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In-Situ Cleaning, Passivation, Functionalization, and Atomic Layer Deposition on Germanium and Silicon-Germanium

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy in Materials Science and Engineering

by

Tobin Adar Kaufman-Osborn

Committee in charge:

Professor Andrew Kummel, Chair
Professor Shadi Dayeh
Professor Vitali Nesterenko
Professor William Trogler
Professor Paul Yu

2014
The dissertation of Tobin Adar Kaufman-Osborn is approved, and it is acceptable in quality and form for publication on microfilm and electronically:

Chair

University of California, San Diego

2014
DEDICATION

To my grandfather, Irving Kaufman, who overcame incredible challenges in his life and inspired me through his love of physics and engineering.
EPIGRAPH

“the highest forms of understanding we can
achieve are laughter and human compassion”

- Richard Phillips Feynman
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CHAPTER 4

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<tbody>
<tr>
<td>A</td>
<td>Ampere</td>
</tr>
<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>Sb</td>
<td>Antimony</td>
</tr>
<tr>
<td>AC</td>
<td>Alternating Current</td>
</tr>
<tr>
<td>Al</td>
<td>Aluminum</td>
</tr>
<tr>
<td>$V_{\text{applied}}$</td>
<td>Applied Voltage</td>
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<tr>
<td>(aq)</td>
<td>Aqueous Phase</td>
</tr>
<tr>
<td>Ar</td>
<td>Argon</td>
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<tr>
<td>ALD</td>
<td>Atomic Layer Deposition</td>
</tr>
<tr>
<td>C</td>
<td>Carbon</td>
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<tr>
<td>C</td>
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<td>Centimeter</td>
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<tr>
<td>Cl</td>
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<tr>
<td>CMOS</td>
<td>Complementary Metal-Oxide-Semiconductor</td>
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<tr>
<td>CB</td>
<td>Conduction Band</td>
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<tr>
<td>$E_C$</td>
<td>Conduction Band Energy</td>
</tr>
<tr>
<td>I</td>
<td>Current</td>
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<tr>
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<tr>
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<tr>
<td>$D_{it}$</td>
<td>Density of Interface Traps</td>
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<tr>
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<td>Density of States</td>
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</table>
eV  Electron Volt
E  Energy
EOT  Equivalent Oxide Thickness
$E_F$  Fermi Energy
Fig.  Figure
(g)  Gas Phase
Ge  Germanium
>  Greater Than
Hf  Hafnium
Hz  Hertz
H  Hydrogen
$\text{H}_2\text{O}_2$  Hydrogen Peroxide
-OH  Hydroxyl
K  Kelvin
kj  Kilojoule
L  Langmuir
LEED  Low Energy Electron Diffraction
<  Less Than
LL  Load Lock
LT  Low Temperature
MOSFET  Metal-Oxide-Semiconductor Field Effect Transistor
mm  Millimeter
<table>
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<tr>
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<td>Millitorr</td>
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<tr>
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</tr>
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</tr>
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<tr>
<td>MMA</td>
<td>Monomethylaluminum</td>
</tr>
<tr>
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<td>Nanoampere</td>
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<tr>
<td>m</td>
<td>Nanometer</td>
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<tr>
<td>PAW</td>
<td>Projector Augmented-Wave</td>
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<tr>
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<td>Perdew-Burke-Emzerhof</td>
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<tr>
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<td>Phosphorous</td>
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<td>Picometer</td>
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<td>Pressure</td>
</tr>
<tr>
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<tr>
<td>PBN</td>
<td>Pyrolytic Boron Nitride</td>
</tr>
<tr>
<td>RMS</td>
<td>Root Mean Squared</td>
</tr>
<tr>
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<tr>
<td>STM</td>
<td>Scanning Tunneling Microscope</td>
</tr>
<tr>
<td>STS</td>
<td>Scanning Tunneling Spectroscopy</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
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<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>sec</td>
<td>Second</td>
</tr>
<tr>
<td>Si</td>
<td>Silicon</td>
</tr>
<tr>
<td>SiGe</td>
<td>Silicon-Germanium</td>
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<tr>
<td>Ta</td>
<td>Tantalum</td>
</tr>
<tr>
<td>TMA</td>
<td>Trimethylaluminum</td>
</tr>
<tr>
<td>( I_t )</td>
<td>Tunneling Current</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra High Vacuum</td>
</tr>
<tr>
<td>VASP</td>
<td>Vienna \textit{ab initio} simulation code</td>
</tr>
<tr>
<td>V</td>
<td>Volt</td>
</tr>
<tr>
<td>VB</td>
<td>Valance Band</td>
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<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>Zr</td>
<td>Zirconium</td>
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non-disruptive cleaning of Ge(100) using H₂O₂(g) and atomic hydrogen”,
Surface Science (2014).

Chapter 3, in part or in full, is a reprint of the following material. The dissertation author is the primary investigator and author of this paper:

T. Kaufman-Osborn, E. Chagarov, A. Kummel, “Atomic imaging and
modeling of H₂O₂(g) surface passivation, functionalization, and atomic layer
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Physics, 140, 204708 (2014).

Chapter 4, in part or in full, is a reprint of the following material. The dissertation author is the primary investigator and author of this paper:

imaging and modeling of passivation, functionalization, and atomic layer
deposition nucleation of the SiGe(001) surface via H₂O₂(g) and
VITA

EDUCATION

2014  Doctor of Philosophy in Materials Science and Engineering  
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2007  Bachelor of Arts in Physics and Astronomy  
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PUBLICATIONS


2. T. Kaufman-Osborn, E. Chagarov, S.W. Park, B. Sahu, A. Kummel, “Atomic imaging and modeling of passivation, functionalization, and atomic layer deposition nucleation of the SiGe(001) surface via H₂O₂(g) and trimethylaluminum dosing”, Submitted to *Surface Science*, (2014).


**FIELD OF STUDY**

Major Field: Materials Science and Engineering (Surface Science)

Studies in Semiconductor Surface Passivation and Functionalization
Professor Andrew C. Kummel

Studies in Dry Cleaning Semiconductor Surfaces
Professor Andrew C. Kummel
ABSTRACT OF THE DISSERTATION

In-Situ Cleaning, Passivation, Functionalization, and Atomic Layer Deposition on Germanium and Silicon-Germanium

by

Tobin Adar Kaufman-Osborn

Doctor of Philosophy in Materials Science and Engineering

University of California, San Diego, 2014

Professor Andrew Kummel, Chair

In recent years, germanium (Ge) and silicon-germanium (SiGe) have drawn significant interest as replacements of conventional silicon in the search for alternative materials for use in complementary metal-oxide-semiconductor (CMOS) devices due to their high electron and hole mobilities. In order to effectively implement Ge or SiGe as a replacement for silicon, two major challenges must be overcome: non-disruptive cleaning and surface passivation/functionalization.

As electrical devices are increasingly scaled, it becomes especially crucial to effectively clean each unit cell on the Ge/SiGe surface without causing major disruption or damage to the surface. If air-induced defects or contaminants persist on the surface after cleaning, these defect sites may be un-reactive for functionalization.
and thereby will hinder device performance and/or the ability to aggressively scale device size. If a cleaning method is too aggressive leaving a rough or disordered surface, this can lower the mobility at the interface which will worsen device performance. For these reasons, it is necessary to develop a non-disruptive cleaning process that cleans each unit cell leaving a flat, ordered, and reactive surface.

Once the Ge or SiGe surface is cleaned, in order to achieve a good electrical quality interface and a high nucleation density on the surface, all surface atoms must be passivated and functionalized allowing for aggressive device scaling. The interface must remain electrically passive in order to not inhibit electrical performance of the device.

This study uses scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), and x-ray photoelectron spectroscopy (XPS) to develop and analyze a completely in-situ non-disruptive cleaning method of the Ge surface using H$_2$O$_2$(g) and atomic hydrogen. After cleaning, the Ge or SiGe surface is passivated and functionalized using H$_2$O$_2$(g) as a method to improve upon the conventional H$_2$O(g) passivation method by more than doubling the reactive –OH groups on the surface. Once a high density of –OH chemisorbates passivate and functionalize the surface, trimethylaluminum is dosed onto the surface forming a thermally stable and electrically passive monolayer which can serve as an ideal template for further high-k oxide deposition.
Chapter 1

Experimental Setup

1.1 The Chamber

The research conducted in this dissertation was performed in an ultra high vacuum (UHV) chamber. The UHV chamber (Omicron NanoTechnology) has two main chambers: the preparation chamber and the analysis chamber. The analysis chamber has a low temperature scanning tunneling microscopy (LT-STM) capable of operating in the range of 4.2-300K. Topographical (scanning tunneling microscopy) and electrical analysis (scanning tunneling spectroscopy) is performed in the analysis chamber while the pressure is maintained below 2×10^{-11} Torr. The preparation chamber is equipped with an Omicron Nanotechnology monochromatic x-ray photoelectron spectroscopy (XPS) system (XM 1000 MkII/SPHERA) and a low energy electron diffraction (LEED) system (Omicron NanoTechnology). For sample preparation and processing, the preparation chamber has a Veeco hot tungsten filament atomic hydrogen source, a Nonsequitur Technologies (Model 1403) ion gun, and a pyrolytic boron nitride (PBN) heater for sample annealing. The base pressure of the preparation chamber is 1×10^{-10} Torr. The pressure is maintained in the preparation and analysis chamber with Varian Starcell ion pumps.

Attached to the preparation chamber is a custom built dual chamber load lock (LL) / atomic layer deposition (ALD) chamber. Samples are introduced into the chamber via the LL. The ALD chamber attached to the LL is capable of heating the sample. In the ALD chamber, precursors (water, hydrogen peroxide,
trimethylaluminum) are delivered to the sample via a series of valves. Alternatively, the ALD chamber can be equipped with an Othos McCarroll cavity and microwave generator (Sairem Model GMP 03 K/SM) to dose atomic hydrogen at higher pressures (compared to the preparation chamber atomic hydrogen source). The ALD chamber has a base pressure of 1×10⁻⁷ Torr. A schematic of the entire chamber is shown in Figure 1.1.

1.2 Scanning Tunneling Microscopy

This dissertation focuses on cleaning, passivating, and functionalizing semiconductor surfaces for oxide deposition. One of the most powerful techniques to study the atomic and electronic structure of the semiconductor/oxide interface is scanning tunneling microscopy (STM). STM collects surface morphology information on an atomic level while also having the capability to gather surface density of state information via scanning tunneling spectroscopy (STS).

STM was invented in 1981 by G. Binnig and H. Rohrer and capitalizes on quantum mechanical tunneling of electrons between the tip and sample. [1-3] A schematic diagram of the basic principle of STM is shown in Figure 1.2. The metallic tip, usually tungsten, is placed approximately 10Å away from the surface. A voltage is then applied to either the tip or the sample. This bias generates quantum mechanical tunneling between the tip and the sample surface and is proportional to the distance between the tip and the sample. The current generated due to this tunneling is given by:

\[ I \propto Ve^{-kz} \]  

(1.2.1)
where $V$ is the applied voltage between the tip and the sample, $k$ describes the decay of the wave through the vacuum barrier, and $z$ is the distance between the sample and the tip.

During STM imaging, the tip scans above the surface in the $x$ and $y$ plane while measuring the tunneling current. In constant current mode, the tip to sample distance is changed via a feedback loop in order to maintain a constant tunneling current while the height is recorded. The vertical movement of the tip maps the surface with atomic resolution. The resulting STM image is a convolution of the electronic and topographic structure of the surface. Adjusting the voltage bias between the tip and the sample probes different surface states in the material. Figure 1.3 shows a schematic of the tunneling process between a semiconductor surface and the metal tip. When the tip has a positive bias relative to the surface, this lowers the Fermi level of the tip below the valance band edge of the semiconductor resulting in electrons tunneling from the semiconductor to the tip and is known as filled state imaging. Empty state imaging results when the tip has a negative bias relative to the semiconductor and the Fermi level of the tip is above the conduction band edge resulting in electrons tunneling from the tip to the semiconductor.

1.3 Scanning Tunneling Spectroscopy

STS is another powerful capability of a scanning tunneling microscope. During STS, the tip’s height relative to the surface is fixed while the voltage bias is modulated. This technique is used to measure the density of states (DOS) of the sample surface. Fig. 1.4 shows a basic schematic diagram of the circuit used for STS.
Tersoff’s tunneling theory states that the differential conductance (dI/dV) acquired during STS is proportional to the DOS of the sample surface. [4; 5] To collect this information, the sample bias is swept in the desired range in order to collect current and voltage data. While doing this, an AC signal is applied as well, and the signal is sent to a lock-in amplifier. The lock-in amplifier uses the AC signal to extract the differential conductance and the surface DOS can be calculated using the following equation:

$$\frac{(dI/dV)}{(I/V)} \propto DOS_{\text{sample}}(E_F-eV)$$  (1.1.2)

STS can be used to measure the Fermi level (defined as 0V sample bias) of the surface relative to the valance band (VB) and conduction band (CB). This analysis technique is useful when determining whether a surface is pinned or unpinned. Detailed resources describing the STS technique can be found in the literature. [4-14]

### 1.4 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) uses photo-ionization to excite a sample thereby emitting photoelectrons. The kinetic energy distribution of the emitted photoelectrons contains information regarding the composition and electronic state of each element. Each element has a characteristic binding energy associated with each core atomic orbital. When excited via x-rays, atoms near the surface (with ~10nm) emit photoelectrons with a kinetic energy proportional to that of the incoming x-rays and the respective binding energy of the elements.

In addition to collecting compositional information, XPS collects chemical shift information which is affected by changes in oxidation states or the chemical or physical environment of the atoms. This chemical shift data is very useful in
explaining the atomic bonding taking place near the surface of the sample. In this dissertation, XPS was used to quantify the amount of adsorbates on a surface after a given dose of precursors or to verify cleanliness and reduction of contaminants on the surface. XPS data complements STM and STS data to provide a more clear understanding of the quality, bonding structure, and elemental composition of sample surfaces.

1.5 Density Functional Theory

Density functional theory (DFT) is an ab-initio quantum mechanical modeling method used to investigate the electronic structure of many body systems. In this dissertation, DFT is used to theoretically model the ground state (lowest energy) of surface reconstructions, bonding structures, density of state information, and bonding energies. DFT models are correlated with experimental data acquired via STM to verify bonding structures of precursors reacted to semiconductor surfaces. DFT DOS simulations are compared to STS in order to further describe the electronic interaction between chemisorbates and the semiconductor surface.

1.6 Outline of the Dissertation

This dissertation focuses on two semiconductor materials that are garnering increasing attention due to limitations in silicon based electronic devices. Germanium (Ge) and Silicon-Germanium (SiGe) are quite attractive replacements for pure silicon based devices due to their high hole and electron mobilities. The first part of this dissertation describes cleaning of the pure germanium surface while the second part describes passivating, functionalizing, and nucleating ALD on the Ge and SiGe surfaces. Throughout both sections, the surfaces are analyzed via STM, STS, and XPS.
Chapter 2 reports upon developing a non-disruptive in-situ dry process to effectively clean the Ge surface. Air exposed Ge surfaces are cleaned of carbon contamination via H$_2$O$_2$(g) dosing at 300°C. The resulting oxide left on the surface after H$_2$O$_2$(g) dosing is removed via one of two methods: > 550°C annealing or atomic hydrogen dosing at 300°C. While using atomic hydrogen at 300°C leaves a contaminant free surface, only using high temperature annealing (> 600°C) will produce a flat and ordered surface that can be imaged via STM.

In chapter 3, H$_2$O$_2$(g) is used to passivate the Ge surface. H$_2$O$_2$(g) functionalizes the Ge surface with a high density of hydroxyl (-OH) groups which are reactive to metal precursors. STM imaging and DFT modeling confirms H$_2$O$_2$(g) functionalizing improves upon conventional H$_2$O(g) functionalization techniques by more than doubling the density of reactive –OH groups while adding thermal stability. Trimethylaluminum (TMA) is then reacted with the surface forming a thermally stable Ge-O-Al monolayer. While the H$_2$O$_2$(g) dosed Ge surface has a Fermi level pinned p-type, dosing TMA followed by annealing successfully unpins the surface leaving an electrically passive thermally stable monolayer that can serve as an excellent template for further high-k deposition.

Chapter 4 presents an STM, XPS, and DFT based study that explores the passivation and functionalization of the SiGe surface via H$_2$O$_2$(g) dosing. The SiGe surface after sputter and annealing is terminated with a full Ge monolayer. Dosing H$_2$O$_2$(g) at 300K onto the surface results in a high density of reactive –OH groups bonded to the surface Ge atoms. Upon annealing the surface, the oxygen atoms in the surface –OH groups induce a place exchange between Ge and Si pulling Si to the
surface while pushing Ge subsurface due to the difference in bond strength of Si-O vs. Ge-O. This –OH functionalized surface is subsequently dosed with TMA forming an ordered monolayer on the surface. The H$_2$O$_2$(g) dosed surface is pinned p-type but is unpinned upon dosing of TMA. The Si-O-Al monolayer formed after dosing is thermally stable and electrically unpinned and can serve as an excellent template for further high-k deposition, especially because any persistent un-reacted Si atoms at the surface can be passivated via forming gas.
Figure 1.1 Schematic of the UHV chamber. The scanning tunneling microscopy chamber (left) has a base pressure of $2 \times 10^{-11}$ Torr. The STM chamber contains a Omicron Low Temperature Scanning Tunneling microscope (LT-STM) capable of performing STM and STS. The preparation chamber has a base pressure of $2 \times 10^{-10}$ Torr. The preparation chamber is equipped with an Omicron Nanotechnology monochromatic x-ray photoelectron spectroscopy system (XM 1000 MkII/SPHERA), a low energy electron diffraction (LEED) system (Omicron NanoTechnology), a Veeco hot tungsten filament atomic hydrogen source, a Nonsequitur Technologies (Model 1403) ion gun, and a pyrolytic boron nitride (PBN) heater. Both the preparation and analysis chambers are pumped via Varian starcell ion pumps. The load lock (LL) / atomic layer deposition (ALD) chambers have a base pressure of $1 \times 10^{-7}$ Torr and are pumped via turbomolecular pumps. Oxidant and reductant precursors and atomic hydrogen can be dosed in the LL/ALD chamber at room temperature or elevated temperatures.
Figure 1.2 Simplified schematic diagram of a STM circuit.
Figure 1.3 Schematic of STM tunneling process. Schematic diagram illustrating the tunneling process between a semiconductor surface and a metal tip during STM operation. (a) Empty state imaging. (b) Filled state imaging.
Figure 1.4 Simplified schematic of a STS circuit.
Chapter 2

In-situ non-disruptive cleaning of Ge(100) using H$_2$O$_2$(g) and atomic hydrogen

2.1 Abstract

In-situ gas phase cleaning of the Ge(100) surface was studied at the atomic level using scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) while chemical analysis of the surface was performed using x-ray photoelectron spectroscopy (XPS). High purity H$_2$O$_2$(g) dosing removed carbon contamination from an air exposed Ge(100) sample. The oxide formed via H$_2$O$_2$(g) dosing was subsequently removed via either atomic hydrogen exposure at 300°C or 550-700°C annealing. STM imaging showed an air exposed Ge(100) surface after H$_2$O$_2$(g) dosing and 600-700°C annealing produced a flat and ordered surface while STS verified the density of states (DOS) is equal to that of a Ge(100) surface which has been cleaned via sputter (500°C) and annealing (700°C). Combining H$_2$O$_2$(g) with atomic hydrogen dosing or annealing removed carbon via oxidation and oxygen via thermal desorption or reduction from an air exposed Ge(100) surface.

2.2 Introduction

Germanium has drawn significant interest as an alternative material for use in electronic devices as a replacement of conventional silicon based devices due to its high electron and hole mobilities. In order to effectively employ germanium as a replacement for silicon, a non-disruptive cleaning mechanism is needed which leaves
the surface atomically flat and defect-free allowing for nucleation in each surface unit cell for gate oxide growth and contact deposition. Many defects that persist on the Ge surface are carbon based. It is well known that carbon contaminants are difficult to remove from a Ge surface and can pin surface steps between terraces on a Ge(100) surface.[15; 16] During device fabrication or material deposition, carbon based contaminants can block or act as nucleation sites, change the order of a reaction during growth, or erroneously appear as growth features. For example, any persisting un-reactive defect sites on the Ge surface can increase the required gate oxide thickness to maintain low leakage. Therefore, a non-disruptive (i.e. without ion bombardment) method is needed to effectively clean the entire Ge(100) surface.

There are many different methods for cleaning a Ge(100) surface. Most commonly, cyclic sputtering and annealing is used to clean the surface. [17-19] This is usually done with 400-1000 eV Ar+ or Ne+ at normal to 45° incidence. The final step is high temperature annealing (550-800°C) in attempt to eliminate damage caused by sputtering. However, either very long duration anneals or very high temperatures are needed to achieve a flat highly ordered surface and to drive any sputter embedded ions out of the surface. [20-27]

Alternatively, wet chemical etching followed by formation of a sacrificial oxide passivation layer which desorbs in vacuum at elevated temperature can be used to form a clean Ge surface. This process results in varying contamination levels and surface roughness depending on the cleaning and passivation methods. [15; 16; 19; 28-31] A Ge buffer layer is sometimes grown after oxide desorption to increase sample cleanliness and order while minimizing roughness. [19; 31-33]
Purely in-situ chemical cleaning methods followed by high temperature anneals have also been studied to remove carbon contamination from surfaces[34; 35]. Both ozone and oxygen plasma have been shown to successfully reduce carbon contamination; however, even after this treatment, the Ge surface may still have carbon based protrusions.[19]

The goal of this study is to develop an understanding of the surface chemistry for a completely in-situ and low temperature non-disruptive method which completely removes all contaminants from an air exposed Ge(100) surface. First, high purity H$_2$O$_2$(g) is shown to completely remove carbon contamination from an air exposed Ge surface consistent with formation of volatile carbon oxides and non-volatile germanium oxides. Second, after H$_2$O$_2$(g) dosing to remove carbon, atomic hydrogen dosing at 300°C was shown to remove the germanium oxide formed during H$_2$O$_2$(g) cleaning by chemical reduction. Alternatively, H$_2$O$_2$(g) treatment followed by a high temperature anneal leaves a flat, ordered, contaminant-free surface consistent with thermal desorption of germanium oxides. Cleanliness of the surface was verified using in-situ x-ray photoelectron spectroscopy (XPS), scanning tunneling microscopy (STM), and scanning tunneling spectroscopy (STS).

### 2.3 Experimental Details

Sb-doped n-type Ge(100) wafers (0.005-0.020 Ωcm, Wafer World Inc.) were diced into 12mm x 4.5mm pieces and degreased via ultrasonication with acetone, methanol, and deionized water then dried with N$_2$ gas. The Ge samples were quickly (< 10 min) introduced into the UHV chamber with a base pressure of 2 × 10$^{-10}$ Torr and degassed via a pyrolytic boron nitride heater at 400°C. The samples were
subsequently transferred into a separate “dosing” chamber with a base pressure of $2 \times 10^{-8}$ Torr in order to clean the Ge surfaces. The reaction pressures were measured using a convectron gauge, and the exposure was estimated in Langmuirs (1 Langmuir (L) = $1 \times 10^{-6}$ Torr · 1 sec).

After loading the Ge(100) samples into the “dosing” chamber, the samples were exposed to high purity $\text{H}_2\text{O}_2(g)$ while the samples temperature was maintained at 300°C. The high purity $\text{H}_2\text{O}_2(g)$ source is built by RASIRC® and is maintained at 40°C. Glass and Teflon tubing were employed in order to minimize $\text{H}_2\text{O}_2(g)$ decomposition on the tubing or stainless steel dosing chamber. The reported doses of $\text{H}_2\text{O}_2(g)$ in Langmuir are presented assuming a 0% dissociation rate of $\text{H}_2\text{O}_2(g)$.

After high purity $\text{H}_2\text{O}_2(g)$ dosing, the samples were given one of two treatments to remove the oxide formed during $\text{H}_2\text{O}_2(g)$ dosing. The samples were either dosed with atomic hydrogen at modest temperatures, 300°C, to chemically reduce the oxide, or annealed at high temperature, up to 700°C, to desorb the oxide. For oxide removal via atomic hydrogen plasma, the samples were transferred into the “dosing” chamber and exposed to an atomic hydrogen plasma while the sample temperature was maintained at 300°C. The atomic hydrogen plasma was generated in an Opthos McCarroll cavity using a microwave generator (Sairem Model GMP 03 K/SM). Inside of the McCarroll cavity, the plasma was generated in a sapphire discharge tube with a power of 30W. The pressure during dosing of atomic hydrogen was ~300mTorr and the dosing gas was composed of 5% $\text{H}_2(g)$ and 95% $\text{Ar}(g)$. The atomic H doses reported assume 100% dissociation and, therefore, only represent an upper limit. For oxide desorption via heating, samples were heated via direct heating
in the UHV chamber using a controlled heating ramp rate of 1°C/sec while the sample temperature was monitored by a pyrometer. GeO is known to desorb from the Ge(100) surface starting around 400°C for submonolayer coverage while GeO$_2$ will decompose into GeO and desorb between 550-600°C.[36-38]

In-situ analysis of the sample surface was conducted after each surface treatment. A monochromatic XPS (XM 1000 MkII/SPHERA, Omicron Technology) was employed to examine the surface elements and their relative intensities. The XPS data was acquired in constant analyzer energy mode with a pass energy of 50eV and a line width of 0.1eV using an Al Kα source (1486.7 eV). XPS spectra were collected with a takeoff angle of 30° from the sample surface (i.e. close to the surface parallel) with an acceptance angle of ± 7°. Analysis of the spectra was performed using CASA XPS v.2.3 using a Shirley background subtraction method. The relative XPS elemental intensities were quantified by calculating the peak area divided by the XPS sensitivity factor. The elemental ratios reported display the best fit of the data while the reported errors bars represent the largest deviations of potential fits of the spectra. The topography analysis of the sample surfaces was performed using a STM (LT-STM, Omicron Nanotechnology). All STM and STS data were obtained at room temperature (RT) in a UHV chamber with a base pressure of 1 × 10$^{-11}$ Torr. The STM was operated in constant-current mode (I$_{sp}$ = 0.2nA) with an applied sample bias of -1.8V. The electronic structure of the surfaces of the samples was measured using STS operating in variable-z mode using a modulation signal (0.1V, 650 Hz) supplied by an external lock-in amplifier while sweeping the sample bias from -1 to +1V.

2.4 Results and Discussion
2.4.1 Chemical Analysis: XPS results

Fig. 2.1 shows the relative elemental ratios acquired via XPS of carbon (black) and oxygen (red) contaminants normalized to the Ge signal on a Ge(100) sample after several surface treatments. Column A shows the ratios of contaminants to germanium of a Ge(100) sample after ex-situ degreasing and subsequent air exposure during sample transfer and loading into the chamber. The degreased Ge(100) sample (Fig. 2.1, Column A) has a multilayer coverage of carbon and oxygen contaminant on the surface due to hydrocarbon and water adsorption during air exposure. After degassing the sample at 400°C (Column B), all of the oxygen and native oxide desorbed from the sample consistent with the dominant ambient Ge oxide, formed during short air exposure (< 10 min), being a suboxide (see XPS chemical shift data below); however, some remaining carbon contamination persists on the surface. Column C shows the carbon and oxygen on the sample after a subsequent 20 second exposure of high purity $\text{H}_2\text{O}_2(\text{g})$ at 300mTorr ($6\times10^6$ L) while the sample temperature was maintained at 300°C. $\text{H}_2\text{O}_2(\text{g})$ reacts with carbon on the surface forming volatile carbon and reaction by-products which readily desorb at 300°C reducing the carbon signal in XPS while also forming a germanium oxide (Column C) (see XPS chemical shift data below). Subsequently, heating the sample to 700°C desorbs the oxide formed during $\text{H}_2\text{O}_2(\text{g})$ dosing eliminating oxygen contamination on the surface while the carbon signal does not change (Column D). The 20 second high purity $\text{H}_2\text{O}_2(\text{g})$ dose at 300mTorr ($6\times10^6$ L) + 700°C anneal was repeated (Column E) and showed a decrease of carbon. To accelerate the carbon removal, the $\text{H}_2\text{O}_2(\text{g})$ dose was increased. Column F shows a
contaminant free surface after an additional 80 second (2 min total or 3.6×10⁷ L) of high purity H₂O₂(g) dosing (300mTorr) at 300°C followed by a 700°C anneal.

Figure 2.2 shows the progression of the carbon signal in XPS after the H₂O₂(g) + 700°C anneal cleaning procedure. The air exposed sample shows a carbon peak with a large feature with binding energy near 284.5eV consistent with hydrocarbons or Ge-C (orange peak) and also a broad higher binding energy peak (blue) near 286.5eV consistent with C-O bonding.[39-41] When the sample is degassed at 400°C, the carbon signal decreases consistent C-O desorption (reduction in higher binding energy blue peak) while the hydrocarbon/Ge-C feature persists. After a 20 second dose of H₂O₂(g), the higher binding energy feature (C-O bonding) is completely eliminated while the hydrocarbon/Ge-C feature (284.5eV) is reduced. The subsequent 700°C anneal has no impact on the carbon signal. After a subsequent 20 second H₂O₂(g) dose + 700°C anneal, the carbon peak is further decreased. A additional 80 sec H₂O₂(g) dose (2 min total or 3.6×10⁷ L) followed by a 700°C anneal shows a completely carbon free surface consistent with removal of both hydrocarbons/Ge-C and C-O.

Figure 2.3 shows the progression of the Ge 3d peak during the cleaning process. The degreasing step ending with a water rinse which completely dissolved the GeO₂ native oxide that formed during extended air exposure.[15] The air exposed (< 10 min air exposure) sample shows a Ge bulk peak (green curve) near 29.5eV and also a higher binding energy peak consistent with a native oxide formed during short air exposure being GeOₓ (x < 2) ( red curve). It is known that GeO₂ will slowly form on the clean Ge surface after long exposure times (on the order of hours to days).[42; 43] In addition, the binding energy of GeO₂ is at 32.8-33.2eV verifying that the majority
of the native oxide formed during air exposure during transfer from degreasing to
UHV chamber is suboxide.[42; 44; 45] After degassing the sample at 400°C, the GeOₙ
(x < 2) feature is completely eliminated and the XPS spectrum shows only a Ge bulk
feature. Note this bulk like peak will obscure a Ge-C feature since it is expected to
have a nearly zero chemical shift since C and Ge have similar electronegativities.
After 20 seconds of H₂O₂(g) dosing to remove carbon from the surface, the high
binding energy feature returns and is consistent with a variety of germanium oxidation
states due to many potential bonding configurations after H₂O₂(g) dosing (Ge-OH,
GeO, Ge₂O₃, GeO₂) therefore it is referred to as GeOₙHₙ (x ≤ 2, 0 ≤ y ≤ 1) (red curve).
[46] A 700°C anneal completely desorbs the GeOₙHₙ feature leaving only a bulk Ge
feature. Subsequent H₂O₂(g) dosing and annealing further decreases the carbon
contamination on the surface as seen in Fig. 2.1 & 2.2 while the Ge 3d only shows a
bulk Ge feature after each 700°C anneal.

In order to reduce the thermal budget required for obtaining a contaminant free
Ge(100) surface, a chemical reduction was investigated which removes oxygen from
the surface at a lower temperature. Figure 2.4 shows the XPS contaminant:Ge ratios of
the H₂O₂(g) dosed Ge(100) surface followed by atomic H dosing. Figure 2.4 shows the
amount of oxygen and carbon on the Ge(100) surface after a 2 min exposure to high
purity H₂O₂(g) (300mTorr, 300°C, 3.6×10⁷L). As previously shown, a 2 min H₂O₂(g)
dose was able to completely strip all carbon contaminants from an air exposed
Ge(100) surface (Fig. 2.1 Column F) and the carbon contamination level during the
entire atomic H dosing procedure remained consistently below 3%. This carbon
contamination is attributed to background oil vapor from a mechanical pump. The
Ge(100) sample was subsequently dosed with atomic H for increasing exposure times while the sample temperature was maintained at 300°C. Figure 2.4 shows a ~2.8:1 O:Ge ratio after a 2 min high purity H₂O₂(g) dose. Exposure estimates for atomic hydrogen dosing are presented assuming a 100% dissociation of the 5% H₂(g) in the gas mixture. After a 5 minute exposure to 300mTorr of the gas mixture (9 ×10⁶L of atomic hydrogen), the O:Ge ratio was decreased by a factor of 4. Increasing the exposure time of atomic hydrogen to 10 min (1.8×10⁷L), 30 min (5.4×10⁷L), or 40 min (7.2×10⁷L) demonstrates the ability to remove oxygen contaminants down to < 2% compared to the Ge signal. In contrast to the plasma generated in the quartz discharge tube (see supplemental material), the plasma from the sapphire discharge tube minimizes the oxygen contamination on the Ge(100) surface.

Fig. 2.5 shows the progression of the Ge 2p peak after the 2 min H₂O₂(g) dose and subsequent atomic hydrogen dosing. The Ge 2p peak after a 2 min H₂O₂(g) dose (300mTorr, 300°C, 3.6×10⁷L) has a dominant oxide feature (red curve) between 1219-1222 eV consistent with a variety of potential bonding configurations including Ge-OH, GeO, Ge₂O₃, GeO₂. After 5 min of atomic H dosing (9 ×10⁶L, 300°C, 300 mTorr), the oxide peak is reduced while the germanium bulk signal (green curve) increases. After 10 min of atomic H dosing (1.8×10⁷L, 300°C, 300 mTorr), the oxide feature decreases while the bulk feature continues to increase. Also, the oxide feature shifts to a slightly lower binding energy indicating a preferential reduction of the GeO₂ oxide. 30 min of atomic H dosing (5.4×10⁷L, 300°C, 300 mTorr) further decreases the oxide feature as it shifts to a lower binding energy demonstrating significant reduction of oxygen off the surface. After a total of 40 min of atomic H dosing (7.2×10⁷L,
300°C, 300 mTorr) the higher binding energy feature (red curve) is almost completely eliminated indicating successful removal of contaminants off the Ge(100) surface.

2.4.2 Topographical and Electronic Analysis: STM & STS results

While H\textsubscript{2}O\textsubscript{2}(g) + atomic hydrogen dosing forms a contaminant free surface, to form a well-ordered surface with low roughness, higher annealing temperatures are required. In order to better analyze the quality of the Ge(100) surface after contaminant removal, STM and STS were implemented. STM requires long range order and long range surface flatness to obtain atomically resolved images over large regions due to the relative bluntness of the tip. Multiple STM studies were performed with lower temperature anneals and atomic order could only be observed in small regions; long range order required a >600°C anneal.

Figure 2.6 shows an STM image of a Ge(100) sample cleaned via H\textsubscript{2}O\textsubscript{2}(g) and subsequently annealed at 700°C for 5 minutes (Fig. 2.6a) or 600°C for 1 hour (Fig. 2.6b). The topography is compared to a sputter and annealed Ge(100) surface (Fig. 2.6d). Longer duration anneals are required to achieve increased surface ordering needed for STM and STS, especially at lower temperatures. H\textsubscript{2}O\textsubscript{2}(g) dosing followed by 700°C annealing produced a flat surface with a 0.17nm RMS (root mean squared) roughness over 100×100 nm. A typical Ge(100) sample that was thoroughly sputtered and annealed has an average 0.13 nm RMS roughness over 100×100 nm. The H\textsubscript{2}O\textsubscript{2}(g) + <600°C anneal cleaned surface shows large amounts of atomic order with no large etch pits with a small percentage of Ge adatoms (< 5% of the surface) sit on top of terraces (highlighted by blue arrows). The carbon signal on these surfaces are below the detection level of XPS and the characteristic (2x1) (yellow arrow) and c(4x2)
(white arrow) reconstructions seen on the sputtered/anneal Ge(100) surface are also seen in the H$_2$O$_2$(g) dosed + >600°C anneal cleaned surfaces (in Fig. 2.4b & 2.4c). The adatoms on the 700°C annealed surface and larger RMS roughness compared to a sputtered/annealed sample are most likely caused by insufficient annealing.

Line trace analysis (Fig. 2.7a) taken at 5 different locations (each line trace offset by 100nm) on the chemically cleaned surface (Fig. 2.6a) shows periodic row spacing of 7.9Å with a standard error of .1Å which is nearly identical to the row spacing on the ideal clean Ge(100) surface (8Å).[47] STS verifies the electronic structure (density of states) of the surface after this cleaning procedure is equivalent to that produced using sputter and annealing as seen by the strong agreement between the orange and blue STS curves in Fig. 2.7c. The data is consistent with the 600-700°C anneal being required to restore surface order since the GeO$_x$ desorbs at > 400°C leaving a slightly rougher surface.

2.5 Conclusion

Air exposed Ge(100) samples were cleaned of surface contaminants using high purity H$_2$O$_2$(g) followed by either atomic hydrogen dosing at 300°C or a high temperature anneal (550°C- 700°C). High purity H$_2$O$_2$(g) dosed on an air exposed surface at 300°C reacted with carbonaceous species on the surface forming volatile compounds. The H$_2$O$_2$(g) dosing removed all the carbon contamination on the Ge(100) surface while also forming a GeO$_x$H$_y$ layer. The oxide formed during H$_2$O$_2$(g) dosing can be removed via reduction by one of two methods: annealing or atomic H dosing. Atomic hydrogen dosing reduced the germanium oxide layer forming volatile by-products at 300°C thereby removing oxygen from the surface. While H$_2$O$_2$(g):
atomic H dosing is successful at removing all contaminants from the Ge(100) surface, STM verifies a 600-700°C anneal leaves a flat and ordered Ge(100) surface. STS verified the high temperature annealed surface has a density of states on the surface equivalent to that of a sample cleaned via sputter and annealing.

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Chapter 2, in part or in full, has been submitted for publication of the material as it may appear in T. Kaufman-Osborn, K. Kiantaj, C.-P. Chang, and A. C. Kummel, *In-situ non-disruptive cleaning of Ge(100) using H$_2$O$_2$(g) and atomic hydrogen*, Surface Science (2014). The dissertation author was the primary investigator and author of this paper.
Figure 2.1 XPS elemental ratios of carbon and oxygen on a Ge(100) surface during cleaning. XPS showing carbon and oxygen reduction following dosing of high purity H$_2$O$_2$(g) and 700°C annealing. Column A shows ratios on an as-loaded Ge(100) sample. Column B shows ratios after 400°C degassing. Column C shows ratios after a subsequent 20 sec dose of H$_2$O$_2$(g). Column D shows ratios after a subsequent 700°C anneal. Column E shows ratios after an additional 20 sec dose of H$_2$O$_2$(g) and subsequent 700°C anneal. Column F shows a contaminant free surface after additional 80 sec (2 min total) H$_2$O$_2$(g) dose and subsequent 700°C anneal.
Figure 2.2 XPS carbon 1s spectra during $\text{H}_2\text{O}_2(\text{g})$ dosing and annealing. Carbon 1s spectra during cleaning procedure involving $\text{H}_2\text{O}_2(\text{g})$ dosing and 700°C annealing corresponding with procedure outlined in Fig 2.1.
Figure 2.3 XPS Ge 3d spectra during H₂O₂(g) dosing and annealing. Ge 3d spectra during the cleaning procedure involving H₂O₂(g) dosing and 700°C annealing corresponding with procedure outlined in Fig. 2.1 & 2.2.
Figure 2.4 XPS elemental ratio of oxygen and carbon during $\text{H}_2\text{O}_2(\text{g})$ and subsequent atomic hydrogen dosing (sapphire discharge tube). XPS showing oxygen on the Ge(100) surface after 2 min of $\text{H}_2\text{O}_2(\text{g})$ cleaning followed by increasing exposure to atomic hydrogen generated in a sapphire discharge tube. Atomic hydrogen reduces oxygen contamination down to $< 2\%$ on the Ge(100) surface.
Figure 2.5 XPS Ge 2p spectra during H$_2$O$_2$(g) dosing followed by atomic hydrogen dosing. Ge 2p spectra during the cleaning procedure involving H$_2$O$_2$(g) dosing and subsequent atomic hydrogen dosing corresponding with the procedure outlined in Fig. 2.4.
Figure 2.6 STM of a Ge(100) surface cleaned via H$_2$O$_2$(g) dosing + annealing or sputtering and annealing (a) 40×40nm$^2$ STM image of the Ge(100) surface after H$_2$O$_2$(g) dosing and 700°C annealing (5 min). A large amount of ordering is observed while a few Ge adatoms (blue arrows) sit atop some terraces. (b) 20×10nm$^2$ inset of Ge(100) surface shown in (a) highlighting ordering and (2×1) (yellow arrow) and c(4×2) (white arrow) reconstructions. (c) 20×10nm$^2$ STM image of the Ge(100) surface after H$_2$O$_2$(g) dosing and 600°C annealing (60 min) (d) 20×10nm$^2$ STM image of a Ge(100) cleaned via sputter and 700°C annealing showing (2×1) (yellow arrow) and c(4×2).
Figure 2.7 Line trace analysis and STS of the chemically cleaned Ge(100) surface. (a) Line trace analysis acquired at five different locations on the chemically cleaned Ge(100) surface (Fig. 2.6a) showing periodic row spacing of 7.9Å with a standard error of .1Å. (b) STS acquired on the chemically cleaned Ge(100) surface compared to a sputter/anneal cleaned Ge(100) surface showing identical DOS.
Chapter 3

Atomic imaging and modeling of H$_2$O$_2$(g) surface passivation, functionalization, and atomic layer deposition nucleation on the Ge(100) surface

3.1 Abstract

Passivation, functionalization, and atomic layer deposition (ALD) nucleation via H$_2$O$_2$(g) and trimethylaluminum (TMA) dosing was studied on the clean Ge(100) surface at the atomic level using scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS). Chemical analysis of the surface was performed using x-ray photoelectron spectroscopy (XPS) while the bonding of the precursors to the substrate was modeled with density functional theory (DFT). At room temperature, a saturation dose of H$_2$O$_2$(g) produces a monolayer of a mixture of –OH or –O species bonded to the surface. STS confirms that H$_2$O$_2$(g) dosing eliminates half-filled dangling bonds on the clean Ge(100) surface. Saturation of the H$_2$O$_2$(g) dosed Ge(100) surface with TMA followed by a 200°C anneal produces an ordered monolayer of thermally stable Ge-O-Al bonds. DFT models and STM simulations provide a consistent model of the bonding configuration of the H$_2$O$_2$(g) and TMA dosed surfaces. STS verifies the TMA/H$_2$O$_2$/Ge surface has an unpinned Fermi level with no states in the band gap demonstrating the ability of a Ge-O-Al monolayer to serve as ideal template for further high-k deposition.

3.2 Introduction
To scale complementary metal-oxide-semiconductor (CMOS) devices, new materials with high carrier mobility have been investigated as potential replacements of the conventional silicon channel. Germanium has drawn significant interest due to its high electron and hole mobilities. However, Ge native oxide has very poor electronic properties due to a high interface trap density between Ge and Ge native oxide. This has caused challenges during MOSFET fabrication because most Ge based devices, even devices incorporating high-k gate oxide materials, have a GeO\textsubscript{x} interfacial layer which can negatively affect device performance and/or increase equivalent oxide thickness (EOT). [48; 49]

In order to minimize the defect density that occurs at the interface between Ge and the gate oxide, a proper passivation method is required prior to gate oxide growth. Many different passivation methods have been studied on Ge including oxidation[50-54], sulfurization[55; 56], nitridation[57-60], halogenations[61-63], and epitaxial growth of Si.[64; 65] These passivation methods must eliminate the dangling bonds on the Ge surface while remaining of angstrom thickness to minimize the EOT in a MOSFET. Not only should the passivation method satisfy the bonding requirements of atoms on the semiconductor surface, but it should also serve to functionalize the surface for subsequent atomic layer deposition (ALD) precursor deposition. ALD, in recent years, has gained significant attention as a superior method of depositing films of uniform thickness while maintaining excellent compositional control.[66-68] As this work describes, ALD gate oxide growth has the potential to bond to the Ge surface leaving an electrically passive and ideal interface which should not inhibit electrical performance of the full device. Recent work has shown promising results
using H₂O(g) as a passivation and functionalization method to grow Al₂O₃ via ALD.[69] However, H₂O(g) has some limitation in this application. A Ge surface dosed with a saturation dose of H₂O(g) leaves a large density of dangling bonds which act as interface traps, and H₂O(g) lacks thermal stability on Ge surfaces due to recombinative desorption at temperatures above 100°C.[60]

This study aims to improve on the water passivation mechanism by substituting H₂O₂(g). By selecting an oxidant with weak internal bonds, saturation of the Ge surface with reactive –OH chemisorption species becomes much more effective. When a Ge surface is exposed to a saturation dose of H₂O₂(g), greater than 97% of surface Ge atoms become terminated with hydroxyl species which are more thermally stable than the chemisorptions species, -H and –OH, on a H₂O(g) dosed Ge surface. By increasing the hydroxyl saturation coverage, trimethylaluminum (TMA) is able to nucleate in nearly every unit cell on the Ge surface, thereby resulting in a very low density of dangling bonds or interface trap states and a nearly ideal monolayer passivation and ALD nucleation layer. This study demonstrates for the first time the ability to electrically passivate all the dangling bonds on the Ge surface by combining an oxidant and reductant precursor while maintaining an electrically unpinned Fermi level thereby creating an ideal semiconductor-oxide interface.

A very thin interfacial Al₂O₃ layer is known to improve device performance demonstrating the need for an high density and electrically passive monolayer of Al₂O₃.[70; 71] In this study, the reaction of H₂O₂(g) only and H₂O₂(g) + TMA on the Ge(100) surface was studied at the atomic level using UHV experimental techniques. The thermal behavior of these surfaces was studied by annealing in UHV conditions
while the surface was analyzed between each step using *in-situ* x-ray photoelectron spectroscopy (XPS), scanning tunneling microscopy (STM), and scanning tunneling spectroscopy (STS). Atomic models of the reaction of H₂O₂(g) on a clean Ge surface and TMA on a H₂O₂(g) functionalized Ge surface were developed based on density functional theory (DFT). Both experimental and theoretical results are consistent with H₂O₂(g) and TMA ALD on the Ge surface producing an electrically passive ideal interface that serves as an excellent template for further high-k deposition.

### 3.3 Experimental Details

Sb-doped n-type Ge wafers (0.005 – 0.020 Ωcm, Wafer World Inc.) were diced into rectangular pieces (12mm x 4.5 mm) and degreased via ultrasonication with acetone, methanol, and deionized water then dried with N₂ gas. All samples were loaded into a UHV chamber with a base pressure of 2 × 10⁻¹⁰ Torr. The samples were cleaned via repeated sputter and anneal processes. The sputtering was performed using a 1-1.5keV of Ar⁺ ion beam (Model 1403 ion gun, Nonsequitur Technologies) with a beam current of 0.6-0.9 μA and at an incident angle of 45° for 30 min while the sample temperature was maintained at 500°C via direct heating to avoid the adsorption of trace oxygen on the Ge sample. Following each sputter process, the samples were annealed at 700°C for 20 min. The samples were STM imaged with atomic resolution to confirm a contaminant free surface thereby verifying surface cleanliness before proceeding with each experiment.

The samples were transferred into a separate “dosing” chamber with a base pressure of 2 × 10⁻⁸ Torr to react precursors with the Ge surfaces. H₂O₂(g) and TMA were dosed by back filling the dosing chamber with the precursor vapors without
carrier gas. Both H₂O₂(g) and TMA exposures were controlled by throttling valves on the H₂O₂(g) and TMA. The reaction pressures were measured using a convectron gauge, and the exposure was estimated in Langmuirs (1 Langmuir (L) = 1 x 10⁻⁶ Torr · 1 sec). All dosing was performed at RT. A 30% solution of H₂O₂(aq) was employed which is known to produce a vapor containing 2.67% H₂O₂(g) at 25°C.[72] Although glass and Teflon tubing was employed, some of the H₂O₂(g) may have decomposed in the tubing or on the walls of the stainless steel dosing chamber. Therefore, the reported doses for H₂O₂(g) are the upper limits of the actual doses of H₂O₂(g) reacting with the surface. Since all results in this study employed saturation doses, knowledge of the exact dose is not material.

After H₂O₂(g) or TMA exposure, the samples were transferred to the main chamber for thermal annealing. The samples were heated via direct heating using a controlled heating ramp rate of 1°C/sec while the sample temperature was monitored by a pyrometer. In-situ analysis of the topography of the sample surfaces was performed using a STM (LT-STM, Omicron Nanotechnology). All STM and STS data were obtained at RT in a UHV chamber with a base pressure of 1 × 10⁻¹¹ Torr following each surface treatment. STM images were acquired using constant-current mode STM (Iₛₚ = 0.2nA) with an applied sample bias between -1.8 and -2.0V. The electronic structure of the surfaces of the samples was measured using STS operating in variable-z mode using a modulation signal (0.1V, 650 Hz) supplied by an external lock-in amplifier, while sweeping the sample bias from -1 to +1V or -1.5 to +1.5V.

An in-situ monochromatic XPS (XM 1000 MkII/SPHERA, Omicron Nanotechnology) was employed to examine the surface elements and their relative
intensities. The XPS was operated in constant analyzer energy mode with a pass energy of 50eV and the line width of 0.1 eV using an Al Kα source (1486.7 eV). The takeoff angle was 30° from the sample surface with an acceptance angle of ± 7°. Data and peak shape analysis was performed using CASA XPS v.2.3 using a Shirley background subtraction method. The relative XPS intensity of each core-level spectra (C 1s, Al 2p, and O 1s) was quantified by calculating the peak area divided by the XPS sensitivity factor.

3.4 Computational Details

All presented DFT simulations were performed with the Vienna *ab initio* simulation code (VASP) using the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional and projector augmented-wave (PAW) pseudopotentials (PPs).[73-78] The choice of PBE functional and PAW PP was confirmed by parametrization calculations indicating good reproducibility of experimental lattice constants, bulk moduli, and cohesive energies for bulk crystalline Ge. The STM simulations were performed using the Tersoff–Hamann approach.[4; 5] The Ge slabs were built as 2x2x3 supercell (96 atoms) using PBE-optimized Ge unitcell lattice constants. The three bottom Ge layers were permanently fixed in bulk-like positions, and bottom Ge atoms were passivated by two relaxed hydrogen atoms each to simulate continuous bulk. The Ge slabs with or without passivation layer were relaxed using conjugate-gradient algorithm at 5x5x1 Gamma-centered K-point grid below force tolerance level of 0.05 eV/Å.

3.5 Results and Discussion

3.5.1 H₂O₂(g) Passivation/Functionalization of Ge(100)
An atomically flat, sputter and anneal cleaned Ge(100) sample is shown in Fig. 3.1a showing the two surface reconstructions that occur at RT on the clean Ge(100) surface. The clean surface was dosed at RT with \(2.25 \times 10^5\) L of \(\text{H}_2\text{O}_2(g)\), a near saturation dose. In STM of Ge, reaction with –H, –OH, or –O produces dark sites, and the residual unreacted dangling bonds appear bright.[60; 79] The \(\text{H}_2\text{O}_2(g)\) reacts with the Ge(100) surface giving a coverage greater than 0.97ML of dark sites as shown in Fig. 3.1b.

During \(\text{H}_2\text{O}_2(g)\) dosing, dissociative chemisorption of \(\text{H}_2\text{O}_2(g)\) terminates the dangling bonds on Ge dimers with –OH or –O species resulting in a variety of surface chemisorbates bonding configurations shown in Fig. 3.1c. These various surface bonding configurations change the electronic structure and, therefore, the STM tunneling current, resulting in a difference of brightness in constant current STM imaging. The two different surface bonding configurations are highlighted inside the green and blue boxes. Simple bonding models were developed based on bond enthalpies and confirmed below by DFT calculations. The green box highlights the bonding configuration where \(\text{H}_2\text{O}_2(g)\) has dissociated on a Ge dimer leaving each Ge atom terminated with an –OH species. The blue box highlights the bonding configuration where \(\text{H}_2\text{O}_2(g)\) has dissociated on a Ge dimer terminating each Ge atom with an –OH species and an additional –O atom has inserted into the Ge dimer bond. The mechanism of this –O insertion is discussed below and is a variant of the O insertion mechanism of Mui et al.[80] There are a few percent of unreacted Ge dangling bond sites which have a high tunneling current and are imaged as very bright spots on the surface; one dangling bond site is highlighted in the red box.
H₂O₂(g) dosing, background H₂O(g) is present. It is hypothesized that this did not affect the reaction of H₂O₂(g) with the Ge(100) surface due to the increased reactivity of H₂O₂(g) compared to H₂O(g).[81] However, if H₂O(g) dissociatively chemisorbed to the surface, the resulting Ge-H bond would be quickly replaced with a Ge-OH bond due to the difference in bond strength of Ge-O (659 kJ/mol) vs Ge-H (327 kJ/mol)[82] causing the following reaction: Ge-H + H₂O₂(g) → Ge-OH + H₂O(g).

Scanning tunneling spectroscopy (STS) measurements yield \((dI/dV)/(I/V)\) curves which effectively plot the local density of states on the surface.[4; 7; 83] STS measurements were conducted to further probe the electronic states of the H₂O₂(g) dosed Ge(100) surface. Only n-type samples were studied because pinning of the Fermi level on the Ge(100) surface results in the Fermi level being at the valence band edge, therefore, if p-type samples were used, it would be impossible to determine whether the Fermi level is pinned or not.[60; 84] On the clean n-type surface, Ge(100) has a Fermi level position (0V in STS) just above midgap. This is attributed to the \(\frac{1}{2}\) filled dangling bonds on surface Ge atoms even on a perfectly ordered clean Ge(100) surface.[85] Fig. 3.2 compares the STS curves acquired from the dangling bond sites on unreacted sites of the H₂O₂/Ge surface (Fig. 3.1 red box) with the H₂O₂(g) chemisorption sites (i.e Ge-OH or Ge-O, Fig. 3.1 blue or green boxes) on Ge(100).

While the clean n-type Ge(100) surface shows a Fermi level slightly above the middle of the band gap, the H₂O₂(g) dose pins the Fermi level near the valence band most likely due to the large surface dipole caused by the oxygen containing adsorbates on the surface (blue arrow).[84] The dangling bond sites have states near +0.4eV consistent with the presence of conduction band edge dangling bonds. Conversely, on
the H$_2$O$_2$(g) chemisorption sites, the states near +0.4eV are completely eliminated demonstrating that the –OH chemisorbed species passivate the dangling bond states (red arrow).

XPS data shown in Fig. 3.3(a) compares the oxygen coverage on Ge(100) surfaces dosed with equivalent doses (9×10$^5$ Langmuir) of H$_2$O(g) or H$_2$O$_2$(g) at 25°C. Fig. 3.3(b&c) shows the peak shape analysis of the Ge 2p signal and associated chemical shifts after a saturation dose of H$_2$O(g) or H$_2$O$_2$(g), respectively.

As seen in Fig. 3.3(a), more oxygen adsorbs to the surface when dosed with H$_2$O$_2$(g) compared to H$_2$O(g). H$_2$O(g) dosing at 25°C results in less than half a monolayer of Ge-OH chemisorption sites and less than half a monolayer of Ge-H chemisorption sites.[60] The H$_2$O$_2$(g) saturation coverage on Ge(100) results in at least two oxygen atoms per available Ge surface dimer from a combination of Ge-OH bonds and O-Ge-OH bonds, which is more than double the oxygen coverage compared to the H$_2$O(g) saturated Ge(100) surface.

The XPS spectra in Fig. 3.3(b) shows the H$_2$O(g) dose results in a 1.3eV higher binding energy peak (red peak) than bulk Ge (blue peak) consistent with Ge-OH bonds. Fig. 3.3(c) shows the H$_2$O$_2$(g) dosing results in the formation of two new higher binding energy peaks consistent with two different surface Ge-O/Ge-OH bonding configurations. The H$_2$O$_2$(g) dose gives a large number of Ge-OH bonds which is 1.3eV higher in binding energy compared to the bulk peak(red peak) as well as Ge surface atoms which are bonding to two -O/-OH species giving an even higher 2.1eV binding energy shift (yellow peak) consistent to what is seen in the STM images in Fig. 3.1(a) and DFT models below.
The differences in H$_2$O$_2$(g) vs H$_2$O(g) saturation coverage are not simply the result of H$_2$O(g) dissociation producing both Ge-OH and Ge-H sites. The 25°C H$_2$O$_2$(g)/Ge(100) has a lower density of dangling bond sites and higher density of Ge-OH compared to 25°C H$_2$O(g)/Ge(100). A previous report analyzed STM images of the H$_2$O(g) saturated Ge(100) surface and showed that a saturation dose of H$_2$O(g) at 25°C provides 85% coverage on the Ge(100) surface and a dangling bond density of 15%.[60] while, as seen in Fig. 3.1(b), a saturation dose of H$_2$O$_2$(g) at 25°C provides a saturation coverage of >97% and a dangling bond density below 3%.

Fig. 3.4 present a heuristic model of the H$_2$O(g) and H$_2$O$_2$(g) dissociation mechanism on Ge(100). It is hypothesized that H$_2$O(g) requires two neighboring empty sites to dissociatively chemisorb due to the high HO-H bond strength while H$_2$O$_2$(g) does not require neighboring sites due to its weak internal bonds and ability to insert into Ge-Ge dimer bonds. This mechanism suggests when H$_2$O(g) dissociates across a pair of dimers, isolated empty sites are created which are unreactive to H$_2$O(g) thereby creating the high density of dangling bonds at 25°C. It is hypothesized that H$_2$O$_2$(g) does not leave isolated unreactive sites due to a much weaker HO-OH bond. Therefore, a saturation dose of H$_2$O$_2$(g) on Ge(100) leaves Ge dimers terminated with either two or three oxygen species consistent with the STM image (Fig. 3.1) and DFT calculations below.

To investigate the thermal behavior of the H$_2$O$_2$(g) chemisorbed species on Ge(100), the 25°C H$_2$O$_2$(g) dosed sample was annealed to 100°C and 150°C for 10 min. Fig. 3.5(a) shows a filled state STM image of the Ge(100) surface after a 2.25×10$^5$ L H$_2$O$_2$(g) dose and a subsequent 100°C anneal. Fig. 3.5(b) shows STS
measurements of the 100°C annealed H\textsubscript{2}O\textsubscript{2}/Ge surface (blue curve) compared to the RT H\textsubscript{2}O\textsubscript{2}/Ge surface (red curve) and the clean Ge(100) surface (green curve).

For 100°C annealing, Fig. 3.5(a), no additional dangling bond sites are formed, but there is a change in overall bonding configuration to a zig-zag symmetry consistent with either H\textsubscript{2} desorption from the surface or rearrangement of hydroxyl bonding configurations. XPS data (not shown) verifies that the oxygen coverage on the 100°C annealed surface is within 10% of the oxygen content on the un-annealed surface while the Ge-OH peak shifts to a slightly lower binding energy by about .1eV compared to the RT dosed surface. This is likely attributed to some of the hydroxyl groups inserting into the Ge dimer bonds consistent with the DFT model of the annealed surface proposed below. However, when the H\textsubscript{2}O\textsubscript{2}(g) saturated surface is annealed to temperatures above 150°C, XPS shows the oxygen content decreases, and STM shows that the Ge dangling bonds are formed consistent with H\textsubscript{2}O(g) desorption. This is in contrast to the H\textsubscript{2}O(g) dosed Ge surface which exhibits recombinative desorption of H\textsubscript{2}O(g) when annealed to only 100°C.[60]

As seen in Fig. 3.5(b), the effect of a 10 min 100°C anneal was studied to determine the effect of annealing on the electronic structure of H\textsubscript{2}O\textsubscript{2}/Ge(001). While the RT as-dosed surface shows a Fermi level very near the valence band consistent with a large surface dipole (red arrow), annealing the surface to 100°C shifts the Fermi level towards the conduction band (blue arrow) likely due to the decrease of surface dipole caused by the change in surface bonding configuration.

3.5.2 ALD Nucleation on the H\textsubscript{2}O\textsubscript{2}/Ge(100) Surface via TMA Dosing
To investigate the effect of using H$_2$O$_2$(g) in ALD nucleation, STM and XPS measurements were performed on a Ge(100) pre-dosed with H$_2$O$_2$(g) and subsequently dosed with TMA. Fig. 3.6(a) shows an STM image of the Ge(100) surface that was been pre-dosed with 6 × 10$^4$ L of H$_2$O$_2$(g) at 25°C followed by 2.3 × 10$^4$ L of TMA at RT and subsequently annealed at 200°C for 5 min. Fig. 3.6(b) shows three line traces acquired on ordered vertical rows. Fig. 3.6(c) shows STS analysis of the n-type Ge(100) surface dosed with H$_2$O$_2$(g), annealed at 100°C, then dosed with TMA and subsequently annealed to 200°C. Note the data was collected with slightly less than full saturation of H$_2$O$_2$ and TMA doses allowing defect states to be observed.

The STM image in Fig. 3.6(a) shows ordered vertical rows (blue lines highlight row direction) along the Ge dimer row direction showing chemisorption of TMA onto the H$_2$O$_2$/Ge(100) surface. The line traces in Fig. 3.6(b) show uniform spacing (~8Å) that is consistent with the clean Ge(100) dimer row spacing. The STS in Fig. 3.6(c) shows the TMA/H$_2$O$_2$ dosed Ge surface ordered rows (blue curve) have a slightly larger band gap compared to the clean Ge surface (green curve) consistent with O-Al-O bond formation. The dosed surface has a Fermi level slightly above midgap which is consistent with unpinning as seen on the n-type clean Ge surface STS curve. Bright defect states (red curve) have a large number of conduction band edge states due to either incomplete saturation of the H$_2$O$_2$(g) dose or desorption of H$_2$O$_2$ chemisorption species that did not react with TMA and are volatile at annealing temperatures above 100°C.

Fig. 3.7 shows XPS analysis of a Ge(100) sample dosed with 9×10$^5$ L H$_2$O$_2$ at 25°C followed by 4×10$^5$ L TMA at 25°C. XPS shows that the as-dosed sample has a
O:Al ratio of 1.3 to 1 and a C:Al ratio of 1.9 to 1. As the sample is heated to 220°C and 280°C, the carbon signal decreases to C:Al less than 0.8:1 consistent with methyl desorption. Annealing the sample may also slightly reduce the oxygen signal while the aluminum remains constant consistent with Al-O-Ge bonds being stable on the surface up to 280°C. The 220°C and 280°C annealed surfaces have an O:Al ratio near 1:1 which is consistent with the DFT model of the bonding on the surface proposed below.

3.6 Density Functional Theory Simulations

DFT modeling and STM simulations were performed to verify proposed bonding configurations of the H₂O₂/Ge(100) surface (Fig. 3.1), 100°C annealed H₂O₂/Ge(100) surface (Fig. 3.5), and the TMA dosed and annealed H₂O₂/Ge(100) surface (Fig. 3.6). The DFT models were developed by placing –OH or –O groups from dissociated H₂O₂(g) onto the Ge(100) surface followed by a relaxation. A vacuum layer of around 15 Å was added above the surfaces to eliminate spurious interaction through periodic-boundary conditions. The three bottom layers of the Ge slabs were permanently fixed in their bulk-like positions and the bottom most layer was passivated by H atoms to simulate continuous bulk. All simulated Ge slabs had 12 atomic layers (around 16 Å tall) which, in combination with bulk-like fixation of the 3 bottom layers, was enough to emulate bulk-like behavior and avoid surface to surface interaction.

A variety of bonding configurations were modeled and only the lowest energy models are presented. Fig. 3.8(a) shows a side view of DFT models of the two lowest energy bonding configurations found on the H₂O₂(g) dosed Ge(100) surface. The STM simulations, shown above the DFT models, are consistent with the two bonding
configurations shown in the STM image in Fig 3.8(b). The STM simulations showing the HO-Ge-O-Ge-OH structure (blue box) are consistent with an oxygen insertion imaging as a dark spot in between the hydroxyl terminated Ge atoms. In STM, both these symmetric bright sites have the same brightness because the Ge-OH bond freely rotate at 25°C; it is only an artifact of 0K non-rotating Ge-OH bonds in the STM simulation causing the STM simulation to have asymmetric brightness. The dihydroxyl terminated Ge dimer (green box) is consistent with a brightness covering the entire Ge dimer due to the imaging of the hydroxyls and the Ge dimer bond. In both configurations, the chemisorbates align directly along the Ge dimer rows and cover nearly the full surface.

Fig. 3.9 shows the calculated density of states (DOS) of the clean Ge surface passivated with hydrogen atoms (red curve) representing a defect free surface compared to the Ge surface dosed with H₂O₂(g) (black curve). The band gap of the DFT calculated DOS is smaller than the actual band gap of the system due to the standard PBE band gap underestimation. The H-passivated Ge surface, Fig. 3.9 red curve, shows an unpinned surface with the Fermi level near midgap as shown by the red curve in the enlarged inset in the top left corner of Fig. 3.9. After covering the surface with –O and –OH species via H₂O₂(g) dosing, the Fermi level is pinned p-type most likely due to the surface dipole as shown by the shift of the Fermi level into the valance band (black curve). This is consistent with the STS data shown in Fig. 3.2.

Fig. 3.10 shows a DFT model and STM simulation of the H₂O₂(g) dosed Ge surface annealed to 100°C. Annealing the H₂O₂/Ge(100) surface to 100°C induces H₂ desorption and insertion of one oxygen species into the Ge dimer bond. Fig. 3.10(c)
confirms the STM of the 100°C annealed H₂O₂/Ge(100) with the zig-zag structure formed via the anneal is consistent with STM simulation overlaid on the image.

Total energy calculations from the DFT models of each of the H₂O₂/Ge bonding configurations were compared to determine relative thermodynamic stability. In order to compare the total energy of each system relative to the initial clean surface, gas phase species were included in each total energy calculation to ensure all systems had the same number of atoms. Fig. 3.11 shows the total energies of each system, including gas phase reaction products and reacted surfaces. In Fig. 3.11, the fourth column shows the total surface energy while the fifth column displays ΔE, the energy of each system relative to system A, which is the bonding configuration of the clean Ge surface with six gas phase H₂O₂(g) molecules. System B & C depict the two room temperature H₂O₂(g) dosed isolated Ge bonding configurations. System D depicts the mixed surface with half B and half C bonding configurations. Systems E and F depict the mixed surface D bonding configuration after 100°C anneal. System E and F show two different total energies due to the two different potential reactions that could occur which leave differing gas phase products. System E depicts the reaction where all gas phase species are formed due to water recombinative desorption off the Ge surface while system F depicts the reaction that has partial water recombinative desorption and also remaining gas phase H₂O₂ and H₂. As shown in Fig. 3.11, the surface becomes more stable (lower total energy) as more H₂O₂(g) chemisorbs to the surface via the mechanism proposed in Fig. 3.4, and the 100°C anneal transforms the mixed surface to a more thermodynamically stable configuration.
DFT simulations were performed to confirm the bonding structure and DOS of TMA dosed onto the H$_2$O$_2$(g) functionalized Ge surface and are shown in Fig. 3.12. This model was calculated by bonding monomethylaluminum (MMA) to the oxygen species on the HO-Ge-O-Ge-OH structure shown in the blue box of Fig 3.8(a). Subsequently, the model was relaxed. During relaxation, the aluminum atoms pulled the oxygen that had previously inserted into the Ge dimer bond out of the dimer bond and instead bridge bonded between two aluminum atoms above the dimer. The relaxed structure has a ratio of Al, C, and O that is similar to what is seen in the XPS results in Fig. 3.7. The relaxed model is also consistent with the STM image of the TMA/H$_2$O$_2$/Ge(100) (Fig. 3.6a) which has rows directly above the Ge dimer rows. As seen in the DOS of the H-passivated Ge defect free surface (Fig. 3.9a), the DOS of this surface shows no states in the band gap, consistent with the STS results in Fig. 3.6b demonstrating that the TMA/H$_2$O$_2$/Ge provides as good of an interface as the clean H-passivated Ge surface. The band gap of the DFT calculated DOS is smaller than the actual band gap of the system due to the PBE simulation method.

3.7 Conclusion

Functionalization and passivation of the Ge(100) surface was demonstrated using H$_2$O$_2$(g). 25$^\circ$C dosing of H$_2$O$_2$(g) leaves surface Ge dimers terminated with either two or three oxygen species while passivating the dangling bonds on the surface. Compared to conventional H$_2$O(g) functionalization of the Ge(100) surface for ALD, H$_2$O$_2$(g) more than doubles the oxygen concentration on the surface and provides a higher saturation coverage which thereby decreases the density of dangling bond defects during ALD of Al$_2$O$_3$. H$_2$O$_2$(g) also gives increased thermal stability
compared to the H$_2$O(g) dosed Ge(100) which is important for potential applications as an ALD precursor. TMA was dosed on the H$_2$O$_2$(g) saturated Ge(100) surface and it formed a high density electrically passive monolayer of thermally stable Al-O bonds. DFT modeling and STM simulations verified all of the bonding configurations on the surface and were consistent with STM results. Using H$_2$O$_2$(g) as an oxidant precursor allows for a smaller amount of oxidant pre-pulsing, a more complete passivation of surface dangling bonds, an increased number of reactive ALD nucleation sites, and an increased thermal budget during ALD.

3.8 Acknowledgements

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Chapter 3, in full, is a reprint of the material as it appears in The Journal of Chemical Physics 2014. T. Kaufman-Osborn, E. A. Chagarov, A. C. Kummel, Atomic imaging and modeling of H$_2$O$_2$(g) surface passivation, functionalization, and atomic layer deposition nucleation on the Ge(100) surface, 140, 204708 (2014). The dissertation author was the primary investigator and author of this paper.
Figure 3.1 STM image of clean and $2.25 \times 10^5$ L $\text{H}_2\text{O}_2(g)$ dosed Ge(100) (a) Filled state STM image ($10 \times 10$ nm$^2$, $V_s = -1.8$V, $I_t = 0.2$nA) of a clean Ge(100) surface showing both (2×1) and c(4×2) reconstructions (b) Filled state STM image ($10 \times 10$ nm$^2$, $V_s = -1.8$V, $I_t = 0.2$nA) of a $2.25 \times 10^5$ L $\text{H}_2\text{O}_2(g)$ dosed Ge(100). The $2.25 \times 10^5$ L $\text{H}_2\text{O}_2(g)$ dose at RT produces 0.97 ML of $\text{H}_2\text{O}_2(g)$ dark chemisorption sites (blue and green boxes) on a Ge(100) surface. Bright spots (red box) are unreacted sites with $\frac{1}{2}$ filled dangling bonds. (c) Schematic diagrams of surface bonding configurations that correspond to the blue, green, and red boxes in the STM image.
Figure 3.2 STS of clean and H$_2$O$_2$/Ge(001) STS of a H$_2$O$_2$(g) dosed Ge(100) surface at RT. STS measured on H$_2$O$_2$ sites (blue curve) shows reduction of dangling bond states (red arrow) compared with dangling bond sites (red curve). Blue arrow highlights the Fermi level shift and pinning near the valence band.
Figure 3.3 XPS comparison of $9 \times 10^5$ L H$_2$O(g) vs H$_2$O$_2$(g) dosing at 25°C on Ge(100) (a) XPS data showing peak area ratios of oxygen 1s to germanium 3d after relative sensitivity factor adjustment comparing oxygen coverage for equivalent 25°C room temperature doses of H$_2$O(g) and H$_2$O$_2$(g) on a sputter cleaned Ge(100) surface. (b) XPS peak shape analysis of the Ge 2p peak after dosing H$_2$O(g) on a clean Ge(100) surface. A Ge-OH feature appears with a peak shift of 1.3 eV (c) XPS peak shape analysis of the Ge 2p peak after dosing H$_2$O$_2$(g) on a clean Ge(100) surface. Two Ge-O$_x$H$_y$ features appear with peak shifts of 1.3 eV and 2.1 eV.
Figure 3.4 Heuristic model of H\textsubscript{2}O(g) and H\textsubscript{2}O\textsubscript{2}(g) dissociation mechanism on Ge(100) (a) Neighboring empty dimer sites available for dissociative chemisorption of H\textsubscript{2}O(g). (b) Neighboring dimer sites with H\textsubscript{2}O(g) dissociatively chemisorbed across the dimer row leaving two separated empty sites (red) which are unavailable for dissociative chemisorption of H\textsubscript{2}O(g). (c) Neighboring empty dimer sites available for dissociative chemisorption of H\textsubscript{2}O\textsubscript{2}(g). (d) Neighboring dimer sites with H\textsubscript{2}O\textsubscript{2}(g) dissociatively chemisorbed across the dimer row leaving two separated empty sites. H\textsubscript{2}O\textsubscript{2}(g) is still able to dissociatively chemisorb on each single empty site and form a bridge bonded oxygen species in the dimer.
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Figure 3.11  Total energies of DFT unit cell models of clean Ge and H₂O₂(g) dosed Ge at 25°C and 100°C (a) Clean Ge(100) surface unit cell total energy with six H₂O₂(g) molecules. (b & c) Two possible H₂O₂(g) dosed Ge room temperature bonding configuration unit cell total energies (d) Mixed unit cell consisting of both b & c H₂O₂(g)/Ge bonding configuration unit cell total energy. (e & f) Mixed unit cell bonding configuration (d) annealed to 100°C total unit cell energy.
Figure 3.12 DFT model and DOS of TMA/H$_2$O$_2$/Ge(100) DFT model and DOS of the H$_2$O$_2$(g) dosed Ge(100) surface bonded to MMA species and relaxed to the lowest energy configuration. Green circles correspond to germanium atoms, red circles correspond to oxygen atoms, blue circles correspond to aluminum atoms, grey circles correspond to carbon atoms, and white circles correspond to hydrogen atoms. DOS shows no states in the band gap which was experimentally verified using STS as seen in Fig. 3.6b.
Chapter 4

Atomic imaging and modeling of passivation, functionalization, and atomic layer deposition nucleation of the SiGe(001) surface via H₂O₂(g) and trimethylaluminum dosing

4.1 Abstract

Passivation, functionalization, and atomic layer deposition (ALD) via H₂O₂(g) and trimethylaluminum (TMA) dosing was studied on the clean Si₀.₆Ge₀.₄(001) surface at the atomic level using scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS). Chemical analysis of the surface was performed with in-situ x-ray photoelectron spectroscopy (XPS) while density functional theory (DFT) was employed to model the bonding of H₂O₂(g) chemisorbates to the substrate. A room temperature saturation dose of H₂O₂(g) covers the surface with a monolayer of –OH and –O chemisorbates. XPS and DFT demonstrate that the room temperature H₂O₂/SiGe surface is comprised of only Ge-OH and Ge-O bonds while annealing induces an atomic layer exchange bringing Si to the surface to bond with –OH or –O while pushing Ge subsurface. The resulting Si-OH and Si-O surface is optimal because it can be used to nucleate high-k ALD and Si dangling bonds are readily passivated by forming gas. After H₂O₂(g) functionalization, TMA dosing, and a subsequent 230°C anneal, ordering along the dimer row direction is observed on the surface. STS verifies that the TMA/H₂O₂/SiGe surface has an unpinned Fermi level.
with no states in the band gap demonstrating the ability to serve as an ideal template for further high-k deposition.

4.2 Introduction

To further scale complementary metal-oxide semiconductor (CMOS) devices, materials with high carrier mobility have been studied. Much attention has been given to using SiGe as a channel material due to its high hole mobility and the facility to place Si channels or low Ge content SiGe under biaxial tensile strain for electron mobility enhancement in NMOS or to have a SiGe channel compressively strained by a higher Ge content SiGe or pure Ge to enhance hole mobility. [86-88] However, one of the main challenges in employing SiGe as a channel material is achieving a high quality interface between SiGe and a gate oxide. [89] As the oxide thickness is scaled down on the SiGe surface, a large drop in mobility is observed which is most likely caused by the poor quality Ge containing oxide which exists at the SiGe-oxide interface. [90] Therefore, a high quality and low defect density interlayer must be deposited between the semiconductor and the gate oxide.

Several strategies have been studied to optimize the SiGe/oxide interface. On Ge(001), a good oxide/SiGe interface can be formed by growing a high quality GeO₂ layer using high temperature and high pressure oxidation[38; 53; 91; 92]. However, oxidation of the SiGe surface to form an insulating layer is difficult because typical thermal oxidation preferentially oxidizes the Si leaving a Ge rich layer or Ge suboxide near the semiconductor-oxide interface which negatively affects the oxide properties.[93] Even if SiO₂ and GeO₂ could simultaneously be formed on SiGe, GeO₂ is problematic due to its water solubility and limited thermal stability. Another
possible solution is to deposit an ultra-thin Si capping layer [94-98]. The Si capping layer can be very effective at reducing interface traps (D
<i>n</i>). [97] However, optimizing the Si cap thickness is crucial because too thin a cap can result in leakage current while too thick a Si cap can increase sub-threshold swing and lower hole mobility. [98]

In an effort to improve performance on Si and SiGe devices, multilayered oxides (SiO₂/Ta₂O₅, Ta₂O₅/ZrO₂, ZrO₂/HfO₂, SiO₂/ZrO₂, etc.) have been studied with the goal of lowering EOT, reducing leakage current, increasing interfacial layer stability, suppressing dopant diffusion, and improving reliability. Many multilayered oxides include a low-k SiO₂ layer in an effort to optimize the semiconductor/oxide interface quality. [99-104]

The goal of this study is to eliminate the need for the Si/SiO₂ capping layer by generating a Si-OH and Si-O terminated surface via H₂O₂(g) dosing and annealing which can directly nucleate high-k ALD and subsequently be treated with forming gas anneal process to passivate any persistent Si dangling bonds at the interface.[105-108] The effect of reacting H₂O₂(g) and TMA on the Si₀.₆Ge₀.₄(001) surface is analyzed because it has previously been shown on Ge, Si, and SiGe that a very thin interfacial Al₂O₃ can improve device performance.[70; 71; 109]

The present study reports upon the formation of a thermally stable passivation layer of monolayer thickness on Si₀.₆Ge₀.₄(001) which leaves the Fermi level unpinned while preventing low quality Ge sub-oxide formation eliminating the need for a low-k SiO₂ buffer layer. The surface bonding configurations and thermal behavior of the Si₀.₆Ge₀.₄(001) surface after H₂O₂(g) and TMA dosing was studied by
annealing in ultrahigh vacuum conditions and analyzing the surface between each step using \textit{in-situ} x-ray photoelectron spectroscopy (XPS), scanning tunneling microscopy (STM), and scanning tunneling spectroscopy (STS). Atomic models of the H$_2$O$_2$(g) passivated Si$_{0.5}$Ge$_{0.5}$(001) surface were developed using density functional theory (DFT) and were consistent with experimental results. H$_2$O$_2$(g) + TMA dosing on the SiGe surface was shown to produce an electrically passive interface which acts as an ideal template for additional high-k deposition; DFT modeling of the monolayer of aluminum oxide on SiGe(001) are consistent with an ordered electrically passive interface.

4.3 Experimental Details

N-type Si$_{0.6}$Ge$_{0.4}$(001) wafers doped with 4x10$^{19}$ cm$^{-3}$ P (Applied Materials) were diced into 12mm x 5 mm pieces. Samples were degreased using acetone, methanol, and deionized water then dried with N$_2$ gas. Samples were loaded into a custom Omicron UHV chamber with a base pressure of 2×10$^{-10}$ Torr then cleaned via repeated sputter and anneal processes. The sputtering was performed using a 1-1.5keV of Ar$^+$ ion beam (Model 1403 ion gun, Nonsequitur Technologies) with a beam current of 0.6-0.9 μA for 30 min while the sample temperature was maintained at 500°C via direct heating. Following each sputter process, the sample temperature was maintained at 500°C for 20 min. Sample cleanliness was verified via STM before proceeding with each experiment.

SiGe surfaces were reacted with precursors in a separate “dosing” chamber with a base pressure of 2×10$^{-8}$ Torr. Without carrier gas, H$_2$O$_2$(g) and TMA were dosed by back filling the dosing chamber with the precursor vapors. The doses of
both H$_2$O$_2$(g) and TMA were controlled by throttling valves on the H$_2$O$_2$(g) and TMA. The reaction pressures were measured using a convectron gauge, and the exposures were estimated in Langmuirs (1 Langmuir (L) = 1 x 10$^{-6}$ Torr · 1 sec). The SiGe(001) samples were maintained at 300K during dosing. A 30% solution of H$_2$O$_2$(aq) was employed as the surface oxidant source. The H$_2$O$_2$(aq) solution is known to produce a vapor containing 2.7% H$_2$O$_2$(g) at 25°C.\[^{[72]}\] Glass and teflon tubing and teflon valves were employed to minimize the decomposition of the H$_2$O$_2$(g); however, some H$_2$O$_2$(g) may have reacted with the walls of the stainless steel dosing chamber. Therefore, the estimates of H$_2$O$_2$(g) exposures on the Si$_{0.6}$Ge$_{0.4}$(001) surfaces are the upper limits of the actual doses of H$_2$O$_2$(g). However, knowledge of the exact dose is not material to the results because all results in this study employed saturation doses.

After dosing H$_2$O$_2$(g) or TMA, samples were transferred to the UHV chamber for thermal annealing. The sample temperature was monitored by a pyrometer during direct heating using a controlled heating ramp rate of 1°C/sec. The sample surface topography was analyzed using \textit{in-situ} analysis via an STM (LT-STM, Omicron Nanotechnology). After each surface treatment, STM (scanning tunneling microscopy) and STS (scanning tunneling spectroscopy) data were obtained at RT in a UHV chamber with a base pressure of 1 × 10$^{-11}$ Torr. STM images were acquired using constant-current mode STM (I$_{sp}$ = 0.2nA) with an applied sample bias between -1.8 and -2.0V. STS, operating in variable-z mode using a modulation signal (0.1V, 650 Hz) supplied by an external lock-in amplifier while sweeping the sample bias from -1 to +1V or -1.5 to +1.5V, was implemented to measure the electronic structure of sample surfaces.
Chemical analysis was performed using an *in-situ* monochromatic XPS (XM 1000 MkII/SPHERA, Omicron Nanotechnology) to examine the surface elements and their relative intensities. XPS data was acquired in constant analyzer energy mode with a pass energy of 50eV and a line width of 0.1 eV using an Al Kα source (1486.7 eV). The takeoff angle was 30° from the sample surface (i.e. close to the surface parallel) with an acceptance angle of ± 7°. Peak shape and data analysis was performed using CASA XPS v.2.3 using a Shirley background subtraction method.

4.4 Computational Details

All presented first-principle simulations were performed with the Vienna Ab-Initio Simulation Package (VASP)[74; 75] applying projector augmented-wave (PAW) pseudopotentials (PP)[73; 76] and PBE (Perdew-Burke-Ernzerhof) exchange-correlation functional[77; 110]. The choice of PBE functional and PAW pseudopotentials was validated by parametrization runs demonstrating good reproducibility of experimental lattice constants and bulk moduli of crystalline bulk Si and Ge. The systems were relaxed by conjugate-gradient algorithm with force tolerance level of 0.02 eV/Å. The 3 bottom layers of the slabs were fixed in bulk-like positions and passivated by H atoms to simulate continuous bulk.

4.5 Results and Discussion

Atomically flat and clean Si$_{0.6}$Ge$_{0.4}$(001) surfaces were prepared via multiple cycles of sputtering and annealing. Fig. 4.1(a&b) shows a typical filled-state STM image of a clean Si$_{0.6}$Ge$_{0.4}$(001) surface. The surface of clean Si$_{0.6}$Ge$_{0.4}$(001) is known to be terminated with a high percentage of Ge atoms due to segregation of Ge to the surface. [111-114] This consistent with the SiGe(001) surface being more
thermodynamically stable when covered with under coordinated Ge atoms rather than under coordinated Si atoms. To determine the electronic structure of the clean $\text{Si}_{0.6}\text{Ge}_{0.4}(001)$ surface, scanning tunneling spectroscopy (STS) measurements were performed. STS measurements generate $(\text{d}I/\text{d}V)/(I/V)$ data which shows the local density of states on the surface.\cite{4,7,83} Fig. 4.1(c) shows an average of 12 STS curves taken on the clean $\text{Si}_{0.6}\text{Ge}_{0.4}(001)$ surface shown in Fig. 4.1(a) (blue curve). STS was only conducted on n-type samples because the Fermi level pins on the SiGe(001) surface near the valence band edge as shown by the average of STS curves acquired on a SiGe(001) sample which was damaged via sputtering without annealing. The sputter damaged surface (STS - Fig. 4.1(c) green curve, STM image not shown) shows the surface pins p-type consistent with a large density of valence band edge states. Therefore, if p-type samples were used, one would be unable to determine whether pinning had occurred. The clean n-type $\text{Si}_{0.6}\text{Ge}_{0.4}(001)$ surface has an unpinned Fermi level position ($0\text{V in STS}$) which is slightly above midgap. The Fermi level on clean n-type $\text{Si}_{0.6}\text{Ge}_{0.4}(001)$ being slightly above midgap is identical to the Fermi level position on clean Ge(001) surface. This is consistent with the presence of $\frac{1}{2}$ filled dangling bonds on surface Ge dimers on the Ge-terminated ordered sputter cleaned $\text{Si}_{0.6}\text{Ge}_{0.4}(001)$ surface.\cite{85}

In order to passivate and functionalize the $\text{Si}_{0.6}\text{Ge}_{0.4}(001)$ surface, the surface was exposed to a near saturation dose of $2\times10^4 \text{ L of } \text{H}_2\text{O}_2(\text{g})$ at room temperature (RT). Fig. 4.2 shows an STM image of the $\text{H}_2\text{O}_2(\text{g})$ dosed $\text{Si}_{0.6}\text{Ge}_{0.4}(001)$ surface; the $\text{H}_2\text{O}_2(\text{g})$ induced dark site formation. DFT analysis shown later determined that $\text{H}_2\text{O}_2(\text{g})$ dosing of the $\text{Si}_{0.6}\text{Ge}_{0.4}(001)$ surface results in $\text{–OH}$ and $\text{–O}$ adsorbates
bonded to the surface. This is consistent with both STM imaging and STM simulations of –OH and –O adsorbates on the H\textsubscript{2}O\textsubscript{2}(g) dosed Ge(001) surface which also image as dark sites.[115] Models of the –OH or –O species are shown in Fig. 4.2(b). Unreacted sites (Fig 4.2, red box) are imaged as bright due to their dangling bonds while reacted sites have an altered electronic structure resulting in a difference of brightness when imaged in constant current mode STM. This allows differentiation between the two different bonding configurations which are highlighted inside the blue and green boxes in Fig. 4.2. The proposed models were developed using bond enthalpy calculations and are confirmed below using DFT calculations. As previously shown on the pure Ge(001) surface, the bonding configuration shown in the green box occurs when H\textsubscript{2}O\textsubscript{2}(g) dissociates on a Ge dimer terminating each Ge atom with an –OH species. [115] The blue box shows the bonding configuration where an –O atom has inserted into the Ge dimer bond which is already terminated by two –OH species. The OH-Ge-O-Ge-OH site appearing darker in filled state imaging than the OH-Ge-Ge-OH site is consistent with the bridging O atoms causing the valence electrons to be more tightly bound. This difference in STM imaging is consistent with STM simulations previously shown on the H\textsubscript{2}O\textsubscript{2}(g) dosed Ge(100) surface.[115] The red box highlights the small portion of the surface that remains unreacted leaving undercoordinated surface atoms with dangling bonds which have a high tunneling current and image as very bright spots.

During the dosing of H\textsubscript{2}O\textsubscript{2}(g), background H\textsubscript{2}O(g) is present. However, H\textsubscript{2}O(g) has a very low reactivity with the Ge(100) surface at room temperature.[81] It is hypothesized that the background H\textsubscript{2}O(g) did not affect the reaction of H\textsubscript{2}O\textsubscript{2}(g) with
the SiGe(100) surface. If H₂O(g) dissociatively chemisorbed to the SiGe surface, the reaction Ge-H + H₂O₂(g) → Ge-OH + H₂O(g) would quickly occur eliminating the Ge-H bond due to the difference in bond strength of Ge-O (659 kJ/mol) vs Ge-H (327 kJ/mol).[82]

STS curves were taken on the H₂O₂(g) dosed Si₀.₆Ge₀.₄(001) surface and are shown in Fig. 4.2(c). As shown by the red arrow, H₂O₂(g) shifts the Fermi level towards the valence band edge consistent with the oxygen containing adsorbates shifting the Fermi level towards the valence band edge due to the large dipole on the surface. [84]

After H₂O₂(g) dosing onto the Si₀.₆Ge₀.₄(001) surface, XPS was employed to verify that the surface was terminated with Ge atoms and show the progression of SiGe(001) surface bonding as the annealing temperature was raised. Fig. 4.3 shows the evolution of the Ge 3d and Si 2p peaks after a variety of surface treatments. Fig. 4.3(a) shows the Ge 3d and Si 2p peaks after repeated cycles of sputtering and annealing until the Si₀.₆Ge₀.₄(001) sample was free of contaminants. The cleanliness was verified by STM imaging and verified as contaminant free in XPS. The Si₀.₆Ge₀.₄(001) surface was subsequently dosed with 2×10⁵ L of H₂O₂(g) at RT. While the Ge 3d peak on the clean Si₀.₆Ge₀.₄(001) surface in Fig. 4.3(a) only shows a bulk-like component, H₂O₂(g) dosing at room temperature (RT) generated a higher binding energy peak which is assigned as GeOₓHᵧ. As previously shown, dosing H₂O₂(g) onto a Ge surface results in a variety of bonding configurations involving a complete –OH and –O termination. [115] Therefore, the resulting bonding configurations on the surface have been collectively assigned as a single broad GeOₓHᵧ peak centered at ~1.5 eV higher than
the bulk Ge feature. However, the RT H$_2$O$_2$(g) dose has no effect on the Si 2p peak shown in Fig 4.3(b). This is consistent with the sputter cleaned Si$_{0.6}$Ge$_{0.4}$(001) surface being completely terminated with Ge-Ge dimers and indicates that H$_2$O$_2$(g) dosing at RT results in no subsurface oxidation of Si$_{0.6}$Ge$_{0.4}$(001).

The sample was subsequently annealed at 180°C inducing a large reduction in the GeO$_x$H$_y$ peak and formation of a SiO$_x$H$_y$ peak (see Fig. 4.3(c)). This is consistent with the –OH and –O adsorbates pulling the subsurface Si atoms to the surface to form Si-OH or Si-O bonds upon heating to 180°C. This phenomenon has been seen in a similar system where Cl atoms on a Ge terminated SiGe surface induce place exchange when annealed resulting in Si-Cl bonding.[116] Fig. 4.3(d) shows the XPS spectra of H$_2$O$_2$/ Si$_{0.6}$Ge$_{0.4}$(001) after a 300°C anneal; there are no Ge-OH nor Ge-O bonds remaining on the surface consistent with complete Si/Ge place exchange. The complete Si/Ge place exchange is also consistent with the growth of the SiO$_x$H$_y$ peak in Fig. 4.3(d) compared to Fig. 4.3(c). This place exchange results from the difference in bond strengths between Ge-O (659.4 kj/mol) and Si-O (799.6 kj/mol) bonds.[82]

The ability to manipulate the H$_2$O$_2$(g) dosed SiGe(001) surface from Ge termination to Si termination is beneficial for device fabrication because the Si-OH terminated surface should form stable strong bonds to high-k ALD metal precursors. Furthermore, if any dangling bonds persist after oxide deposition, the dangling bonds will be on Si which can be passivated using forming gas thereby minimizing D$_{it}$. [105-108]

Once the Si$_{0.6}$Ge$_{0.4}$(001) surface was functionalized via H$_2$O$_2$(g) dosing, TMA was dosed in order to emulate typical ALD processing for growth of Al$_2$O$_3$;
afterwards, STM and STS measurements were performed. Fig. 4.4(a) shows an STM image of a Si$_{0.6}$Ge$_{0.4}$(001) surface dosed with 4×10$^5$ L of H$_2$O$_2$(g) and subsequently dosed with 5×10$^4$ L of TMA and annealed at 230°C for 20 min. Vertical rows are observed along the SiGe dimer row direction demonstrating chemisorption of the TMA onto the H$_2$O$_2$/SiGe(001) surface. The TMA/H$_2$O$_2$/SiGe STM image has inferior resolution than the clean SiGe surface due to the many weakly bound adsorbates covering the surface making it difficult to maintain high resolution STM tip stability; however, line trace analysis, STS, XPS, and DFT (shown below) can be employed for definitive structure identification. Line trace analysis was performed on 20 different locations on the image; for each of the 20 traces, the spacing over at least 3 rows was measured to increase accuracy. The average row spacing was 8.3Å with a standard deviation of 1.0 Å and with a standard error of 0.023 Å. Fig. 4.4(b) shows four line trace profiles taken on the STM image showing consistent spacing of the ordered rows which corresponds with the dimer row spacing on the clean Si$_{0.6}$Ge$_{0.4}$(001) surface.

STS measurements were used to analyze the electronic structure of the TMA/H$_2$O$_2$/SiGe surface and are shown in Fig. 4.5. By dosing the H$_2$O$_2$/SiGe surface (Fig. 4.2c red curve) with TMA, the Fermi level is shifted back to a position identical to that on the clean surface as shown by the good agreement in Fermi level position between the clean SiGe surface (Fig. 4.5 blue curve) and the TMA/H$_2$O$_2$/SiGe surface (Fig. 4.5 green curve).

Fig. 4.6 shows XPS analysis of a SiGe(100) sample dosed with 4×10$^5$ L of H$_2$O$_2$(g) and subsequently dosed with 5×10$^4$ L of TMA and annealed at 230°C for 20 min. The sample was subsequently annealed at 310°C for 20 min. As the sample is
headed to 310°C, XPS shows the carbon signal decreases consistent with methyl desorption. Annealing the sample may also slightly reduce the oxygen signal while the aluminum signal remains constant. This is consistent with Al-O-Si/Ge bonds being stable up to 310°C demonstrating thermal stability after H₂O₂(g) and TMA dosing.

4.6 Density Functional Theory Simulations

DFT modeling was performed to verify proposed bonding configurations and to study the thermodynamic stability of the bonding configuration of the H₂O₂/SiGe during annealing. The DFT models were established by placing –OH or –O groups from dissociated H₂O₂(g) onto the SiGe(100) surface, with either Si or Ge termination, followed by a relaxation. Multiple bonding configurations were modeled and the lowest energy models are presented. Fig. 4.7 shows a side view of six different bonding configurations calculated for the reaction products of H₂O₂(g) on the Si₀.₅Ge₀.₅(001) surface. Note the experiments were performed on Si₀.₆Ge₀.₄(001) while the DFT model is for Si₀.₅Ge₀.₅(001) to simplify the calculations; the differences are not expected to be important. The top row of DFT models show the SiGe(001) surface with Ge termination on (a) the clean surface, (b) the –OH passivated surface, and (c) the –OH passivated surface with an additional –O atom inserted into the Ge dimer bond. The bottom row of DFT models show the same three surface bonding configurations on SiGe(001) but instead with Si termination.

In order to compare the relative thermodynamic stability of each system, gas phase species were added to ensure each system has the same number of atoms. Column (a) compares the total energy of the clean SiGe(001) surface terminated in either Ge dimers or Si dimers. As shown Fig. 4.7, the clean Ge terminated surface has
a lower total energy than the Si terminated surface. This is consistent with the surface being more thermodynamically stable with Ge dangling bonds; since Ge bonds are weaker than Si bonds, it is reasonable the thermodynamically preferred under-coordinated atoms are Ge. Columns (b & c) compare the total energy of the SiGe(001) surface in the two most stable H₂O₂(g) dosed SiGe(001) bonding configurations. In contrast to the clean surface, the systems are now more stable when they are terminated with Si atoms (bottom row) rather than Ge atoms (top row). This is due to the stronger bond that is formed during Si-OH or Si-O bonding compared to Ge-OH or Ge-O bonding.

DFT simulations were performed to verify the bonding configuration and DOS of TMA dosed onto the H₂O₂(g) functionalized SiGe surface and are shown in Fig. 4.8. This model was developed by bonding monomethylaluminum (MMA) to the oxygen species on the OH-Si-O-Si-OH structure shown in the bottom row of column C in Fig. 4.7. The model was subsequently relaxed. During relaxation, the aluminum atoms pulled the oxygen that had previously inserted into the Si/Ge dimer bond out of the dimer bond to form an oxygen bridge bonded between two aluminum atoms above the dimer. This structure is consistent with the STM image and line traces of TMA/H₂O₂/SiGe (Fig. 4.4 a&b) with row spacing identical to the clean surface. The DOS of this structure was calculated and shows no states in the band gap, consistent with STS results in Fig. 4.5 (green curve) verifying that the TMA/H₂O₂/SiGe structure provides an electrically passive unpinned interface with no mid-gap defect states. The band gap of the DFT calculated DOS is smaller than the actual band gap of the system.
due to the standard PBE band gap underestimation. Note exact atomic positions of all atoms in the DFT models presented herein are included in the supplementary material.

4.7 Conclusion

H$_2$O$_2$(g) was employed to functionalize and passivate the Si$_{0.6}$Ge$_{0.4}$(001) surface. The clean Si$_{0.6}$Ge$_{0.4}$(001) surface is terminated with Ge dimers; RT dosing of H$_2$O$_2$(g) onto the clean surface results in either two or three oxygen species per surface Ge dimer successfully passivating the dangling bonds on the surface Ge dimers. When the RT H$_2$O$_2$/Si$_{0.6}$Ge$_{0.4}$(001) surface is annealed above ~150°C, the atoms near the surface undergo a “flip” or place exchange pushing Ge atoms subsurface while bringing Si to the surface. This occurs because, upon thermal activation, it is most thermodynamically favorable for Si to bond to oxygen containing adsorbates. This phenomenon allows for manipulation of the H$_2$O$_2$/SiGe interface by annealing. By “flipping” the Ge and Si surface atoms and terminating the SiGe(001) surface in Si-OH and Si-O, high-k ALD precursors can directly react to the Si terminated surface. Once the surface has been functionalized with H$_2$O$_2$(g), TMA is dosed resulting in a high nucleation density of Al-O bonds. Dosing TMA onto the H$_2$O$_2$/Si$_{0.6}$Ge$_{0.4}$(001) surface results in an electrically passive thermally stable monolayer of Al-O-Si bonds which serves as an ideal template for further high-k deposition. DFT modeling verified the bonding configuration of the H$_2$O$_2$(g) only and TMA + H$_2$O$_2$(g) dosed Si$_{0.5}$Ge$_{0.5}$(001) surface, and the total energy calculations were consistent with experimental data demonstrating the Ge-Si “flip” phenomenon on the H$_2$O$_2$/SiGe surface. Using H$_2$O$_2$(g) as an oxidant precursor provides a high density of reactive oxygen containing adsorbates which nucleate Al$_2$O$_3$ growth when dosed with TMA. It
is expected that the Si-OH functionalized surface can directly form strong bonds to most high-k ALD metal precursors and, if any unpassivated sites remain on this Si-terminated surface after oxide deposition, they can be passivated via forming gas anneal.

4.8 Acknowledgements

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Chapter 4, in part or in full, has been submitted for publication of the material as it may appear in T. Kaufman-Osborn, E. A. Chagarov, S. W. Park, B. Sahu, and A. C. Kummel, Atomic imaging and modeling of passivation, functionalization, and atomic layer deposition nucleation of the SiGe(001) surface via H$_2$O$_2$(g) and trimethylaluminum dosing, Surface Science (2014). The dissertation author was the primary investigator and author of this paper.
Figure 4.1 STM and STS of clean SiGe(001) (a) Filled state STM image (50 x 50 nm², \(V_s = -1.8V, I_t = 0.2nA\)) of sputter and anneal cleaned SiGe(001). (b) 10 x 10 nm² inset of black square outline in (a) showing surface reconstruction (c) STS of clean (blue) and sputter damaged (green) SiGe(001) surface. The clean surface is unpinned with a Fermi level (0V) slightly above midgap and the sputter damaged surface is pinned p-type consistent with large high density of valence band edge states. Dotted green line shows conduction band edge of sputter damaged surface.
Figure 4.2 STM image and STS of $2 \times 10^4$ L $\text{H}_2\text{O}_2$ (g) dosed SiGe(001) (a) Filled state STM image (15×15 nm$^2$, $V_s$ = -1.8V, $I_t$ = 0.2nA) of $2 \times 10^4$ L $\text{H}_2\text{O}_2$ (g) dosed onto clean SiGe(001). The $\text{H}_2\text{O}_2$ (g) dose at RT produces a nearly full monolayer of $\text{H}_2\text{O}_2$ (g) dark chemisorptions sites (blue and green boxes) on a SiGe(001) surface. Bright spots (red box) are unreacted sites with half filled dangling bonds. (b) Schematic diagrams of surface bonding configurations that correspond to the blue, green, and red boxes in the STM image. (c) STS of $\text{H}_2\text{O}_2$ (g) dosed SiGe(001) surface at RT (red curve) shows Fermi level shift towards the valence band (red arrow) compared to STS of clean surface (blue curve).
Figure 4.3 Ge 3d and Si 2p spectrum of H₂O₂/SiGe(001) (left) Ge 3d spectrum showing formation of a GeOₓHᵧ peak after a RT H₂O₂(g) dose and reduction of the GeOₓHᵧ peak as sample is annealed to 300°C. (right) Si 2p spectrum showing absence of a SiOₓHᵧ peak after RT H₂O₂(g) dose and formation of a SiOₓHᵧ peak as sample is annealed to 300°C.
Figure 4.4 STM and line trace of TMA/H$_2$O$_2$/SiGe(001) (a) 16×20nm$^2$ STM image of SiGe(001) pre-dosed with $4 \times 10^5$ L of H$_2$O$_2$(g) at RT followed by $5 \times 10^4$ L of TMA at RT and subsequently annealed at 230°C for 20 min. (b) Line trace analysis of four different areas of STM image. Vertical ordering is seen in the STM image and line trace analysis confirms uniform row spacing of 8.3Å with a standard error of 0.023 Å.
Figure 4.5 STS of TMA/H$_2$O$_2$/SiGe STS of clean SiGe(001) surface (blue curve) and TMA/H$_2$O$_2$/SiGe surface (green curve). STS of the ordered rows on the TMA/H$_2$O$_2$/SiGe surface shows no defect states in the band gap and a Fermi level position slightly above midgap identical to the clean surface and consistent with removal of the surface dipole from OH termination.
Figure 4.6 XPS of $5 \times 10^4$ L of TMA dosed on a SiGe(100) surface that was predosed with $4 \times 10^5$ L of H$_2$O$_2$(g) vs. annealing temperature XPS showing elements on the SiGe surface after a 25°C $4 \times 10^5$ L of H$_2$O$_2$(g) and $5 \times 10^4$ L of TMA after a 220°C and 280°C anneal. XPS sensitivity for core-level spectra was taken into account to compare intensities from different elements. All the data presented are derived from the ratios to the (Si2p + Ge3d) peak feature intensity.
Figure 4.7 DFT models and total energy of the H₂O₂/SiGe system. DFT models and total energies of (Column A) clean SiGe(001) surface Ge dimer terminated (top) or Si dimer terminated (bottom) (Column B) two hydroxyls bonded to each Ge dimer terminated SiGe(001) (top) or Si dimer terminated SiGe(001) (bottom) (Column C) two hydroxyls with an inserted bridge bonded oxygen atom on each Ge dimer terminated SiGe(001) (top) or Si dimer terminated SiGe(001) (bottom). The total energies of all the systems are compared showing that the clean surface is more thermodynamically stable with Ge termination while the H₂O₂(g) dosed surface is more stable with Si termination.

<table>
<thead>
<tr>
<th>Gas Phase Species</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge Termination</td>
<td>6 × H₂O₂(g)</td>
<td>2 × H₂O₂(g)</td>
<td>6 × H₂(g)</td>
</tr>
<tr>
<td>Total Energy (eV)</td>
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<td>-642.731</td>
<td>-650.933</td>
</tr>
<tr>
<td>Si Termination</td>
<td>6 × H₂O₂(g)</td>
<td>2 × H₂O₂(g)</td>
<td>6 × H₂(g)</td>
</tr>
<tr>
<td>Total Energy (eV)</td>
<td>-618.647</td>
<td>-645.754</td>
<td>-661.096</td>
</tr>
</tbody>
</table>

Germanium =  Green, Silicon = Yellow, Oxygen = Red, Hydrogen = Black.
Figure 4.8 DFT model and DOS of TMA/H₂O₂/SiGe(001) DFT model and DOS of the H₂O₂(g) dosed SiGe(100) surface bonded to MMA species and relaxed to the lowest energy configuration. Yellow circles correspond to silicon atoms, green circles correspond to germanium atoms, red circles correspond to oxygen atoms, blue circles correspond to aluminum atoms, grey circles correspond to carbon atoms, and white circles correspond to hydrogen atoms. DOS shows no states in the band gap which was experimentally verified using STS as seen in Fig. 4.5 (green curve).
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