substrate undergoing silicon surface segregation in the presence of chlorine surface termination at 275°C. Both the Si\textsubscript{0.5}Ge\textsubscript{0.5}(110) and Si\textsubscript{0.7}Ge\textsubscript{0.3}(001) surfaces contain residual chlorine following one complete ALD reaction cycle due to the strong N-H (431kJ/mol) and Si-Cl (377 kJ/mol) bonds making it difficult to produce the HCl(g) desorption byproduct at a low deposition temperature.

Figures 4.2 (a), (b), and (c) show the raw XPS peak areas for Si 2p, N 1s, and Ge 2p peaks on the as-loaded wet cleaned Si\textsubscript{0.5}Ge\textsubscript{0.5}(110) surface following an 1800 Langmuir atomic hydrogen dose at 330°C, an additional 400 MegaLangmuir N\textsubscript{2}H\textsubscript{4} dose at 285°C, and following an additional 20 SiN\textsubscript{x} ALD cycles at 285°C. The large shifted Si 2p peak (~68% of the total Si 2p signal) indicative of SiO\textsubscript{x}N\textsubscript{y} is located at a binding energy of 101.7 eV, and the N 1s peak is located at 397.7 eV. A small higher binding energy Ge 2p component is seen at 1219.1 eV indicative of GeO\textsubscript{x}N\textsubscript{y} surface bonding after the N\textsubscript{2}H\textsubscript{4} dose, with slightly more nitrogen found bonded to silicon (25% of Si 2p total corrected peak area signal) than nitrogen bonded to germanium (15% of Ge 2p total corrected peak area signal) as predicted by the large silicon and germanium nitride formation enthalpy differences of -177 and -15 kcal/mol. Following the 20 SiN\textsubscript{x} ALD cycles, the intensity of the Ge 2p signal decreases by a factor of 5 indicating Ge-N bonds are localized at the SiO\textsubscript{x}N\textsubscript{y}/SiGe interface.
Similar results are shown on the as-loaded wet cleaned Si$_{0.5}$Ge$_{0.5}$(001) (Fig 4.2 (d) to (f)) and wet cleaned Si$_{0.7}$Ge$_{0.3}$(001) (Fig 4.2 (g) to (i)) for comparison. After the initial N$_2$H$_4$ dose, the large shifted SiO$_x$N$_y$ peak, located at 101.7 eV, makes up ~70% of the total Si 2p signal on Si$_{0.5}$Ge$_{0.5}$(001) and ~60% of the total Si 2p signal on Si$_{0.7}$Ge$_{0.3}$(001), and the N1s peak is located at 397.7 eV on both 30% Ge and 50% Ge SiGe(001) surfaces. After the initial N$_2$H$_4$ dose, the GeO$_x$N$_y$ surface high binding energy component, located at binding energy 1219.1 eV, makes up ~15% of the total Ge 2p signal on the Si$_{0.5}$Ge$_{0.5}$(001) and Si$_{0.7}$Ge$_{0.3}$(001) surfaces. Following an additional 20 SiN$_x$ ALD cycles the intensity of the Ge 2p signal decreases by a factor of 10 and 8 on Si$_{0.5}$Ge$_{0.5}$(001) and Si$_{0.7}$Ge$_{0.3}$(001) surfaces showing that on both higher and lower Ge content SiGe(001) surfaces the SiO$_x$N$_y$ thin film provides a protective diffusion barrier preventing Ge out diffusion to the surface.

The XPS corrected peak areas were normalized to the sum of the unshifted Si 2p and Ge 3d peaks as shown in Figure 4.3 to more clearly illustrate the nitride film growth and for quantification of the film thickness and stoichiometry. These substrate normalized XPS ratios are shown following an 1800 Langmuir atomic hydrogen dose at 330°C, an additional 400 MegaLangmuir N$_2$H$_4$ dose at 285°C, 20 SiN$_x$ ALD cycles at 285°C, and a final 1800 Langmuir atomic hydrogen dose at 285°C on Si$_{0.5}$Ge$_{0.5}$(110), Si$_{0.5}$Ge$_{0.5}$(001), and Si$_{0.7}$Ge$_{0.3}$(001) surfaces. The final atomic hydrogen dose was employed after 20 ALD cycles in order to reduce residual chlorine species in the deposited film. The equation \( \ln(I/I_o) = -t/\lambda \) was used to calculate the estimated deposited SiN$_x$ film thickness, where I is the intensity of the sum of unshifted Si 2p and Ge 3d peaks following the N$_2$H$_4$ dose and 20 SiN$_x$ ALD cycles, I$_o$ is the intensity of the sum of
unshifted Si 2p and Ge 3d peaks following the N$_2$H$_4$ dose, “t” is the thickness of the deposited SiN$_x$ layer, and $\lambda$ is the inelastic mean free path of the Si 2p and Ge 3d collected electrons (2.1 nm). The thickness is multiplied by cosine of the emission angle (60°) to account for the glancing angle (30°) of detection. The deposited film is estimated to be a thin silicon rich SiN$_x$ film of ~0.4 nm thick on the Si$_{0.5}$Ge$_{0.5}$(110) surface, and ~0.6 nm thick on the Si$_{0.5}$Ge$_{0.5}$(001), and Si$_{0.7}$Ge$_{0.3}$(001) surfaces.

The stoichiometry of the deposited film was calculated by comparing the actual amount of silicon in a shifted oxidation state detected in the SiON to the theoretical amount of silicon that would be in a shifted oxidation state if the SiON was stoichiometric. The amount of “stoichiometric” SiO$_x$N$_y$ is calculated (a) from the amount of O and N after subtracting the small amount of GeON, and (b) assuming the oxidized Si is in an alloy of SiO$_2$ and Si$_3$N$_4$ to calculate the percentage of silicon in stoichiometric SiO$_x$N$_y$.

(1) Stoichiometric SiO$_x$N$_y$ = Si$_{x/2}$ + $3y/4$ O$_x$N$_y$ = 0.5*(O XPS peak) + 0.75*(N XPS peak – shifted Ge XPS peak)

If there is Si rich silicon sub-oxynitride then the experimental XPS Si signal from SiO$_x$N$_y$>>calculated Si in ideal stoichiometric SiO$_x$N$_y$ = Si$_{x/2}$ + $3y/4$ O$_x$N$_y$ from equation (1). Note, the calculated SiO$_x$N$_y$ from equation (1) does not account for surface carbon and residual chlorine species bonding to silicon.

Figure 4.3 shows the amounts of oxygen, nitrogen, and oxidized silicon and germanium species on the Si$_{0.5}$Ge$_{0.5}$(110) (a), Si$_{0.5}$Ge$_{0.5}$(001) (b), and Si$_{0.7}$Ge$_{0.3}$(001) (c) surfaces after 20 ALD cycles. It is assumed that all GeO$_x$N$_y$ is substoichiometric GeN
due to the small chemical shift found on surface Ge and because oxygen initially bonds only to silicon. The XPS signals shown in Figure 4.3 does not account for variation in film thicknesses nor the depth distributions of O, N, and shifted Si species. For Si$_{0.5}$Ge$_{0.5}$(110), using Eq (1) if all the SiON was stoichiometric (i.e. a mixture of SiO$_2$ and Si$_3$N$_4$) then the shifted Si peak should be 0.56 = calculated stoichiometric SiO$_x$N$_y$ from equation (1); however, the experimental shifted Si is 0.70, therefore the real SiO$_x$N$_y$ is 25% silicon rich (0.70/0.56 = 1.25). Similarly on Si$_{0.5}$Ge$_{0.5}$(001), if all the SiON was stoichiometric (Eq 1), then equal 0.62 but the experimental shifted Si XPS peak is 0.82 indicating the film is 32% silicon rich. On Si$_{0.7}$Ge$_{0.3}$(001), if all the SiON was stoichiometric (Eq 1), then SiO$_x$N$_y$ should equal 0.75, while the shifted Si XPS peak is 0.95 indicating the film is 26% silicon rich. As shown below in the DFT calculations, a silicon rich SiO$_x$N$_y$ may be beneficial since it minimizes formation of Ge-N and Ge-O bonds. 20 ALD cycles on 30% Ge and 50% Ge SiGe(001)/(110) surfaces leaves a substoichiometric silicon rich SiO$_x$N$_y$ film where it is hypothesized that residual Si-Cl and trace Si-O species in the thin deposited film serve to block nitrogen from fully nitriding silicon to stoichiometric Si$_3$N$_4$. The SiO$_x$N$_y$ peak is located at binding energy 101.7 eV on all SiGe(001)/(110) surfaces. Stoichiometric amorphous Si$_3$N$_4$ has a binding energy of 102 eV$^{55}$ and stoichiometric SiO$_2$ has a binding energy of 104 eV$^{56}$ making the measured binding energy in these films consistent with a silicon rich SiO$_x$N$_y$ film predominantly made of SiN$_x$.

4.4.2 STS of SiN$_x$ on SiGe(001) and SiGe(110)
STS measurements probing the local surface density of states of the SiOₓNᵧ/SiGe surface were performed at room temperature as shown in Figure 4.4 (a) – (f). Bilinear fits are shown in Fig. 4.4 (dotted blue and pink lines) so that band edge states are properly fitted; however, for the discussion of the bandgap size, the outer bandgap is reported and, therefore, represents the full bandgap in the presence of band edge states. Therefore, the estimate of the band gaps does not include the VB and CB edge states observed in the narrow band gap spectra, nor the VB band edge states observed in the wide band gap regions. States outside the bandgap of SiGe and near the SiGe band edges are best evaluated with MOSCAP measurements. The Si₀.₅Ge₀.₅(110) surface contains the thinnest deposited film (~0.4 nm from XPS data), and has the largest range of measured band gap energies with 60% of the curves containing a larger band gap of ~1.4 ± 0.02 eV (Fig. 4.4 (a)), and 40% showing a narrow band gap (~1.0± 0.02 eV) (Fig. 4.4 (d)) more reflective of the SiGe substrate, indicating the presence of varying nitride stoichiometry across the surface after the initial 1-3 monolayers of SiNₓ nucleation and growth on the surface. It is hypothesized that the SiOₓNᵧ ALD nucleation on the (110) surface is more difficult because this surface contains smaller domains and increased disorder and roughness, as previously shown in STM and STS studies comparing SiGe(001)/(110) surfaces. The narrow SiNₓ band gap (1 - 1.6 eV) has been previously reported for subnanometer SiNₓ films on Si(001) surfaces by STS measurements at both low and high deposition temperatures. It has been reported that when subnanometer SiNₓ films are deposited at low temperatures (<600°C), SiNₓ grows in a layer by layer fashion and silicon and nitrogen atoms are limited in diffusion across the surface and tend to form incomplete non-stoichiometric Si₃N₄ in which the N atoms have less than
three bonds to Si. The Si$_{0.5}$Ge$_{0.5}$(001) contains a thicker deposited SiO$_x$N$_y$ film (~0.6 nm by XPS) with 90% of surface curves showing a measured averaged band gap of $2.1 \pm 0.02$ eV (Fig. 4.4 (b)), and 10% of the curves showing an averaged narrow band gap (1.1 ± 0.17 eV) (Fig. 4.4 (e)). Similarly, on the Si$_{0.7}$Ge$_{0.3}$(001) surface with ~0.6 nm SiO$_x$N$_y$ film measured by XPS, 90% of surface curves show a measured averaged band gap of $2.1 \pm 0.02$ eV (Fig. 4.4 (c)), and 10% show an averaged narrow band gap (1.09 ± 0.02 eV) (Fig. 4.4 (f)). Note for all surfaces, the absence of midgap states is indicative of surface passivation without formation of unwanted trap defect states. It is hypothesized that with increasing deposited film thickness, the band gap increases towards that expected for a stoichiometric Si$_3$N$_4$ film. Because this work focuses on depositing a thin subnanometer film to passivate the SiGe(001)/(110) surface and protect against germanium out-diffusion, thicker film properties were not investigated. The narrow bandgaps on 10% of the (001) surfaces were not considered an issue since during ALD gate oxide deposition and post deposition anneal, the interfacial silicon will become fully oxidized and, therefore, the interlayer will have a wide bandgap as shown below by the lower gate leakage for devices formed on the N$_2$H$_4$ + Si$_2$Cl$_6$ samples.

4.4.3 SiN$_x$ Interfacial Layer Effect on SiGe/HfO$_2$ MOSCAPs

Following XPS and STS, MOSCAPs were fabricated with and without the insertion of the SiO$_x$N$_y$ layer on both Si$_{0.7}$Ge$_{0.3}$(001) and Si$_{0.5}$Ge$_{0.5}$(001) prior to HfO$_2$ deposition to investigate the electronic structure of the SiO$_x$N$_y$/SiGe interfaces. To deposit a thin SiO$_x$N$_y$ diffusion barrier and still maintain a low EOT, 10-15 cycles of SiN$_x$ ALD (with estimated thickness of 0.2 – 0.3 nm) were employed. In order to determine if
more highly silicon enriched SiN$_x$ film would improve the interface quality, a second SiN$_x$ recipe with half the N$_2$H$_4$ pulse length per ALD cycle was explored for MOSCAP fabrication. MOSCAPs were fabricated following 20 SiN$_x$ ALD cycles with half the N$_2$H$_4$ pulse length per cycle, so that the SiN$_x$ film thickness would be comparable to that from the regular recipe (~ 0.2 – 0.3 nm).

Figure 4.5 shows the C-V characteristics of HfO$_2$/Si$_{0.7}$Ge$_{0.3}$(001) MOSCAPs fabricated following cyclic HF clean (a), 20 cycles of SiN$_x$ ALD with 10 MegaLangmuir N$_2$H$_4$ pulses per cycle (b), and 10 cycles of SiN$_x$ ALD with 20 MegaLangmuir N$_2$H$_4$ pulses per cycle (c). The C-V characteristics were measured for 6 MOSCAPs for each condition shown in (a), (b), and (c). Although the device with HF clean has a higher maximum capacitance in accumulation ($C_{\text{max}}$), it also has a large interface trap feature (known as the $D_{\text{it}}$ bump) observed near the flat band region. In comparison, MOSCAPs with an SiN$_x$ interfacial layer (Figure 4.5 (b) and (c)), showed smaller $D_{\text{it}}$ bumps as well as smaller $C_{\text{max}}$. The lower $C_{\text{max}}$ is consistent with the SiO$_x$N$_y$ layer having a sufficient band gap to prevent accumulation of electrons in the SiO$_x$N$_y$ layer. Moreover, addition of SiN$_x$ at the interface improved the gate leakage characteristics by lowering the maximum gate leakage in accumulation by almost an order of magnitude (Figure 4.5 (d)). While the two MOSCAPs with SiN$_x$ layers have similar $C_{\text{max}}$ values, 10 cycles of SiN$_x$ ALD with the longer N$_2$H$_4$ pulses resulted in smaller $D_{\text{it}}$ bump (Fig. 5c) and lower gate leakage (Fig. 4.5 d), indicating the SiN$_x$ ALD recipe with full saturation of the N$_2$H$_4$ pulse leads to a better interface quality with less chlorine and more nitrogen in the film; note this interlayer is still Si rich (i.e. substoichiometric) compared to a mixture of SiO$_2$ and Si$_3$N$_4$. 
Using the full interface state model for quantitative analysis of the C-V and G-V characteristics, D_{it} versus Fermi energy level (relative to the edge of the valence band) profiles have been extracted for the three above-mentioned MOSCAPs (Figure 4.6). By employing SiN$_x$ ALD, the detectable D_{it} distribution energy range has decreased from 0.15 - 0.65 eV for the HF cleaned sample to 0.15 - 0.51 eV for 20 cycles of SiN$_x$, and 0.15 – 0.45 eV for 10 cycles of SiN$_x$. In addition, the maximum in D_{it} has been lowered by using an SiON interlayer from 1.17 x 10$^{13}$ cm$^{-2}$ eV$^{-1}$ for the HF cleaned sample, to 7.7 x 10$^{12}$ cm$^{-2}$ eV$^{-1}$ and 6.3 x 10$^{12}$ cm$^{-2}$ eV$^{-1}$ for 20 cycles and 10 cycles of SiN$_x$ ALD, respectively. The lower D_{it} comes at the expense of an increase in the equivalent oxide thickness (EOT) as shown in Fig. 4.6 (b). Relative to the HF cleaned sample, ALD deposition of SiN$_x$ resulted in a 0.5 nm EOT increase for 10 ALD cycles and 0.57 nm increase for 20 ALD cycles. Note this increase in EOT is greater than expected from the deposition of 0.2 nm to 0.25 nm of SiN$_x$; the increased EOT may also result from the air exposure after SiN$_x$ deposition and before gate oxide ALD or better nucleation of HfO$_2$ on the SiN$_x$ passivated surfaces. These results are consistent with SiN$_x$ ALD forming an SiON interfacial layer between HfO$_2$ and Si$_{0.7}$Ge$_{0.3}$(001), with bonding states that reduce D_{it} by almost 2x with an EOT increase of just 0.50-0.57 nm.

Figure 4.7 displays the C-V characteristics of HfO$_2$/Si$_{0.5}$Ge$_{0.5}$(001) MOSCAPs fabricated on surfaces with and without SiN$_x$ interfacial layers. Due to low substrate doping and consequently large series resistance, high levels of frequency dispersion in accumulation were observed for Si$_{0.5}$Ge$_{0.5}$(001) MOSCAPs. Therefore, only the low-frequency C-V characteristics (up to 20 kHz) are shown. Relative to the MOSCAPs with cyclic HF clean (Fig. 4.7(a)), addition of SiN$_x$ to the interface (Fig.4.7 (b) and (c)) led to
lower \( C_{\text{max}} \), a smaller \( D_{\text{it}} \) bump, and similar gate leakage in accumulation (Fig. 4.6 (d)). 20 cycles of Si\( N_x \) with 10 MegaLangmuir \( N_2H_4 \) pulse length per cycle (Fig. 4.7 (b)) contains a larger \( D_{\text{it}} \) bump, and an increased false inversion component (observed for \( 1 \text{ V} < V_g < 2\text{ V} \)) in comparison with 15 cycles of Si\( N_x \) ALD with 20 MegaLangmuir \( N_2H_4 \) pulse length per cycle (Fig. 4.7 (c)). In addition, the longer \( N_2H_4 \) pulse length nearly eliminated the false inversion capacitance caused by large density of interface traps closer to the edge of the conduction band of Si\( _{0.5}Ge_{0.5} \) (001). Therefore, a fully saturating \( N_2H_4 \) pulse during Si\( N_x \) ALD results in a better passivation layer on the Si\( _{0.5}Ge_{0.5} \) (001) surfaces consistent with the need for a more nitrogen rich film to reduce Ge out-diffusion for the higher Ge content Si\( _{0.5}Ge_{0.5} \) (001) substrates; note this interlayer is still Si rich (i.e. substoichiometric) compared to a mixture of SiO\(_2\) and Si\(_3N_4\).

### 4.4.4 DFT Simulations of SiO\(_x\)N\(_y\) Interfacial Layers in SiGe/HfO\(_2\) Stacks

DFT molecular dynamics (MD) simulations of a-HfO\(_2\) on a-Si\( N_x \) and a-Si\( O_xN_y \) passivated Si\( _{0.5}Ge_{0.5} \) (001) surfaces are shown in Figure 4.8. Fig. 4.8 (a) shows the gate stack of a-HfO\(_2\) on top of an interfacial layer of substoichiometric a-Si\(_3N_2\) passivating the Si\( _{0.5}Ge_{0.5} \) (001) surface. The calculated HSE06 density of states for the gate stack is shown in Fig. 4.8 (b), where defect states exist across the entire bandgap, and Fig. 4.8 (c) shows the band decomposed charged density visualized for defect states in the energy ranges of \([-0.7; -0.2]\) (eV), and \([-0.2; +0.3]\) (eV) indicated by pink lobes surrounding under-coordinated (3-fold) and over-coordinated (6-fold) silicon atoms with strained bonding inside the a-Si\(_3N_2\) interfacial layer (blue arrows).
Fig. 4.8 (d) shows the gate stack of a-HfO$_2$ on top of a substoichiometric Si-rich a-SiO$_{0.4}$N$_{0.4}$ passivating interfacial layer on the Si$_{0.5}$Ge$_{0.5}$(001) surface. The calculated HSE06 density of states (Fig. 4.8 (e), black curve without H passivation) shows the bandgap decreased by band-edge states and the Fermi level shifted to valence band. To identify sources of these valence band-edge states, the band decomposed charge density was visualized for the energy range of [0, + 0.6] eV (Fig. 4.8 (f)) highlighting a 3-fold under-coordinated germanium atom found below the a-SiON interfacial layer as a primary source of these VBM band-edge states. Dangling bonds on gate-stacks have been passivated experimentally during forming gas annealing in an H$_2$/N$_2$ gas mixture, and to simulate this process a hydrogen atom was inserted to passivate the under-coordinated germanium atom, as shown in Fig. 4.8 (g). The calculated density of states curve (Fig. 4.8 (e), red curve with H passivation) shows that hydrogen passivation of the under-coordinated germanium atom successfully unpins the Fermi level by shifting the Fermi level into the band gap consistent with the experimental STS results for the substoichiometric passivating SiO$_x$N$_y$ layer on the Si$_{0.7}$Ge$_{0.3}$(100) and Si$_{0.5}$Ge$_{0.5}$(100) surfaces.

Figure 4.9 (a) shows the DFT simulation of a-HfO$_2$ on top of an interfacial bilayer of stoichiometric a-SiO$_{0.8}$N$_{0.8}$ passivating the Si$_{0.5}$Ge$_{0.5}$(001) surface. The HSE06 calculated density of states for a stoichiometric a-SiO$_{0.8}$N$_{0.8}$ layer (Fig. 4.9 (a)), and a substoichiometric a-SiO$_{0.4}$N$_{0.4}$ interfacial layer (Fig. 4.8 (d)) gate stacks are shown overlayed in Fig. 4.9 (b), which shows that defect states almost eliminated the band gap for the stoichiometric a-SiO$_{0.8}$N$_{0.8}$ interfacial layer. When comparing the silicon rich substoichiometric a-SiO$_{0.4}$N$_{0.4}$ layer and stoichiometric a-SiO$_{0.8}$N$_{0.8}$ layer, the a-SiO$_{0.8}$N$_{0.8}$
layer contains strained Si-Ge and Si-Si bonds, Ge-O bonds, and Ge-N bonds with oxygen and nitrogen atoms penetrating below the interface and into the SiGe bulk. The silicon rich a-SiO$_{0.4}$N$_{0.4}$ layer contains no Ge-O nor Ge-N bonds, and no strained substrate bonds. The silicon rich a-SiO$_{0.4}$N$_{0.4}$ gate stack has no oxygen or nitrogen penetrating into the SiGe bulk, as oxygen and nitrogen thermodynamically favor bonding with silicon over germanium. As the calculated density of states shown in Figure 4.9 (b) shows that the a-SiO$_{0.4}$N$_{0.4}$ interfacial layer gate stack contains a band gap free of defect states showing the silicon rich film is electrically passivating with higher quality interfacial bonding.

Figure 4.9 (c) shows the DFT simulation of a-HfO$_2$ on top of an interfacial layer of stoichiometric a-Si$_3$N$_4$ passivating the Si$_{0.5}$Ge$_{0.5}$(001) surface. Figure 4.9 (d) shows the corresponding calculated density of states for the model shown in Fig. 4.9 (c) with an overlay of the substoichiometric a-Si$_3$N$_2$ interfacial layer gate stack shown in Fig. 4.8 (a). The calculated density of states for both gate stacks contains defect states throughout the band gap with Fermi level pinning. The stoichiometric a-Si$_3$N$_4$ interfacial layer contains Ge-N bonds and over-coordinated silicon atoms, and similarly the substoichiometric a-Si$_3$N$_2$ layer contains over-coordinated and under-coordinated silicon atoms. The DFT results show stoichiometric a-SiO$_{0.8}$N$_{0.8}$ and a-Si$_3$N$_4$ films pin the surface Fermi level with defect states present throughout the band gap. Both theoretical and experimental results confirm the silicon rich a-SiO$_x$N$_y$ layer electrically passivates the SiGe surface as no defect states are found inside the band gap.

4.5 Conclusions
ALD of a silicon rich SiN_x control layer on Si_{0.7}Ge_{0.3}(001), Si_{0.5}Ge_{0.5}(001), and Si_{0.5}Ge_{0.5}(110) surfaces has been achieved by sequential pulsing of Si_2Cl_6 and N_2H_4 precursors at a substrate temperature of 285°C as shown by XPS. XPS measurements on SiGe(001) and SiGe(110) surfaces indicate the SiO_xN_y thin film creates a diffusion barrier preventing Ge out diffusion as the germanium signal is largely attenuated following SiN_x ALD cycles, with Ge-N bonds localized to the SiO_xN_y/SiGe interface. STS measurements and DFT simulations confirm the silicon rich SiO_xN_y interfacial control layer forms a passivating interfacial layer on the SiGe(001) surface, as the surface Fermi level was unpinned and the electronic structure was free of midgap trap states. DFT calculations show that a Si rich a-SiO_{0.4}N_{0.4} film produces a lower interfacial defect density than stoichiometric a-Si_3N_4 and stoichiometric a-SiO_{0.8}N_{0.8}. MOSCAP device fabrication on p-type Si_{0.7}Ge_{0.3}(001) and Si_{0.5}Ge_{0.5}(001) substrates with the insertion of an SiO_xN_y interfacial control layer show a decrease in frequency dispersion, and midgap trap states for a comparable C_{max} value.

4.6 Acknowledgements

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Chapter 4, is in part or full, reprinted with permission from M. Edmonds, K. Sardashti, S. Wolf, E. Chagarov, M. Clemons, T. Kent, J. H. Park, K. Tang, P. McIntyre, N. Yoshida, L. Dong, W. Tsai, H. Luan, Z. Fang, D. Alvarez, R. Holmes, and A. C. Kummel, “Low Temperature Thermal ALD of a SiN_x Interfacial Diffusion Barrier and Interface Passivation Layer on Si_xGe_{1-x}(001) and Si_xGe_{1-x}(110),” (manuscript submitted
4.7 Supplemental Materials

4.7.1 DFT molecular dynamics generation of a-SiO$_x$N$_y$/SiGe interlayers

The sub-stoichiometric a-SiO$_x$N$_y$ interlayers on the SiGe substrate were generated placing N and O atoms randomly on a SiGe slab terminated with two layers of Si with a DFT-optimized lattice constant for bulk SiGe. The interlayer topmost semiconductor layer originally included Ge atoms which were later substituted by Si atoms to form a-Si$_x$N$_y$ and a-SiO$_x$N$_y$ interlayers. The N and O atoms were added individually at random locations avoiding strong agglomeration. The N and O atoms were added in two steps: sufficient O and N were added to form subnitride (Si$_3$N$_2$) or sub-oxynitride (SiO$_{0.4}$N$_{0.4}$); the bilayer of silicon contained 16 Si atoms so 11 N atoms or 7 O and 7 N atoms were added for the subnitride and suboxynitride. The initial configurations for the interlayer formation are presented in Fig. 4.10. The dashed boxes delineate bulk SiGe and the interlayer. The bulk has 40 Si and 40 Ge atoms. The 3 bottom layers of the SiGe slab were permanently fixed in the bulk-like positions and saturated by relaxed H atoms to simulate a continuous bulk.

After placement of the interlayer atoms for the subnitride and suboxynitride, the stack was DFT-MD annealed at 800K for 1000 fs with timestep 1 fs, cooled to 0K for 200 fs and relaxed to the ground state configuration below force-tolerance level of 0.05 eV/Å. For stoichiometric Si$_3$N$_4$ and SiO$_{0.8}$N$_{0.8}$, after the slabs were annealed and relaxed, the 2$^{nd}$ layer of O/N atoms (11 N atoms or 7 O and 7 N atoms were added for the
subnitride and suboxynitride) was deposited randomly; subsequently, the slab was again annealed-cooled-relaxed using the same sequence as described previously.

The relaxed configurations are presented in Fig. 4.11. The a-Si$_3$N$_2$ interlayer includes 16 Si and 11 N atoms (Fig. 4.11 (a)), the a-Si$_3$N$_4$ interlayer includes 16 Si and 21 N atoms (Fig. 4.11 (b)). The a-SiO$_{0.4}$N$_{0.4}$ interlayer includes 16 Si, 7 O, and 7 N atoms (Fig. 4.11 (c)), the a-SiO$_{0.8}$N$_{0.8}$ interlayer includes 16 Si, 13 O, and 13 N atoms (Fig. 4.11 (d)). N$_2$ and O$_2$ left the stacks several times during annealing, and the escaped molecules were returned to the surface and annealing-cooling-relaxation was continued.

### 4.7.2 Validation of a-HfO$_2$/a-SiO$_x$N$_x$/SiGe DFT-MD simulations

To investigate variation of obtained interface electronic properties as a function of simulation parameters two stacks - a-HfO$_2$/a-SiO$_{0.4}$N$_{0.4}$/SiGe and a-HfO$_2$/a-SiO$_{0.8}$N$_{0.8}$/SiGe were re-simulated with 2 simulation variations. As a first variation, annealing temperature was changed from 800K to 600K followed by same cooling and relaxation. As a second variation, annealing time at 800K was increased from 1000 fs to 2000 fs followed by the same cooling and relaxation procedure. These 2x2 variations generated 4 additional a-HfO$_2$/a-SiO$_x$N$_x$/SiGe stacks. The calculated HSE06 DOS curves for these stacks are summarized in Fig. 4.12.

For the sub-stoichiometric a-HfO$_2$/a-SiO$_{0.4}$N$_{0.4}$/SiGe stack, the switching of annealing temperature from 800K to 600K had a minor effect on DOS curve slightly decreasing the CBM band-edge state and increasing the bandgap (Fig. 4.12 (a)). The increasing annealing time at 800K from 1000 fs to 2000 fs had a greater effect on the DOS increasing the CBM band-edge state and decreasing the bandgap (Fig. 4.12 (a)).
For the fully-stoichiometric a-HfO$_2$/a-SiO$_{0.8}$N$_{0.8}$/SiGe stack the switching of annealing temperature from 800K to 600K showed minor effects on DOS curve slightly shifting the seriously reduced bandgap vs. Fermi level (Fig. 4.12 (b)). The increasing annealing time at 800K from 1000 fs to 2000 fs had a more significant effect on DOS curve increasing the bandgap and shifting Fermi level from CBM to VBM region (Fig. 4.12 (b)). The simulation variations are consistent with the suboxynitride a-HfO$_2$/a-SiO$_{0.4}$N$_{0.4}$/SiGe forming a more stable interlayer-SiGe interface while the a-HfO$_2$/a-SiO$_{0.8}$N$_{0.8}$/SiGe forms a less stable a-HfO$_2$/a-SiO$_{0.8}$N$_{0.8}$/SiGe. This is likely due to high propensity of the stoichiometric a-SiO$_{0.8}$N$_{0.8}$ to form dangling bonds in the IL and disrupt the SiGe substrate creating dangling bonds.

4.7.3 Typical raw XPS peak areas showing ALD Saturation on Si$_{0.5}$Ge$_{0.5}$(110) and Si$_{0.7}$Ge$_{0.3}$(001)

Figure 4.13 shows the XPS raw peak areas collected during the course of ALD Saturation on Si$_{0.5}$Ge$_{0.5}$(110) (4.13 (a) – (c)) and Si$_{0.7}$Ge$_{0.3}$(001) (4.13 (d) –(f)) surfaces. XPS raw peak areas of Si 2p (both the total Si 2p peak area and the higher binding energy component of Si 2p), N 1s, and Ge 2p are shown to emphasize surface saturation. XPS peaks are shown following an 1800 Langmuir atomic hydrogen dose at 330°C, 400 MegaLangmuir N$_2$H$_4$ dose at 285°C, 1X Si$_2$Cl$_6$ dose at 285°C, 3X additional Si$_2$Cl$_6$ dose at 285°C, 1X N$_2$H$_4$ dose at 285°C, and 3X N$_2$H$_4$ dose at 285°C. Note, the typical as-loaded wet cleaned Si$_{0.7}$Ge$_{0.3}$(001) shows 40-50% carbon on the surface. Figure 4.14 shows XPS raw peak areas for C1s, O 1s, and Cl 2p on Si$_{0.5}$Ge$_{0.5}$(110) (4.14 (a) – (c)) and Si$_{0.7}$Ge$_{0.3}$(001) (4.14 (d) –(f)) surfaces. XPS peaks are shown following an 1800
Langmuir atomic hydrogen dose at 330°C, 400 MegaLangmuir N$_2$H$_4$ dose at 285°C, 1X Si$_2$Cl$_6$ dose at 285°C, 3X additional Si$_2$Cl$_6$ dose at 285°C, 1X N$_2$H$_4$ dose at 285°C, and 3X N$_2$H$_4$ dose at 285°C. Note, the carbon and oxygen are residual from the combined wet and dry cleaning preparation method to prepare the surface for deposition. A negligible increase in carbon or oxygen is seen during the deposition process.
Figure 4.1 XPS of ALD Saturation on Si$_{0.5}$Ge$_{0.5}$(110) and Si$_{0.7}$Ge$_{0.3}$(001). (a) Si$_{0.5}$Ge$_{0.5}$(110) and (b) Si$_{0.7}$Ge$_{0.3}$(001). XPS corrected peak areas of Si 2p (both the total Si 2p peak area and the higher binding energy component of Si 2p), Ge 3d, O 1s, C 1s, N 1s, and Cl 2p are normalized to the sum of all Si 2p and Ge 3d peaks. Composition based on XPS are shown following an 1800 Langmuir atomic hydrogen dose at 330°C, 400 MegaLangmuir N$_2$H$_4$ dose at 285°C, 1X Si$_2$Cl$_6$ dose (13.5 MegaLangmuir) at 285°C, 3X additional Si$_2$Cl$_6$ dose (40.5 MegaLangmuir) at 285°C, 1X N$_2$H$_4$ dose (20 MegaLangmuir) at 285°C, and 3X N$_2$H$_4$ dose (60 MegaLangmuir) at 285°C. The percent nitrogen is indicated in gold and percent chlorine in magenta. Note, the typical as-loaded wet cleaned Si$_{0.7}$Ge$_{0.3}$(001) shows 40-50% carbon on the surface. (c) Schematic diagram showing the SiGe(001)/(110) surface atomic hydrogen cleaning, initial N$_2$H$_4$ prepulsing, and ALD half cycle surface reactions.
Figure 4.2 XPS Spectra of Si$_{0.5}$Ge$_{0.5}$(110), Si$_{0.5}$Ge$_{0.5}$(001),Si$_{0.7}$Ge$_{0.3}$(001) after ALD with N$_2$H$_4$(g) and Si$_2$Cl$_6$(g). (a) – (c) XPS of ALD on Si$_{0.5}$Ge$_{0.5}$(110); (d) – (f) XPS of ALD Si$_{0.5}$Ge$_{0.5}$(001) ; and (g) – (i) XPS of ALD on Si$_{0.7}$Ge$_{0.3}$(001). XPS fitted raw peak areas are shown for Si 2p, N 1s, and Ge 2p peaks on the as-loaded wet cleaned SiGe surfaces following an 1800 Langmuir atomic hydrogen dose at 330°C, an additional 400 MegaLangmuir N$_2$H$_4$ dose at 285°C, and an additional 20 SiN$_x$ ALD cycles of Si$_2$Cl$_6$(g) and N$_2$H$_4$(g) at 285°C.
Figure 4.3 XPS Derived Surface Compositions of $\text{Si}_{0.5}\text{Ge}_{0.5}(110)$, $\text{Si}_{0.5}\text{Ge}_{0.5}(001)$, $\text{Si}_{0.7}\text{Ge}_{0.3}(001)$ after ALD with $\text{N}_2\text{H}_4(\text{g})$ and $\text{Si}_2\text{Cl}_6(\text{g})$. (a) $\text{Si}_{0.5}\text{Ge}_{0.5}(110)$, (b) $\text{Si}_{0.5}\text{Ge}_{0.5}(001)$ and (c) $\text{Si}_{0.7}\text{Ge}_{0.3}(001)$ XPS corrected peak areas of unshifted Si 2p, unshifted Ge 3d, $\text{SiO}_{x}\text{N}_y$, $\text{GeO}_{x}\text{N}_y$, O 1s, C 1s, N 1s, and Cl 2p normalized to the sum of unshifted Si 2p and unshifted Ge 3d peaks following an 1800 Langmuir atomic hydrogen dose at 330°C, 400 MegaLangmuir $\text{N}_2\text{H}_4$ dose at 285°C, and following an additional 20 SiN$_x$ ALD cycles and final atomic hydrogen dose at 285°C.
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Figure 4.4. STS of Si_{0.5}Ge_{0.5}(110), Si_{0.5}Ge_{0.5}(001), Si_{0.7}Ge_{0.3}(001) after N_2H_4 + Si_2Cl_6 ALD. STS on (a) and (d) p-type Si_{0.5}Ge_{0.5}(110), (b) and (e) p-type Si_{0.5}Ge_{0.5}(001), (c) and (f) p-type Si_{0.7}Ge_{0.3}(001) following an 1800 L atomic H dose at 330°C, an additional 400 MegaLangmuir N_2H_4 dose at 285°C, an additional 20 SiN_x ALD cycles at 285°C, and a final 1800 L atomic H dose at 285°C. Both narrow and wider band gap curves are measured across all surfaces and are reported here. Note the absence of band gap trap states indicative of surface passivation.
Figure 4.5 C-V characteristics of Si$_{0.7}$Ge$_{0.3}$(001) MOSCAPs with 40 cycles of HfO$_2$ deposited by ALD. C-V curves after (a) HF cyclic clean; (b) 20 cycles of SiN$_X$ ALD with 10 MegaLangmuir N$_2$H$_4$ pulse length per cycle; (c) 10 cycles of SiN$_X$ ALD with 20 MegaLangmuir N$_2$H$_4$ pulse length per cycle. Gate leakage characteristics of the three MOSCAPs are shown in (d).
Figure 4.6 Density of interfacial trap states (\(D_{it}\)) and equivalent oxide thicknesses (EOT) for Si\(_{0.7}\)Ge\(_{0.3}\) MOSCAPs with 40 cycles of HfO\(_2\) deposited by ALD. (a) \(D_{it}\) vs. \(E_F - E_v\) for HF cyclic clean, 20 cycles of SiN\(_x\) ALD, and 10 cycles of SiN\(_x\) ALD with 2x longer \(N_2H_4\) pulses. (b) EOT values for HF cyclic clean, 20 cycles of SiN\(_x\) ALD, and 10 cycles of SiN\(_x\) ALD with 2x longer \(N_2H_4\) pulses.
Figure 4.7 C-V characteristics of Si$_{0.5}$Ge$_{0.5}$(001) MOSCAPs with 40 cycles of HfO$_2$ deposited by ALD. C-V spectra of: (a) HF cyclic clean; (b) 20 cycles of SiN$_X$ ALD (10 MegaLangmuir N$_2$H$_4$ pulse length); (c) 15 cycles of SiN$_X$ ALD with 2x longer N$_2$H$_4$ pulses (20 MegaLangmuir N$_2$H$_4$ pulse length). NOTE: Due to low substrate doping and large series resistance, only the low-frequency C-V characteristics at 2 – 20 kHz are shown here. Gate leakage characteristics of the three MOSCAPs are shown in (d).
Figure 4.8 DFT-MD simulations of gate stack a-HfO$_2$/a-Si$_3$N$_2$/SiGe stack with silicon rich substoichiometric a-Si$_3$N$_2$ interfacial layer. (a) a-HfO$_2$/a-Si$_3$N$_2$/SiGe stack with silicon rich substoichiometric a-Si$_3$N$_2$ interfacial layer. (b) HSE06 calculated density of states of gate stack shown in (a). Ef=0.0 eV. (c) band-decomposed charge density of a-HfO$_2$/a-Si$_3$N$_2$/SiGe with silicon rich substoichiometric a-Si$_3$N$_2$ interlayer at [-0.7; -0.2] eV, and [-0.2, + 0.3] eV. Pink lobes surrounds under-coordinated (3-fold) and over-coordinated (6-fold) silicon atoms with strained bonding found inside the a-Si$_3$N$_2$ interfacial layer, as pointed out by the blue arrows. (d) a-HfO$_2$/SiO$_{0.4}$N$_{0.4}$/SiGe stack with silicon rich substoichiometric a-SiO$_{0.4}$N$_{0.4}$/SiGe interfacial layer. (e) calculated density of states of a-HfO$_2$/SiO$_{0.4}$N$_{0.4}$/SiGe stack without (d) and with H passivation (g). Ef=0.0 eV. (f) a-HfO$_2$/SiO$_{0.4}$N$_{0.4}$/SiGe and-decomposed charge density visualized for the energy range [0; + 0.6] eV showing a 3-fold under-coordinated germanium atom found below the a-SiON interfacial layer. (g) Gate stack shown in (d) with the 3-fold coordinated defective germanium atom passivated by a hydrogen atom.
Figure 4.9 DFT simulations of gate stack a-HfO$_2$/stoichiometric SiO$_x$N$_y$ layer/Si$_{0.5}$Ge$_{0.5}$(001). (a) a-HfO$_2$/a-SiO$_{0.8}$N$_{0.8}$/SiGe gate stack with stoichiometric a-SiO$_{0.8}$N$_{0.8}$ interfacial layer. (b) Calculated density of states for a-HfO$_2$/a-SiO$_{0.8}$N$_{0.8}$/SiGe stack (red curve) shown in (a) overlayed with the results for a-HfO$_2$/a-SiO$_{0.4}$N$_{0.4}$/SiGe stack (black curve) shown in Fig. 4.8-d. Ef=0.0 eV for both curves. (c) a-HfO$_2$/a-Si$_3$N$_4$/SiGe gate stack with stoichiometric a-Si$_3$N$_4$ interfacial layer. (d) Calculated density of states for a-HfO$_2$/a-Si$_3$N$_4$/SiGe stack (red curve) shown in (c) overlayed with results for a-HfO$_2$/a-Si$_3$N$_2$/SiGe (black curve) shown in Fig. 4.8-a. Ef=0.0 eV for both curves.
Figure 4.10 Initial atomic configurations for a-Si$_3$N$_2$/SiGe and a-SiO$_{0.4}$N$_{0.6}$/SiGe. Dashed boxes delineate bulk and interlayer regions. Ge-green, Si-yellow, O-red, Al-blue, H-white.
Figure 4.11 DFT-MD annealed, cooled and relaxed a-SiO$_{x}$N$_{y}$/SiGe slabs. Ge-green, Si-yellow, O-red, Al-blue, H-white.
Figure 4.12 HSE06 DOS curves for the a-HfO$_2$/a-SiO$_{0.8}$N$_{0.8}$/SiGe and a-HfO$_2$/a-SiO$_{0.4}$N$_{0.4}$/SiGe stacks with various annealing time and temperature. $E_F=0$ eV for all curves.
Figure 4.13 XPS raw peak areas showing ALD Saturation on Si$_{0.5}$Ge$_{0.5}$(110) and Si$_{0.7}$Ge$_{0.3}$(001). Si$_{0.5}$Ge$_{0.5}$(110) (4.13 (a) – (c)) and Si$_{0.7}$Ge$_{0.3}$(001) (4.13 (d) –(f)). XPS raw peak areas of C1s, O 1s, and Cl 2p are shown. XPS peaks are shown following an 1800 Langmuir atomic hydrogen dose at 330°C, 400 MegaLangmuir N$_2$H$_4$ dose at 285°C, 1X Si$_2$Cl$_6$ dose at 285°C, 3X additional Si$_2$Cl$_6$ dose at 285°C, 1X N$_2$H$_4$ dose at 285°C, and 3X N$_2$H$_4$ dose at 285°C. Note, the carbon and oxygen are residual from the combined wet and dry cleaning preparation method to prepare the surface for deposition. A negligible increase in carbon or oxygen is seen during the deposition process.
Figure 4.14 XPS raw peak areas for C 1s, Cl 2p, O 1s on Si$_{0.5}$Ge$_{0.5}$(110) and Si$_{0.7}$Ge$_{0.3}$(001). Si$_{0.5}$Ge$_{0.5}$(110) ((a) – (c)) and Si$_{0.7}$Ge$_{0.3}$(001) ((d) – (f)). XPS peaks are shown following an 1800 Langmuir atomic hydrogen dose at 330°C, 400 MegaLangmuir N$_2$H$_4$ dose at 285°C, 1X Si$_2$Cl$_6$ dose at 285°C, 3X additional Si$_2$Cl$_6$ dose at 285°C, 1X N$_2$H$_4$ dose at 285°C, and 3X N$_2$H$_4$ dose at 285°C. Note, the carbon and oxygen are residual from the combined wet and dry cleaning preparation method to prepare the surface for deposition. A negligible increase in carbon or oxygen is seen during the deposition process.
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