ULTRATHIN HIGH-K OXIDES FOR AREA-SELECTIVE DEPOSITION AND CHARACTERIZATION BY BALLISTIC ELECTRON EMISSION MICROSCOPY AND X-RAY PHOTOEMISSION SPECTROSCOPY

by

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ABSTRACT

Insulators play an important role in the architecture and resulting performance of semiconductor devices manufactured today. Materials such as HfO₂ and Al₂O₃ are utilized as gate oxides and spacers to control leakage current and enable bottom-up self-aligned patterning of device features. Understanding the electrostatic barrier that forms at the metal-oxide-semiconductor (MOS) interface is crucial in the development of field effect transistors and other devices, especially as the scaling of device features continues to shrink into the nanoscale. Characterization of the barrier height using current-voltage (IV) and capacitance-voltage (CV) techniques provides only a spatially averaged view of the interface, and is incapable of accounting for local nonuniformity which arises at nanoscale dimensions. Additionally, common lithographic strategies for patterning small feature oxides are limited by printing misalignments such as edge placement error (EPE), and in order to achieve smaller pitch sizes lithography steps must be repeated multiple times which adds time and cost to the process. The feasibility of uniform, cost-effective insulator films at the 5 nm technology node and beyond relies on the development of new deposition strategies.

In this thesis, hafnium oxide grown using atomic layer deposition (ALD) is examined with ballistic electron emission microscopy (BEEM). Localized nonuniformities in the barrier height are found to exist for two identically prepared samples which reveal three distinct electrostatic barriers at the buried Au/HfO₂/SiO₂/Si-p interface, including a novel barrier found at 0.45 eV due to ultrathin HfO₂. The results uncover changes in electrostatic behavior of the film which are otherwise impossible to detect using spatially averaged techniques. These variations in barrier height are visualized in a novel way that produces spatial maps showing transitions between high energy and lower energy barriers across a few nanometers. The resolution of this mapping technique is determined by comparing the measured barrier heights of Au/Si(001) and Au/Si(111) interfaces. Momentum conservation and electron scattering result in slightly different barrier heights for both interfaces that depends on metal thickness. The Rayleigh criterion is applied to the barrier height distributions as a function of metal thickness, resulting in a 10 meV resolution.
Both aluminum oxide and hafnium oxide are also selectively grown on patterned metal / low-k silicon wafers using ALD. Self-assembled monolayer (SAM) materials such as octodecanethiol (ODT) and dodecanethiol (DDT) - which are functionalized to metal - are first deposited on the copper lines in order to block high-k film deposition on metal. Both HfO$_2$ and Al$_2$O$_3$ are shown to selectively cover the low-k lines for linespace pitches greater than 100 nm and 5 mM concentration of SAM, and better selectivity is achieved for smaller pitches using lower SAM concentrations. Selectivity is measured qualitatively and quantitatively using x-ray photoemission spectroscopy and confirmed with transmission electron microscopy.
CHAPTER 1
INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

The transistor was arguably one of the most important inventions of the last century, paving the way for most of our modern devices and technologies. Signal amplification using transistors changed the telecommunication industry first, being used in radios, telephones, and other speaker devices. Current transistors are used in most power devices, and rely on the underlying physics of semiconductors - such as silicon - to provide technologies such as solar cells, radiation detectors, and of course computing devices. At the same time as transistors were beginning to change the landscape of technology manufacturing, American physicist Richard Feynman delivered a famous lecture where he discussed the pursuit of the nanoscale [2]. The talk was as much philosophical as it was scientific, and the effects on the scientific community were palpable as it paved the way for exploration of an entirely new field of study.

At the core of the semiconductor industry and transistor itself is the concept of rectification - or diodic electrical behavior. Oppositely doped silicon substrates in thermal contact form a diode which, when a bias voltage is applied across the substrates, can either allow or block the flow of electrons depending on the sign of the bias. In this way, by changing the sign of the supplied bias a switch can be made to turn a current signal on or off. A more efficient diode is created by joining a semiconductor with a metal and is called a Schottky diode, named for German physicist Walter H. Schottky. The switching behavior for a Schottky diode is faster than for a p-n semiconductor junction, and are found in the source and drain contacts of field-effect transistors fabricated today. At the interface of the semiconductor and metal is an electrostatic barrier formed as a result of the energy band alignment and electronic surface states called the Schottky barrier. This barrier is dependent on the materials used and interface preparation, and defines the rectifying behavior of the device. Additionally, dielectric materials such as oxides are utilized in the gate electrode of field-effect transistors, and these MOS or metal / oxide / semiconductor
interfaces also result in rectification. Gate oxides used to consist of SiO$_2$, a naturally occurring oxide on silicon substrates which has a low dielectric constant. As the thermally grown oxide thickness was decreased below 2 nm due to scaling, dielectric breakdown and leakage issues necessitated replacing SiO$_2$ with a high-$\kappa$ alternative such as HfO$_2$. The higher dielectric constant allows for thicker oxides with the same or higher capacitance [3]. Characterization of the electrostatic behavior of HfO$_2$ is needed to confirm the behavior of the oxide film as it begins to scale to smaller thicknesses.

Measurement of the barrier height has been performed using a number of techniques, notably Current-Voltage (I-V), Capacitance-Voltage (C-V), and photoemission [4, 5, 6]. Each of these techniques assesses the barrier across an averaged region, typically on the order of microns or larger, and have been successful in reporting barrier heights for metal / semiconductor and metal / oxide / semiconductor interfaces. With the scaling of devices such as FETs down to submicron dimensions, a technique with nanoscale resolution is required for accurate reporting of the local barrier height for an interface. Ballistic electron emission microscopy (BEEM) is one such technique, employing the lateral resolution of a scanning tunneling microscope (STM) to measure the barrier height to nanoscale dimensions [7]. Electrons are injected from the STM tip into the top electrode of the device by quantum tunneling, and electrons with forward momentum greater than the barrier are collected as current. Spectra are acquired by sweeping the voltage of the tip and the barrier height is derived from a fit to the linearized spectra.

Another consequence of smaller devices is that new techniques must be employed to fabricate them. A common method for printing features in semiconductor devices is photolithography, where photosensitive material is exposed to light and acts like a stencil to produce a desired pattern. Photolithography has been responsible for producing features down to about 80 nm for a single exposure, and by repeating the process the feature dimensions can continue to shrink [8]. The significance of alignment for patterned features at a smaller scale becomes increasingly important, and slight misalignment called edge placement error (EPE) from lithographic processes can cause defective behavior and reduce product yield. In addition, multiple patterning increases the cost of production, potentially limiting the validity of lithography
as a means to produce the next generation of devices while keeping costs down. A method of selective deposition has been offered as a solution to the limitations of patterning, known as atomic layer deposition (ALD). Material is deposited in controlled half-reactions to enable extremely thin, uniform films which are grown only on surfaces that respond to the reactants used.

To promote selectivity using ALD, blocking layers comprised of self-assembled monolayers (SAMs) are utilized. SAMs are chain polymers with a functional head group that adheres to a specific substrate. For patterns of alternating dielectric / metal lines a SAM can be deposited on one substrate to allow selective ALD on the other by blocking the film nucleation [9]. In order to be an effective solution to EPE in photolithography, SAM-enabled selective deposition should work for feature sizes of tens of nanometers. Selectively grown high-κ oxides can become alignment patterns for interconnect printing as well as preventing copper diffusion into the inter-layer dielectric. This has the potential to save chips from shorting and increase yield.

1.2 Literature Review

This chapter will introduce concepts relevant to BEEM and semiconductor devices. An overview of the discovery of rectification in metal-semiconductor contacts is presented first, followed by a discussion of the discovery and use of BEEM for probing the electrostatic properties of these rectifying junctions. Related phenomena which impact the measured barrier height of MS and MOS interfaces, such as electron scattering and dopant density will also be presented. Methods for selective deposition of metals and oxides will be examined and discussed in the context of lithography and ALD. Finally, the history and physics behind X-ray photoelectron spectroscopy will be introduced.

1.2.1 Heterojunctions

Metal-semiconductor junctions were first discovered to exhibit unipolar conduction in 1874 by Ferdinand Braun, who experimented with synthetic and natural metal sulfide samples [10]. By connecting a small metal wire to a copper-sulfide junction, a disparity in electrical resistance was observed based on the direction and intensity of an applied current. This unipolar conducting effect was on the order of a 30 percent
disparity in current response [11]. A theoretical explanation for this divergence from Ohm’s law wouldn’t be found for another 70 years, however multiple innovations to heterojunction design would be proposed in the interim. In 1926 Julius Lilienfeld, a former student of Max Planck, patented the design of what is now called a transistor as a means to provide ‘uni-directional conductivity’ using a thin film of copper sulfide grown on closely spaced metal electrodes [12]. The device was never constructed, however it would bear a striking similarity to the first bipolar junction transistors designed at Bell Labs in the 1940s and 50s.

Prior to the development of the three-terminal bipolar junction transistor, a two-terminal diode called a ‘cat’s-whisker’ was used as a signal detector. Like with Braun’s experiments, a thin tungsten wire was brought into contact with a lead sulfide crystal, and by moving the location of the point contact specific radio signals could be picked up. Improving on this technique, William Shockley, John Bardeen and Walter Brattain of Bell Labs replaced lead sulfide with germanium, and increased the metal-semiconductor contact area by using two contact junctions, greatly improving the efficiency of the device [13]. This bipolar junction transistor delivered on the theoretical proposal of Lilienfeld’s earlier patent, and won the three engineers a Nobel Prize in 1956.

Attempts to model the underlying physics of unipolar conduction were made in the early twentieth century. Early assumptions of the metal-semiconductor interface suggested that a wide potential barrier was formed by thermal contact and that electrons tunneled quantum mechanically through this barrier. However, experimental results showed rectification occured in the opposite direction than calculated by the tunnel method. In 1939 Nevill Mott proposed that rectification was not a product of tunneling, but of the intrinsic nature of the MS junction due to band bending [14]. Electrons require sufficient energy to surpass the potential barrier instead of tunnel through it, and the energy of these electrons is related to the difference between the energy of the lowest conduction band level and vacuum level, known as the work function for metals (\(\phi\)) and electron affinity for semiconductors (\(\chi\)). Mathematically, this is represented by the Schottky-Mott relation:

\[
\phi_B = \phi_M - \chi_S, \tag{1.1}
\]
While in thermodynamic equilibrium, the Fermi level of a metal and semiconductor align, forcing the conduction bands to bend in order to form a continuous contact, where the magnitude of band bending is described by the above relation. Despite the success of this theory in accounting for the direction of current flow for MS junctions, it failed to accurately report the magnitude of the barrier. Work done by Walter Schottky and Eberhard Spenke accounted for ion density at the interface which creates a linearly decaying electric field as opposed to the constant field assumed by Mott [15, 16]. This space-charge layer more accurately represented the potential barrier and became known as the Schottky barrier. Despite being named for Schottky, a more accurate representation of the barrier is described later by Hans Bethe, who shows that the current is limited by thermionic emission of electrons over the barrier [17, 18].

1.2.2 Ballistic Electron Emission Microscopy

Scanning tunneling microscopy (STM) was developed in 1982 as a method of obtaining topographic imaging of surfaces at the atomic scale [19]. This technique has allowed the direct observation of atomic lattice structures and can resolve individual atoms. It also served as the launchpad for a novel, three-terminal measurement developed by L. D. Bell and W. J. Kaiser at Jet Propulsion Laboratory in Pasadena, CA known as ballistic electron emission microscopy (BEEM). The technique employs the atomic precision of the STM tip to inject hot electrons into the base electrode of a MS material stack at discrete locations, and electrons that travel ballistically into the semiconductor are collected as BEEM current [20]. Notably, this is the first technique to probe electrostatic properties of an interface with nanometer spatial resolution - a feat that spatially averaged techniques such as I-V and C-V are incapable of accomplishing. Initially, measurements were limited to Schottky contacts, however future studies have included MOS interfaces, semiconductor heterojunctions, and other interfaces [21].

Ballistic electron emission microscopy is an STM-based technique where hot electrons are injected from a tunneling STM tip into the base electrode of a metal / semiconductor (MS) or MOS device [20, 22, 7]. Electrons that travel ballistically through the metal must surpass the energy of the Schottky barrier height for MS interfaces or the band offset of the dielectric for MOS interfaces to be collected as
BEEM current in the semiconductor [23, 24, 25, 26]. For p-type semiconductors, holes are injected into the metal and the ballistic holes that make it through the interface are measured as current in the semiconductor and called ballistic hole emission microscopy (BHEM) [27, 28]. BEEM current, $I_{BEEM}$, is modeled by the equation:

$$\frac{I_{BEEM}}{I_{Tip}} \propto (V_{Tip} - \phi_B)^n$$

(1.2)

This is the simplified Bell and Kaiser (BK) model, where $I_{BEEM}$ is the BEEM current, $I_{Tip}$ is the tip current, $\phi_B$ is the Schottky barrier, $V_{Tip}$ is the tip bias, and $n$ is a fitting exponent usually expressed as 2 [20, 7]. However, this model assumes a constant distribution of electrons into the metal whereas BEEM produces an exponential distribution of electrons due to quantum mechanical tunneling. Including this quantum transmission factor changes the model parameter $n$ to $n = 5/2$ [29]. Further examination of the factors which impact $I_{BEEM}$ will be discussed later.

Originally, BEEM was employed to investigate Au/Si and Au/GaAs SB heterojunctions, which had been studied extensively by other methods [20]. While Au/Si SBH characteristics were largely reproducible using standard techniques, the Au/GaAs SBH values varied widely by experiment and technique [30]. Early results confirmed that BEEM spectra were in fact direct measurements of the Schottky barrier height. Additionally, it was found that by testing p-type substrates a version of the technique called ballistic hole emission microscopy (BHEM) could be conducted, where ballistic holes are the forward carriers injected by the STM tip into the metal electrode. For both BEEM and BHEM, there exist forward and reverse modes which depend on the relative bias between the STM tip and metal. Only forward BEEM and BHEM will be discussed.

The BK model worked very well in early metal / semiconductor interfaces such as Au/Si(001) and Au/GaAs, assuming that the injected and received energy and momentum distributions from forward carriers were identical. It also predicted BEEM signal loss due to scattering events, the behavior of which were entirely inelastic. This assumption broke down for Si(111) substrates, however; band theory and momentum conservation predicted that the barrier for Au/Si(111) would be much larger than Si(001) due to the lack of surface $k_{||} = 0$ states for Si(111). Carriers injected from the
STM would need higher energy to overcome $k_{\parallel} > 0$, and would result in a larger measured barrier height. Schowalter et al. found an almost identical barrier for Si(111) and Si(001) substrates, indicating a correction to the BK model was needed [31]. Elastic scattering events at the interface would allow carriers additional attempts to penetrate the barrier and broaden the momentum distribution of injected carriers. A Monte Carlo simulation was employed to confirm that elastic scattering events are present and must be included in the analysis of BEEM spectra.

Elastic scattering as a prominent feature of BEEM measurements is further explored by Prietsch [32]. Scattering is believed to randomize momentum of the hot carriers which can impact a carrier’s ability to enter an available semiconductor state by way of an acceptance cone. The acceptance cone is determined by electron energy and material properties and will be discussed in the next chapter. The addition of a silicide interface and grain structure further contributes to scattering behavior [33], and band structure from the semiconductor can also guide ballistic electrons into acceptance cones by way of selective scattering [32]. Each type of scattering has an impact on the power law of the BK model, and a mixture of different types of scattering events is generally assumed.

Au is the often the preferred metal contact for measurements on Si substrates for a number of reasons. It is an inert material when deposited on Si, resisting oxidation and preventing SiO$_2$ formation. It has a relatively high mean-free path for injected electrons reducing the occurrence of inelastic and elastic events in the metal layer. It is also, by virtue of its ubiquity in BEEM measurements, easy to compare with older results and can act as a standard between different research groups. For all of the BEEM work presented here, Au is the metal contact used and is the focus of this literature review.

Another important factor when looking at BEEM spectra collected for the same interface is the distribution of barrier heights. Research by Fowell et al. investigates the Au/CdTe interface which has been subject to much scrutiny due to conflicting barrier height measurements with IV [34]. In tandem with XPS analysis it was found that varying ratios of Cd and Te resulted in discrete changes in the measured barrier height at nanometer spatial dimensions. These variations are not found to relate to surface topography, and are otherwise irreconcilable with spatially averaged
techniques like IV. Other studies which looked at variations in barrier heights across a small region found that the barriers varied by a gaussian distribution [35]. They use differently-doped Si(111) and find a gaussian distribution of barriers across the entire interface with goodnesses-of-fit $\geq 0.95$. Taking a weighted average of barrier heights from the distribution was determined to be a superior method of reporting the Schottky barrier for an interface when compared to IV, CV, and photoelectric (PE) measurements.

Most recently, the atomic lateral resolution of the STM is taken advantage of to track unique BEEM spectra to tip positions. By mapping spectra to STM tip positions one can visualize the local barrier height across an entire interface [36, 37, 38, 39, 40, 41]. Thousands of spectra are collected in a regularly spaced grid and then fit to obtain values of the local barrier height. Histograms of these barrier distributions reveal information about surface chemistry and scattering at the interface [38, 39, 40, 41]. Work using W and Cr on Si find that silicide formation at the interface change the measured barrier height by at least 70 meV, and a Monte Carlo model reveals the extent to which elastic and inelastic scattering impact the barrier. Metal / oxide / semiconductor interfaces show increased scattering events and include multiple discrete barriers across a 100 × 100 nm interface, which are explored in the later chapters of this report.

1.2.3 Material Deposition and Lithography

The deposition of material onto a substrate represents one of the basic processes for chip fabrication in the semiconductor industry. Common techniques can be broadly divided into two categories - physical vapor deposition (PVD) and chemical vapor deposition (CVD) [42]. Physical vapor deposition techniques include sputtering or evaporation of target material onto a substrate, usually under high vacuum conditions, while chemical vapor deposition relies on chemical reactions at high temperatures and fast deposition rates. The latter dates back to incandescent lamp filament coating in the late nineteenth century, and innovation quickly began after World War II which brought CVD into the world of semiconductor fabrication by 1960 [43]. For example, silicon carbide is a widely used material for electronic devices and is typically grown at high temperatures above 1000° C using silane and propane
as precursors for the chemical reaction [44]. Despite its usefulness for fast and thick coatings at close to atmospheric pressures, the high temperature environment limits what substrates can be utilized, and chemical precursors and by-products can be hazardous and toxic, requiring a potentially costly cleanup process [42]. Additionally, it is better suited for large area uniform deposition, but not as successful for small target areas with neighboring non-target areas.

This issue of small target areas is relevant in the world of photolithography, where smaller and smaller feature sizes must be printed on wafers to follow Moore’s Law scaling. The term lithography comes from the Greek litho + graphy which translates as stone writing, and the original lithography technique used limestone to publish theatrical works [45]. While the initial uses for lithography were most prominent in the art world, developments especially for photography would be the building blocks for printing microcircuit devices. Between the 19th and 20th centuries, light exposure was used to change the solubility of compounds which would become known as photoresists [46]. Photoresists come in two flavors, positive tone and negative tone, which determines the impact on solubility caused by incident photon radiation; positive tone resist for example becomes more soluble after light exposure and is removed from the coated surface. By exposing certain photoresist to light, particular features could be added or subtracted from the underlayer. By the 1950s, this process had been successfully implemented in printing transistors [47]. Today, photolithography is a process which follows the following simplified steps:

- A photoresist is coated onto a substrate.
- The photoresist is exposed to a particular wavelength of light, usually through a photomask, such that some of the resist is exposed and some is not.
- The part of the resist that was exposed (or not exposed) is removed and a pattern is left over on the substrate.

Photolithography is dependent on a few key parameters, including the intensity of light irradiation, light wavelength, and photoresist chemistry. Importantly, there is a resolution limit for features printed using photolithography determined by the wavelength, numerical aperture, and Rayleigh resolution considerations [48]. For the
industry standard 193 nm wavelength, feature pitch size is hard-limited to about 80 nm, or a 40 nm half pitch. To bypass this physical limit, a technique called multiple patterning was developed by Flanders et al. which reduced the pitch size to 40 nm [49]. By doubling the lithography step, the spacing between features is halved, as shown in Fig. 1.1. Other solutions such as reducing the wavelength of light (extreme ultraviolet lithography) and adding a liquid medium between the wafer and lensing system (immersion lithography) present unique solutions and added challenges to photolithography, and will not be discussed further [50, 51].

Multiple patterning is still the predominant method for creating features approaching 20 nm [52, 53, 54], however practical considerations limit its usefulness moving forward. Running multiple patterning steps greatly increases the cost of production, making it cost prohibitive to rely on 4+ pattern transfer steps. Additionally, landing patterns on their intended area becomes increasingly difficult with smaller scaling requirements, and a mismatch of the pattern to desired location called edge placement error (EPE) must be rectified. EPE can result in electrical shorting and low yield, which have the potential to ruin whole chips [55, 56].

While engineering solutions to EPE have been introduced, it is possible that an entirely new paradigm may offer the benefits of small feature deposition while removing issues like EPE and cutting down the cost of lithography. A relatively newer technique has been utilized in this capacity - Atomic layer deposition (ALD) [57].
Originally developed and used to coat LCD substrates with ZnS, the ALD process uses two precursors which react to the surface in a self-limiting and controlled way to selectively grow material at lower temperatures (\(< 350^\circ\text{C}\)) than CVD [58, 59]. Each precursor produces a half-reaction and by cycling the precursors, individual layers of the desired material are grown. Controlled, conformal growth of material in this way makes it possible to coat high aspect ratio and three dimensional features. This is especially important when it is necessary to coat one particular surface without coating adjacent surfaces such as in linespace pairs of alternating metal / insulator. Such an approach can be described as a type of area-selective deposition (ASD) and has been used extensively in recent times for back end of the line metal interconnects [60, 61, 62, 63].

1.2.4 Self-Assembled Monolayer

![Dodecanethiol SAM](image).

\textbf{Figure 1.2:} Molecular structure of Dodecanethiol (DDT). The molecule possesses a thiol head group, long hydrocarbon chain, and terminal group.

Both surface and interface properties lead the way for the development of new devices and material stacks. Specifically, surface passivation or diffusion blocking offers control of both the underlying substrate and any potential material overlayer. For example, with metal substrates, surface oxides are commonly formed in atmo-
sphere which potentially impact electrical characteristics and overlayer adhesion. By applying a self-assembled monolayer to the substrate of choice - whether metal, oxide, or semiconductor - the interfacial properties can be tailored [64]. SAMs are materials that possess a head group chosen to adhere to a specific substrate, a long alkane chain, and terminal group to cap the chain as displayed in Fig. 1.2. They are versatile in application and also highly tunable based on factors like temperature [65, 66, 67].

One approach to area-selective deposition (ASD) with ALD involves the use of SAM materials to act as a deposition barrier [68, 69, 70]. Since ALD requires surface reaction with a precursor, a material such as an organic SAM may be used to block precursor from interacting with the substrate. This allows ALD material to attach to a target area without depositing over the area protected by SAMs. Common SAM chemistries include hydrocarbon chains with reactive head groups like thiols and phosphonic acids, and they are chosen based on their propensity to adhere to metallic or dielectric surfaces [71]. Multiple techniques exist to administer SAM films including soft lithography (microcontact printing) [72], sample dipping in solution [73], and vapor deposition [74, 9]. Once the SAM has successfully blocked deposition over a particular area, an etch process can be administered to remove SAM while leaving the desired ALD film.

The effectiveness of SAMs as chemically selective blocking layers for ALD continues to be tested; the tunability of SAMs to specific surface ligands such as -OH for oxide or -H for metal termination is a major advantage, especially since many features in the design of semiconductor devices require control of the metal and oxide components to nanoscale dimensions [75]. Nucleation delay with SAMs has been modest for microcontact printing and sample dipping, usually effective for up to 50 ALD cycles for deposited oxides and a more respectable 100 cycles for metals such as Ru [76]. Avila et al were able to achieve similar ALD cycle rates for dodecanethiol SAM from vapor deposition while also improving SAM packing density. Related work by Hashemi et al. employed a H₂ plasma treatment to significantly increase the number of cycles during which the SAM material was effectively screening high-k nucleation [9].

A practical consideration for the use of SAMs with copper substrates is the propensity for copper to readily oxidize into Cu₂O and CuO, as well as Cu(OH)₂ if
exposed to ambient air [77]. Copper oxidation has the potential to reduce adhesion to the substrate and potentially interfere with SAM chemisorption. The use of organic solvents such as acetic acid is necessary to ensure proper SAM attachment and formation [78]. Since wafers may be moved between different tools in atmospheric conditions, reducing idle time between process and measurement can be critical for limiting oxidation.

1.2.5 X-ray Photoelectron Spectroscopy

In 1887 Heinrich Hertz observed something that was not explainable before quantum physics - conduction between two plates in a spark gap would occur when the apparatus was subjected to UV radiation [79]. Others investigated this phenomenon, where it was agreed that electrons were somehow being emitted by the metal. Lenard for example added in 1902 the discovery that the frequency of light impacted electron emission [80]. This was not accounted for by the wave theory of light, and only when Max Planck and finally Albert Einstein hypothesized in 1905 that light existed in discretized quanta - work for which Einstein was famously awarded the Nobel Prize - was a theory able to be created based on this effect. The so-called photoelectron effect describes the process by which materials that are impinged on by electromagnetic radiation emit characteristic electrons who’s energy depends on the material work function $W$ and frequency of the incoming light wave $\nu$.

$$K_{\text{max}} = h\nu - W$$  \hspace{1cm} (1.3)

Electrons from discrete and well-defined electron orbitals occupy energy states particular to the constituent element, and are only ejected when the energy of the incident photon exceeds this energy, called binding energy. Thus, for a given element the range of emitted electron energies is directly related to the binding energies of that element, providing a means of identification. Work has been done using this basic principle to map the band structure of elements like Ag and Cu [81].

This effect can be taken advantage of by using an electromagnetic beam of known energy directed at a conducting sample [82]. Siegbahn et al. showed how this could be done to collect photoemission spectra of NaCl [83]. Non-monochromated X-rays are reflected off a quartz crystal which focuses the beam onto the sample [84].
X-ray photoemission from the sample is slowed by a bias voltage to improve energy resolution [85]. The slowed electrons are collected in a hemispheric energy analyzer which directs them to a detector along a circular path using an electrostatic field, and the energy of collected electrons is used to identify the composition of the sample. Energy from the sample electrons is superimposed on the background signal caused by Bremsstrahlung radiation, and the background must be subtracted to accurately quantify binding energy peaks. This method has been successfully used in an increasing number of publications - estimated today to be in excess of 9000 new papers annually - as it is able to provide accurate accounts of band structure for any < 100 Å-thick material [86, 87, 88, 89].

The shallow depth of measurement is due to the low escape depth of elastically scattered electrons caused by X-ray photoemission, which puts a limit on the material stack being used for analysis. Since the technique is highly surface sensitive, care must be taken to ensure low surface contamination. The most common surface contaminant is called adventitious carbon, and it is routinely used in peak analysis to calibrate all spectra in a survey [90]. Other surface contaminants have the potential to create surface trap states which lead to charge build up. Positive surface charging represents one of the most common hurdles in quantifying non-metallic samples, and results from negative charge leaving the sample [91]. Aside from post measurement peak calibration, Baer et al. list additional methods used to combat charging, such as changing the X-ray flux, and recommends using a known material like a noble metal or insulating polymer to optimize the charge neutralization system. [90].

One valuable result from X-ray photoemission spectra is to quantify the percent composition of elements in a sample. This is done simply by taking the area under each core-level binding energy spectra for all measured elements and weighting them with a relative sensitivity factor (RSF) [85]. The RSF is experimentally determined, and is typically normalized to a specific signal such as C 1s. Because the value is independent of equipment-specific factors related to the spectrometer and transmission, it is best to use RSF values generated by the instrument being used for all experiments. Additionally, the background radiation must be removed from a peak before analysis. Intrinsic energy loss features occurring from photoexcitation impact the background shape, and three common background models - Linear, Shirley, and Tougaard - are
commonly used to subtract out background counts [92, 90, 85]. Taking this a step further, by comparing XPS spectra peaks between deposition steps, information about the degree of selectivity for deposited material can be obtained [93]. If, for example, a SAM material was known to adhere to metal but not low-k, then XPS spectra taken on a patterned metal / SiO$_2$ linespace sample before and after SAM deposition should show decreased or attenuated copper counts and identical SiO$_2$ counts.

### 1.3 Thesis Overview

This thesis looks at the complicated interface formed by ALD hafnia grown on a $p$-type silicon substrate with a gold capping layer by employing ballistic electron emission microscopy and Schottky barrier visualization. A nonuniform film of hafnium oxide is mapped to nanoscale dimensions and multiple barriers - including a previously undiscovered barrier at 0.45 eV - is found using this technique. The ultimate resolution of Schottky barrier visualization on a modified STM system is also investigated by using BEEM spectra from Au/Si(111) and Au/Si(001) interfaces, and found to be 10 meV. The practical applications of thin film oxides are also explored by attempting to fabricate selectively grown oxide on dielectric lines. Selectivity is achieved by applying blocking material comprised of self-assembled monolayers (SAMs) followed by carefully regulated low temperature growth of the desired oxide film. Characterization of the selective deposition is primarily achieved with x-ray photoelectron spectroscopy which confirms chemical bonding and the presence of desired material. For thiol SAM chemistries, both HfO$_2$ and Al$_2$O$_3$ high-$\kappa$ films are selectively deposited on linespace regions smaller than 100 nm.
CHAPTER 2
THEORY AND RELATED PHENOMENA

2.1 Barrier Height Measurement

2.1.1 Scanning Tunneling Microscopy

The scanning tunneling microscope was developed by Dr. Gerd Binnig and Dr. Heinrich Rohrer from IBM research laboratory in Zurich, Switzerland in 1981. It was the first time a tunneling experiment with an adjustable vacuum gap was utilized to investigate a surface to nanoscale dimensions [94, 95]. This work was awarded the Nobel prize in 1986, and it revolutionized the way surfaces could be imaged. A piezodrive motor allows the STM tip to maintain distance from the surface of interest such that quantum mechanical tunneling is maintained, and vibrational isolation is achieved with a combination of floating air and magnetic levitation to ensure stable tunneling. The STM tip is an atomically sharp metal tip which is capable of injecting electrons into a surface following quantum mechanics; the probability of an electron passing through the vacuum barrier represents the classic potential barrier problem which can be modeled by the time-independent Schrodinger equation:

\[
\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \psi(x) = E\psi(x),
\]  

(2.1)

where \(\psi(x)\) is the wave function, \(E\) is the energy of a free particle, and \(V(x)\) is the barrier potential. For a rectangular potential barrier, there are two conditions to be investigated: \(E < V_0\) and \(E > V_0\). In the first case classical mechanics would not allow for transmission, however a non-zero probability of transmission is possible due to quantum mechanical tunneling. For a free particle, the solution wave equation is represented by

\[
\psi(x) = Ae^{ik_0x},
\]  

(2.2)

where \(k_0\) is the wave number traveling in the positive x direction. For a barrier of thickness \(d\) and potential \(V\), the solution to the Schrodinger equation is made up of
three components listed in the following equations, with wave numbers given below:

\[ \psi_L(x) = Ae^{ik_0x} + Be^{-ik_0x} \quad x < 0 \quad (I) \]  

\[ \psi_C(x) = Ce^{k_1x} + De^{-k_1x} \quad 0 < x < d \quad (II) \]  

\[ \psi_R(x) = Ee^{ik_0x} + Fe^{-ik_0x} \quad x > d \quad (III) \]  

\[ k_0 = \frac{\sqrt{2mE}}{\hbar}, \quad k_1 = \frac{\sqrt{2m(V - E)}}{\hbar} \quad (2.6) \]

These equations govern the particle’s behavior as it travels in the x direction towards a barrier, through the barrier, and past the barrier. In the region from \( x = -\infty \) to \( x = 0 \), there is a component for unhindered forward motion and reflected motion at the barrier, indicated by amplitudes \( A \) and \( B \), respectively. For the region inside the barrier, amplitudes \( C \) and \( D \) represent decay while in the potential field. And past the boundary for \( x > a \), amplitudes \( E \) and \( F \) represent unhindered forward motion and reflected motion, respectively. Since there is no boundary to cause reflected motion, Eqn 2.5 is better represented by:

\[ \psi_R(x) = Ee^{ik_0x} \quad x > d \quad (III) \]  

The ratio of reflected vs incident particles at \( x = 0 \) is represented by \( \frac{|B|^2}{|A|^2} \), and the ratio of particles transmitted vs incident through the barrier is given by \( \frac{k_{III}}{k_I} \ast \frac{|E|^2}{|A|^2} \). In the STM, this represents the tunnel current of injected carriers from the tip into the measured substrate. Carriers such as electrons propagate through the vacuum barrier and are accepted into the conduction band of the sample. The transmission of these electrons across the barrier is given by

\[ T(E) = |t|^2 = 1 + \frac{V_0^2 \sinh^2(k_1d)}{4E(V - E)} \quad (2.8) \]

By applying a bias between the tip and sample as is required for STM measurements, the initial energy state of the region from \( x = -\infty \) to \( x = 0 \) moves relative to
Figure 2.1: The wavefunction of an electron as it reaches a square potential barrier. By multiplying the wavefunction with its complex conjugate, a transmission probability can be calculated - for a square potential transmission is proportional to a square power.

the ground state of the system, causing the rectangular barrier to become a triangular barrier as shown in 2.2. These injected electrons are governed by field emission, and follow the Fowler Nordheim solution to the Schrodinger equation. In this regime, electrons are emitted due to a large electric field between conducting surfaces such as an STM tip and conducting sample. Solving for this potential barrier requires the use of the Jeffreys-Wentzel-Kramers-Brillouin integral [96, 97, 98]

\[ \Psi(L) = \Psi(0)e^{-\frac{\sqrt{2m(V(x)-E)}}{\hbar}L} \]  

(2.9)

The tunneling probability is then the product of the wavefunction times its complex conjugate, which simplifies to the relation

\[ T = e^{\exp\left(-\frac{4\sqrt{2qm}}{3}\frac{\phi_B^{3/2}}{\hbar}\right)} \]  

(2.10)

indicating an exponential dependence on the barrier height to the 3/2 power. Since the barrier height for a vacuum is defined by the thickness of the tunnel gap, this shows the importance of distance between the STM tip and measured substrate.
When a bias is applied to the top electrode, the square barrier becomes a triangular one. This results in a transmission probability proportional to $e^{3/2}$ instead of the square law derived for a square barrier.

### 2.1.2 Schottky Barrier Formation

Schottky barrier formation is important in the semiconductor industry as it gives rise to rectification and is a fundamental principle of interface behavior between metals and semiconductors. The Schottky-Mott relation discussed earlier offers some initial insight into the role of band structure in barrier formation. When a metal and semiconductor are brought into contact with one another, charge is exchanged between the two substrates and a charged depletion layer forms at the interface. The semiconductor Fermi level and metal Fermi level align, causing the valance and conduction bands of the semiconductor to bend. The magnitude of this bending constitutes the electrostatic barrier, and the direction of bending is dependent on the dopant type in the semiconductor. The barrier is modeled by the Schottky-Mott relation (Eqn. 1.1) which is the magnitude of difference between the metal work function $\phi_M$ and semiconductor electron affinity $\chi_S$.

This picture of the barrier height does not hold up to the scrutiny of experimental results, however. Fig. 2.3 shows the discrepancy between theoretical values of
Figure 2.3: Theoretical Schottky-Mott relation for various metals on p-type Si plotted against experimentally determined values of the BHs, with a fit of the experimental data in red. The dependence on metal substrate is less important than predicted by Mott’s theory, prompting a need for a new model to explain the mismatch.

the barrier height versus experimental data for a number of metals on n-type silicon, and the same result is true for p-type silicon as well as other semiconductors such as GaAs. In fact, the choice of metal seems to play a diminished role in the barrier height than predicted by the Schottky-Mott relation. Clearly more is involved in the calculation of the electrostatic barrier, and much work has been done in developing a theoretical model for the barrier [15, 17, 99, 100, 101, 102, 103].

Notably, it was discovered that charge build up at the edge of the depletion layer essentially functions as dipoles between the substrates, and the induced electric field causes the Fermi level of the semiconductor to get pinned at the interface. For negative charges, the Fermi level is lowered and the surface becomes positively charged.
The opposite occurs for positive charge buildup where the Fermi level is raised and the surface is negatively charged. In this way, irrespective of the metal chosen, semiconductor bands would be bent to align with these interface states. To account for the dipole’s influence on the barrier height, an addition to the Mott relation is added such that

$$\phi_B = \Phi_M - \chi_S + eV_{int} \tag{2.11}$$

where $V_{int}$ is the voltage of the interface dipole.

Another way in which interface dipoles are created is through metal-induced gap states (MIGS), which are electronic states that form in the band gap of the semiconductor due to the tunneling of wave function of electrons from the adjacent metal. Heine showed that, again, the choice of metal had little impact on the gap states as the surface state energy of the free electron was stable in most cases [104].

The introduction of an oxide at the metal / semiconductor interface is widely utilized for field-effect transistors and other aspects of the semiconductor industry. In addition to the practical differences of the interfaces such as surface passivation of the semiconductor and diffusion blocking, the electrostatic barrier is also largely dependent on the oxide chosen. Oxide thickness is limiting for STM-based measurements as the oxide contributes large amounts of electron scattering which significantly reduces tunnel current. Barriers measured for interfaces with and without an interfacial oxide yield higher barriers for oxide samples [105, 106]. It should be noted that the mechanism for current flow over the electrostatic barrier is the same for MS and MOS interfaces, and the thermionic emission is modeled by:

$$I = I_0e^{\frac{q(V - IR_s)}{n}kT} \left[1 - e^{-\frac{q(V - IR_s)}{kT}}\right] \tag{2.12}$$

where $q$ is the electron charge, $R_s$ is the series resistance, $k$ is the Boltzmann constant, $T$ is the temperature, and $I_0$ is the saturation current. $I_0$ is determined by

$$I_0 = AA^*T^2e^{-\frac{\Phi_o}{kT}} \tag{2.13}$$

where $A$ is the diode area, $A^*$ is the Richardson constant, and $\Phi_o$ is the barrier height at zero bias.
2.1.3 Ballistic Electron Emission Microscopy

For non-uniform interfaces, few methods exist for determining the barrier height at discrete locations. Thermionic emission measurements, as well as photoemission, provide an average value of the barrier across large contact areas. Ballistic electron emission microscopy offers direct probing of the buried interface electrostatic barrier to nanometer spatial resolution. It requires no prior knowledge of the materials involved, and can diagnose local changes in barrier height with interface defects and scattering sites.

Modeling ballistic electron transport requires collecting the total current density across the interface. Collector current is defined as the current collected by the semiconductor back contact, which means after tunneling across the STM tip to metal gap, ballistic transport through the metal, and across the potential barrier at the interface. The first attempt to model BEEM current comes from Bell and Kaiser (BK) who take the classical physics approach and use an energy independent transmission factor to describe collector current:

\[
I_c = RC \int_{E_{min}}^{E_{max}} D(E_x) dE_x \int_{0}^{E_{max}} f(E) dE_t dE_x ,
\]

(2.14)

where R is the energy independent attenuation constant due to scattering in the metal layer. After integration, a square power law is obtained for \( I_c \)

\[
I_c \propto (V - \phi_B)^2
\]

(2.15)

The square law assumes energy independent ballistic electron attenuation lengths for energy \( E - E_F \) less than 2 eV [7]. They also assume that the effects of scattering in the metal merely reduces collected electrons.

A quantum mechanical approach to the collector current is attempted by Prietsch and Ludeke (PL) who generalize quantum mechanical transmission across a one-dimensional potential step assuming an energy-dependent transmission coefficient. The PL model for collector current is

\[
\dot{j}_c = K \int_{E_{min}}^{E_{max}} D(E_x) dE_x \int_{E_0}^{E_{max}} f(E_x, E_t) T(E_x, E_t) F_\theta(E_{max}, E_t) \Lambda(E_x, E_t) dE_t ,
\]

(2.16)
where integration occurs over the energy variables with momentum vectors normal to \((E_x)\) and transverse to \((E_t)\) the sample surface. Integration occurs over the range of \(E_{min} = E_F - eV - V_0\) to \(E_{max} = r_m(E_x - E_{min})\) and \(E_0 = (eV + E_x)\sin^2 \theta\), where \(V\) is the applied tip bias, \(V_0\) is the conduction threshold voltage, and \(r_m\) is the reduced mass ratio. Notably, \(F_\theta(E_{max}, E_t)\) represents a coordinate transformation for off-normal angles of incidence, which occurs when the STM tip is scanned across rough, nonplanar surfaces. For transmission across a potential step, a generalization of \(T(E_x, E_t)\) is written as

\[
T(E_x, E_t) = 4 \left[ \frac{(m - m_s)(E_{max} - E_t)}{m(eV + E_x)} \right]^{1/2}
\] (2.17)

When \(\theta = 0\) and \(T(E_x, E_t) = 1\), the PL model reduces to the BK model from Eq. 2.14. However for the quantum mechanical energy dependent condition, the resulting expansion provides the power dependence

\[
I_c \propto (V - \phi_B)^{5/2}
\] (2.18)

which is 1/2 power difference from the classical BK model. Both values of \(n\) are used for the simplified BEEM model shown in Eqn 1.2.

2.1.4 BEEM Spectra Fitting

BEEM spectra is understood as the ratio of current collected by the ohmic back contact of the semiconductor and the total current which is emitted from the STM tip shown in Eq. 2.19.

\[
\frac{I_{BEEM}}{I_{Tip}} = A(V_{Tip} - \phi_B)^n,
\] (2.19)

where \(I_{BEEM}\) is the current of electrons which make it through the barrier, \(n\) is the ideality factor, and \(A\) is a fitting parameter. By linearizing this to the form \(y = mx + b\) the values of the barrier height and amplitude can be derived as \(m = \sqrt{A}\) and \(b = \sqrt{A}\phi_B\). In a fitting routine, a starting value is chosen near the onset of measured current - usually the first data point. Regions of about 0.2 eV are defined from the starting value to a fit start value, and incremented sequentially for the linear portion of the BEEM spectra such that for the entire spectrum a fit is calculated.
When this is complete, a new starting value is selected and the process is repeated until all points along the spectra have been selected as the starting value. The fitting procedure is shown in Fig. 2.4.

![Graph](image)

**Figure 2.4:** Fitting routine for BEEM spectra. A starting value (SV) and fitting start value (FSV) are selected over a range of about 0.2 eV and the extrapolated intercept is taken to be the barrier height.

A goodness of fit parameter, $R^2$, is utilized to determine the best fit from the array of fits. The best fit usually falls within 3 to 5 $\sigma$ (0.99 to 0.999999). Once the maximum $R^2$ value is found, the corresponding fit is used to extrapolate the electrostatic barrier.

### 2.1.5 Electron Scattering

Something missing from the initial discussions of BEEM fitting is an accommodation of electron scattering events at the interface which affect the measured barrier height. Two forms of electron scattering - elastic and inelastic - can both occur for electrons injected into the top electrode from an STM tip, both of which impact the electron’s momentum as it travels towards the base electrode.

Elastic scattering is an energy conserving collision, meaning the starting energy and total momentum, $\vec{k}$ of an electron which undergoes elastic scattering remains the same post collision. In order to preserve total momentum, the direction of momentum
Figure 2.5: Elastic scattering events cause a transfer of perpendicular momentum into parallel momentum. This has the potential to lower the perpendicular momentum enough that the electron is no longer able to surpass the electrostatic barrier.

changes, and this has an impact on measured BEEM current. Momentum will be described below as having a parallel and perpendicular component with respect to the interface. For an electron traveling normal to the interface, an elastic collision results in a shift to some parallel motion such that

\[ \vec{k}_T = \vec{k}_\perp + \vec{k}_\parallel, \] (2.20)

Which is depicted in Fig. 2.5. In terms of kinetic energy where \( \vec{k} = m\vec{v} \):

\[ K.E. = \frac{mv_\perp^2}{2} + \frac{mv_\parallel^2}{2}. \] (2.21)

For an electron to surpass the barrier height,

\[ \frac{k_\perp^2}{2m} \geq \Phi_B \text{ or } k_\perp \geq \sqrt{2m\Phi_B}. \] (2.22)

In other words, electrons must possess more than the square root of \( 2m\Phi_B \) in perpendicular momentum to be collected as BEEM current. Since the kinetic energy of electrons is the same as the tip bias from the STM, and forward focused electrons injected from the tip are entirely made up of perpendicular momentum with respect to the interface, then any ballistic electrons ejected from the tip with a bias larger than \( \sqrt{2m\Phi_B} \) as described by Eq. 2.22 should be collected as BEEM current assuming no elastic collision events. This can be illustrated with an energy acceptance cone diagram shown in Fig. 2.6. For electrons that encounter an elastic scattering event, some of their \( \vec{k}_\perp \) may be converted into \( \vec{k}_\parallel \) while maintaining the same total momentum;
Figure 2.6: Acceptance cone of scattered electrons at the electrostatic barrier. As the energy of electrons increases past the BH, more angles are allowed into the barrier.

if those electrons started with sufficient $k_{\perp}$ to surpass the barrier, the translation of momentum from perpendicular to parallel due to elastic scattering may be sufficient to prevent entry into the barrier.

The acceptance cone of electrons is dependent on electron energy, the electrostatic barrier at the interface, and the Fermi energy of the system:

$$\sin^2 \theta_c = \frac{m \ E_e - \Phi_b}{m \ E_F + E_e}$$

where $\theta_c$ is the maximum angle of deflection before an electron becomes incapable of surpassing the barrier height. Since electrons scattered to high angles need energy higher than the barrier height to be recorded, the measured barrier height can be skewed to higher energies for interfaces with a high scattering rate. This is shown in Fig 2.7 for a Au/SiO$_2$/Si interface where the distribution of barrier heights features a shoulder at energies higher than the statistical mean barrier.

Inelastic scattering can also occur for injected electrons, and these events can impact the distribution of measured barrier heights. Unlike elastic collisions, inelastic events are not energy conserving i.e. inelastically scattered electrons lose kinetic...
Barrier height distribution histogram for a Au/SiO$_2$/Si-p interface. Measured barrier heights are found at higher energies due to elastic scattering events.

energy to the environment during a collision. This energy loss is on the order of \( E/2 \) for an average collision. The energy loss is dependent on the momenta of the incident electron and its target, and for the purposes of ballistic transmission inelastic events are shown to decrease the occurrence of collected electrons [107]. BEEM current attenuation can be detrimental for measurements of thick oxides, where signal loss due to scattering renders useful data collection impossible. Garramone et al. describe a method to calculate the inelastic mean free path of an electron through copper using BEEM [108]. Fermi liquid theory is employed to model the behavior of interacting electrons within the metal assuming an energy dependence for inelastic mean free path. By applying Matthiessen’s rule, the sum of elastic and inelastic mean free paths is related to the attenuation length of the material by:
where the inelastic mean free path is an energy dependent component proportional to the electron velocity and lifetime. For electrons at the Fermi level, attenuation length is determined entirely by elastic scattering; as the energy of electrons increases, so does the impact of inelastic scattering on attenuation length, which is proportional to $1/E^2$. For both types of scattering, an effect on the distribution of measured barrier heights is observed, and simulations using a kinetic Monte Carlo modeling approach to highlight the impact of scattering are performed elsewhere [107, 39, 40]. The effects of scattering are observed for data presented in a later chapter, however modeling of the peaks is beyond the scope of this report.

2.2 Area Selective Deposition

2.2.1 X-ray Photoemission Spectroscopy

The modern application of X-ray photoemission spectroscopy was developed by a team at Uppsala University in Sweden in the 1950s. Kai Siegbahn, Nicolaas Bloembergen, and Arthur Schawlow would be awarded the 1981 Nobel Prize in Physics for what they called ‘Electron Spectroscopy for Chemical Analysis (ESCA)’ and what would become known as XPS. While the photoelectric effect had been known for some time, the application of a monochromated X-ray beam to illuminate NaCl crystals revolutionized the way photoexcitation studies were conducted [83]. A general understanding of the effect was that quantized packets of light would collide with core orbital electrons in a target material, ejecting them from the atom and - given electron energy higher than the work function of the material - potentially the surface of the material as well, as shown in Eq. 1.3. Work by Rutherford determined that the energy of an emitted electron was actually related to the binding energy of the electron, $E_b$, in the form:

$$ E_k = h\nu - E_b $$

(2.25)

where the binding energy is dependent on the specific atomic system to which it belongs [109].
To recover these electrons, a hemispheric energy analyzer or spectrometer is utilized which captures a fraction of the electrons generated by photoexcitation. The analyzer uses a retarding voltage at its opening to slow incoming electrons, such that a constant "pass energy" can be maintained. The pass energy is the energy of traveling electrons from the analyzer opening to the detector. A voltage is applied to the inner and outer hemispheres and the entire system can be modeled like:

\[ e(V_{out} - V_{in}) = E_0 \left( \frac{R_{out}}{R_{in}} - \frac{R_{in}}{R_{out}} \right) \]  

(2.26)

where \( V_{out} \) and \( V_{in} \) are the applied voltages on the outer and inner radii, respectively, \( R_{out} \) and \( R_{in} \) are the radii of the hemispheres, and \( E_0 \) is the pass energy. Pass energy is chosen by the operator, and in general, a lower pass energy results in better resolution from the relation \( \Delta E / E_0 = \) a constant value. For a known elemental binding energy, a range of energies can be obtained by varying the pass energy. The detector is laterally sensitive and can identify the energy of the electron based on its distance from the center, dependent on the pass energy and dimensions of the hemispheres. Precision comes at the cost of signal intensity, however, as current through the analyzer is reduced for higher retarding voltages.

Chemical states for an element are denoted by the L-S coupling quantum numbers \( n, l, \) and \( j \), which are the principle quantum number, angular quantum number, and spin projections, respectively. \( n \) and \( l \) are integer values with ranges \((n=1,2,3,...)\) and \((l=0,1,2,...,n-1)\), while \( j \) is a half-integer fractional value. Core level signals with \( l \geq 1 \) have peak doublets of the form: \( \frac{p_2}{2} - \frac{p_1}{2}, \frac{d_5}{2} - \frac{d_4}{2}, \frac{f_7}{2} - \frac{f_5}{2} \) with 2:1, 3:2, and 4:3 theoretical ratios of peak areas, respectively. The exact splitting of binding energies is dependent on steric changes to the material such as oxidation state, and this principle can be used to identify samples of metals like copper which may contain pure metal, +1, and +2 oxidation states. Both satellite peaks and peak broadening occur for Cu 2p with the addition of oxidized species. Peak deconvolution involves breaking down a spectral shape into the component parts, which for an oxidized copper sample means separating the pure metallic from oxidized states. This can be accomplished with reference tables and knowledge of peak ratios for doublets.

XPS is a surface sensitive technique, which is in large part due to the inelastic electron mean free path. For electron energies of hundreds of eV, the mean free path
λ is between 10-25 Å [110]. It is assumed that inelastically scattered electrons largely remain within the surface of the sample, or are scattered to high angles, and are not collected by the analyzer. For a depth x into the sample, signal intensity I₀ is expected to decay exponentially such that:

\[ I = I₀e^{-x/\lambda \cos(\theta)} \] (2.27)

where \( \theta \) is the electron emission angle relative to surface normal. From Eq. 2.27 it is clear that an effective probing depth of 3 \( \lambda \) is expected. The same argument for shallow depth of penetration can be made for the use of high-vacuum conditions.

Since the inelastic mean free path of an electron is inversely proportional to the pressure of the gas medium, by reducing the ambient pressure by a factor of 10, the mean free path of the electron is increased by the same factor. Additionally, the rate of surface particle adsorption is decreased under high-vacuum conditions.

Quantitative information about the elemental composition of a sample is also possible with XPS spectra. Specific to every core-level peak is an experimentally-determined relative sensitivity factor (RSF) which is used to weight the peak intensities of different elements in the same sample. Palmberg shows the experimental process of determining RSF values for their instrument using Auger electron spectroscopy on MgO [111]. Standard RSF values are also tabulated by Moulder et al., however these lack the specificity of experimentally determined values for a particular experimental setup, which adds error [112]. Using carefully determined RSF values, an equation for the molar concentration \( c_x \) of an element is given by:

\[ c_x = \frac{A_x/s_x}{\sum_i A_i/s_i} \] (2.28)

where \( A_x \) is the area under the peak and \( s_x \) is the RSF value. Once RSF values are obtained, background correction must be performed to extract only peak information measured for binding energies of photoexcited electrons. Three commonly applied background models include linear, Shirley, and Tougaard, with the latter two being developed to correlate with physical phenomena [113, 114]. A Shirley background assumes photoelectron flux is directly proportional with the number of inelastic electron collisions which contribute to the background, and both Shirley and linear background
methods are highly dependent on arbitrary end point selection around the peak distribution. The Tougaard method is largely independent of end point selection, and evaluates cross sections for inelastic scattering with dielectric response theory. The differences for a survey spectrum of the Si 2p peak is shown in Fig. 2.8. In the case of this silicon sample, the measured difference of peak areas are very small.

![Background Differences](image)

**Figure 2.8:** Three different background models are applied to a Si 2p XPS spectra. For some peak shapes the different models are necessary for accurate quantitative analysis.

Another consideration when taking XPS data is that surface charging of the sample due to insulator materials or electrical isolation from the analyzer will shift the measured peaks. As negative charges (electrons) leave the surface, a commensurate positive charge is leftover. Due to variations in the subsurface structure, charge can accumulate nonuniformly and cause different variations in measured binding energies across an interface. Studies on thin oxides found a nearly uniform potential step formed by charge buildup at the interface, shifting the binding energy of the oxide [115]. Spectral shape can also be influenced if the potential distribution is nonuniform, leading to distorted peaks. The methods for mitigating charging discussed here all fall under the regime of post measurement corrections, however Baer *et al.* have a comprehensive list of methods to limit charging effects prior to measuring [90]. When charging occurs, a known peak like C 1s is used to compensate for binding energy shifting. The binding energy of adventitious carbon (AdC) is
~284.8 eV and the C 1s signal in a survey spectrum, as well as all other spectra, are shifted such that the C 1s signal matches the AdC value. This method, while expedient, is only moderately useful since the exact chemical composition of AdC is not known nor standard, and contributions to the C 1s peak occur for carbon that is not adventitious. It is still the most utilized method for quick corrections.

Finally, XPS has been shown to be useful for determining the selectivity of deposited materials. Work by Larson, Shah, and Lee describes the methodology for measuring signal attenuation as material is deposited such that the selectivity of the material to an underlying substrate can be quantified [93]. A reference value for the passivation material on the substrate is collected first, and then after a new material is deposited another measurement takes place. The ratio of the peaks in the first and second measurement reveals how well the substrate signal is attenuated relative to a reference, and therefore how selective the deposited material is to the substrate:

\[ GoP = \frac{I_{\text{passivation}}/I_{\text{metal}}}{(I_{\text{passivation}}/I_{\text{metal}})_\text{ref}} \]  

(2.29)

For a ratio equal to 1, ideal selectivity of the passivating material is achieved. A ratio between 0 and 1 indicates non-uniform coverage, and a ratio greater than 1 indicates coverage over the entire substrate, potentially over undesirable regions. This type of analysis is performed on the samples discussed in a later chapter.
CHAPTER 3
Experimental Methods

This chapter details the processes involved with fabricating Schottky devices and techniques involved in area-selective deposition of high-κ films. Included is the deposition of metal cap layers, sample preparation and mounting onto custom STM plates, BEEM measurement setup, as well as XPS characterization and data acquisition.

3.1 BEEM Sample Preparation and Measurement

3.1.1 Substrate Preparation

A proper semiconductor substrate is first chosen to form the base of the Schottky diode prior to metal or insulator deposition. For all experiments reported here, a single crystal silicon substrate with <001> crystallographic orientation is chosen. The <001> orientation is widely utilized by the semiconductor industry, and conveniently cleaves perpendicular to an external stress point such that quadrilateral shaped coupons can be easily obtained. Substrate resistivity is also chosen based on its impact on the depletion layer of the silicon. This depletion layer is typically on the order of micrometers. For n-type silicon the depletion width is roughly 2 μm which is achieved with a silicon resistivity of 100 Ω-cm, or a doping density of \( \approx 10^{13} \text{ cm}^{-3} \). With p-type silicon a depletion width of 0.5 μm is achieved for wafer resistivity of 10 Ω-cm or a doping density of \( \approx 10^{15} \text{ cm}^{-3} \).

Another factor in determining choice of substrate is surface oxidation and cleaning. Different semiconductor substrates such as Si, Ge, and GaN possess dangling bonds at their surface which readily oxidize in atmospheric conditions, forming an amorphous film between 1-2 nm thick [116, 117]. This native oxide can be deleterious to interface characterization using BEEM because electrons injected from the STM tip may be more prone to scattering events within the oxide, changing the measured barrier height. It has also been shown that native oxides such as SiO\(_2\) yield a different electrostatic barrier from their thermally grown counterparts, which has implications for BEEM studies of MOS interfaces [41]. Removal of the native oxide is therefore necessary in the creation of MS interfaces, and this was done on silicon samples by
performing a chemical dip in 49% hydrofluoric acid (HF) for about 5 seconds followed by a DI water rinse. The Si surface becomes passivated by hydrogen during the dip, and resists further oxidation for nearly 20 minutes in atomosphere \cite{118}. To ensure an oxide-free surface, silicon samples etched by HF are brought into UHV conditions within this time frame in a modified metal deposition chamber.

3.1.2 Metal Deposition

Choosing a metal for a Schottky interface has many implications in the semiconductor industry. For example, metals such as chromium and tungsten react with silicon to form a silicide at the interface, which changes the electrostatic properties of the device stack \cite{107}. Copper is also kept away from silicon substrates due to its high diffusion rate into the semiconductor. In this report, gold is utilized as the metal cap layer in each material stack due to its superior properties as an inert diffusion barrier and conductor.

To deposit metal onto the silicon substrate, a UHV molecular beam epitaxy (MBE) system is utilized. The base pressure for this system is $\sim 10^{-11}$ Torr. For the purposes of the measurements examined by this report, gold was the only metal deposited by MBE thermal evaporation using standard Knudsen cells. Deposition temperature for gold is 1380$^\circ$ C, and the deposition rate is $\sim 0.47$ nm/min. Cap layers of both 12 and 20 nm were grown, and the metal is grown in 1x2 mm rectangles by using a shadow mask. The gold used for deposition is 99.99\% pure and is commercially purchased.

3.1.3 Sample Mounting

Immediately following metal deposition, the samples are removed from UHV and cold pressed onto custom BEEM plates shown in Fig. 3.1. Two ohmic electrical contacts are needed for the BEEM measurements to ensure reliable low current acquisition; one is a contact between the top electrode and ground, and the other is a contact between the semiconductor and ammeter in the STM. Before making the first contact onto the top plate, a scribe is used to scratch the bottom of the semiconductor substrate ensuring ohmic behavior. A copper beryllium wire is used to connect the base plate to the top electrode with indium solder. By electrically isolating these
contacts an accurate measurement of the BEEM current can be obtained.

3.1.4 Current-Voltage Spectroscopy

Correctly fabricated and mounted samples will show rectifying behavior when subjected to a current-voltage (IV) measurement. First, before loading into the STM, an ex-situ IV measurement is conducted on a Keithley 2400 source meter at room temperature. If the sample is rectifying, it is brought into the UHV STM chamber where an in-situ IV test is conducted at liquid nitrogen temperatures. The voltage sweep is typically -2 V to +2 V with 40 meV resolution, and both the slope of the IV curve as well as the turn on voltage of the diode are obtained. Using a model for thermionic emission as discussed in an earlier section, an average value of the electrostatic barrier height for the sample can be calculated.

3.1.5 Ballistic Electron Emission Microscopy

Finally the prepared samples are ready to be measured using the BEEM technique. This allows for a probing of the electrostatic properties of a buried interface to nanoscale dimensions, something not possible by using IV or CV spectroscopy. Information about the electrostatic barrier, as well as transport properties like elastic and inelastic scattering can all be examined with BEEM. This is accomplished by injecting
Figure 3.2: Schematic diagram of ballistic hole emission microscopy on a MIS interface. Holes tunnel into the metal contact and must overcome the barrier established by the interlayer dielectric to enter the valance band of the semiconductor. The metal electrode is grounded and semiconductor base is connected by ohmic contact to the electronics of the STM.

hot carriers from the STM tip into the metal at precise locations with subnanometer lateral resolution. The tip is kept in constant current mode by a piezomotor feedback loop which maintains stable tunneling by monitoring the tip current relative to a setpoint. A voltage bias is applied between the STM tip and top electrode of the sample ranging from ± 0.2 V to ± 3.0 V depending on the substrate and types of material layers present. Electrons with sufficient momentum to surpass the electrostatic barrier of the interface make it to the back contact on the semiconductor and are collected as BEEM current as shown in Fig. 3.2.

There are two primary types of BEEM measurements that will be discussed. The first is called forward BEEM, which occurs when the top metal electrode is biased positively relative to the STM tip. This technique is primarily useful for studying n-type semiconductors with surplus donors, where electrons from the STM tip travel through to the semiconductor and are collected as BEEM current. If a negative bias is applied to the metal electrode, holes will be injected from the STM tip and a reverse BEEM spectra will be obtained.

The second type of measurement, which will be discussed prominently here, is called forward ballistic hole emission microscopy (BHEM). Similar to reverse BEEM a negative bias is applied to inject holes into the metal, however the semiconductor for forward BHEM is p-type. Reverse BHEM applies a positive bias to the metal, and injects electrons which generates holes in the substrate via electron hole pair
excitation. The work presented here is largely that of forward BHEM, however some forward BEEM is also discussed.

Forward BHEM measurements were conducted in a modified low temperature UHV STM (Omicron) at \(10^{-11}\) mbar and liquid nitrogen conditions [119]. Specimens were loaded into the UHV environment immediately after mounting and ex-situ testing.

3.1.6 BEEM Mapping

For a typical BEEM measurement an area of \(1 \mu\text{m} \times 1 \mu\text{m}\) is chosen and spectra are collected at unique tip locations spaced 11.7 nm apart in a grid pattern. Nearly 10000 spectra are collected in this way over a 36 hour period. The collection of spectra in an evenly-spaced grid allows a systematic collection of spectra over the desired area. An offset current from an SR 570 pico-ammeter is chosen to cancel out noise effects. Spectra are also collected in the dark to reduce the impact of photocurrent generated by ambient light. Spectra are collected and fit to the BEEM model described in Chapter 2, and a histogram of the fits is produced to show the distribution of barrier heights across the sample area.

A novel interpretation of BEEM data is to map the spectra fits based on their physical x and y coordinates, and by assigning a color value to the barrier height a false color map can be produced showing the electrostatic barrier value at discrete locations across the measured region. This allows for quick identification of the electrostatic uniformity of an interface with nanometer spatial resolution - something that cannot be accomplished by spatially averaged techniques such as IV or CV.

3.2 Area Selective Deposition

Due to the confidential nature of the work being done for area-selective deposition, much of the discussion surrounding experimental methods will be generalized.

3.2.1 SAM Deposition

Both patterned and blanket wafers are utilized in the selective deposition work presented here. Blanket wafers include SiO2, Cu, and SiCOH (low-k), and are all done on silicon < 001 > substrates. SAMs are grown on the blanket substrates uniformly
and range in thickness from 2-5 nm, depending on growth conditions and chemistry. Thickness is measured on a full wafer ellipsometer. Both full wafer and coupon water contact angle (WCA) measurements are also made to qualitatively check SAM adhesion - since the polymer material is hydrophobic the WCA should increase for a wafer that is successfully coated with SAMs. SAMs are also deposited on patterned wafers. These wafers possess multiple different linespace pitches of alternating copper and low-k (SiCOH) lines ranging from 48 nm to 500 nm. Ellipsometry and WCA are insufficient for determining SAM behavior at such small dimensions, so another technique is required.

Once the SAM is deposited, XPS analysis is conducted to characterize the sample. A NOVA full wafer XPS tool is employed with an Al Kα source with a momentum of 1486 eV and width of 0.85 eV. The XPS illuminates a sample with a beam of x-rays, which interact with the bonds of the sample up to a depth of about 100 Å. Electron excitation in the sample atoms result in characteristic photon emission, and by collecting these photons information about the element(s) present can be determined. For example, C-C and C-H bonds from adventitious carbon contamination or hydrocarbon polymer chains result in a characteristic peak at 284 eV as shown in Fig. 3.3. In the case of thiol SAM deposition such as with ODT or DDT, peaks corresponding to carbon and sulfur should appear post application of the SAM onto the substrate, as well as a decrease in peak counts for the underlying substrate material.

For patterned wafers, this characterization requires a little more careful analysis. Due to the relatively large spot size of the XPS, information about the material present in a linespace pair region represents an average value across tens of linespace pairs. For this reason, information about the behavior of SAMs on discrete, nanometer-sized regions of metal or low-k is not possible with XPS - and is extremely difficult using methods like cross section scanning electron microscopy (XSEM) due to limitations of resolution. Fortunately, XPS is still capable of qualitatively describing SAM selectivity. A region of pure low-k is used as reference against linespace regions such that, for ODT-like SAMs, no additional C 1s signal and no S 2p signal should be found in the low-k ”field” region. For low-k-selective SAMS, the SAM signal in the field should be nearly twice the signal in the linespace pair region, since half of
Figure 3.3: XPS spectra for the C 1s peak. Three bonding energies are deconvolved from the peak shape, including C-C, C-O, and C=O bonds.

the latter region is comprised of the non preferred substrate.

3.2.2 High-k Deposition

After SAM has been deposited and analyzed, the wafer is brought into an ALD system to deposit thin high-k material. Different chemical precursors are used to grow the desired film, which in this study is either HfO$_2$ or Al$_2$O$_3$. For hafnia deposition, H$_2$O and Tetrakis(ethylmethylamino)hafnium (TEMAH) are often used as precursors, and temperature plays an important role in the ultimate deposition rate of the hafnia film [120, 121]. Special care is taken in the tuning of precursor conditions, especially for water in the case of hafnia deposition, as this strongly determines the sites for metal precursor adsorption. For aluminum oxide deposition, two distinct precursor chemistries are utilized and compared in this study.

ALD is ideal for work using SAMs as it can be performed at much lower temperatures (< 350°C) than conventional CVD techniques which would destroy the SAM material and also maximizes selectivity of the grown oxide. The tunability of temperature is important when dealing with SAM blocking materials due to the thermal
instability of organic films at modest temperatures (citation needed). The temperature of ALD is modified to observe changes in thickness and selectivity of the desired oxide.

The same XPS analysis for post SAM is performed on each sample post high-k. Peak signals from the oxide film are compared between linespace and field indicating the extent of selective or nonselective growth in the linespace regions. Additionally, by comparing peak signals obtained prior to SAM, post SAM, and post high-k, quantitative information about selective behavior can be obtained.
4.0.1 Results

Figure 4.1: Cross-sectional SEM image of the Au/Si interface. 20 nm of gold is measured.

A cross-sectional SEM image showing 20 nm Au deposited on the hafnia film is displayed in Fig. 4.1, however only the gold grains are visible due to the resolution of the microscope. IV and CV measurements of this interface reveal a built-in potential of -0.43 eV and a doping density consistent with wafer specifications is extracted. The inset IV data shows diode rectification and is displayed in Fig. 4.2. To confirm the presence of hafnia, XPS measurements were conducted and Hf 4f core electron bond energies consistent with HfO$_2$ are detected. The underlying silicon oxide is also found by looking at the Si 2p core electron peaks, however the exact stoichiometry of the film is uncertain due to the resolution of the measurement. Most of the peak counts in Fig. 4.4 are associated with the bulk substrate, while a small secondary peak indicates the ultrathin native oxide formation. A thickness calculation of this interlayer oxide

41
is estimated by looking at the silicon peaks associated with the substrate and the oxide [86], and a thickness of 0.8 nm is determined. Temperature-dependent IV and CV was also conducted on this material stack to observe changes in barrier behavior for a temperature range of 25 to 85 Celsius. The IV spectra are shown in Fig 4.3, and a table showing the extracted barrier heights from thermionic emission described in Eq 2.13 is shown in Table 4.1.

![IV spectra](image)

**Figure 4.2:** IV spectra for a Au/HfO₂/SiO₂/Si interface on p-type silicon taken over a range of 60 degrees Celsius. Current response increases slightly for higher temperatures, and rectification is observed for all temperatures.

The averaged BEEM spectra, as well as linearized fit to the BK model, for this interface are displayed in Fig. 4.5. Data are taken with a positive tip bias, however in order to simplify comparison with the valance band offsets and Schottky barrier heights for p-type semiconductors - which are reported as negative values - units of eV are utilized. The solid line represents the linear region of fit, and the barrier height extracted from the simplified BK model is -0.45 eV.

Two distinct BHEM threshold maps and histograms are produced from two square micron scans of different HfO₂ samples and are displayed in Fig. 4.6. The first region shows a histogram with two broad concentrations of threshold values centered around -1.40 eV and -2.20 eV. The dominant peak is centered at -1.40 eV which is indicated by the inset threshold map - only a few discrete locations near the top of the
Figure 4.3: IV spectra for a Au/HfO$_2$/SiO$_2$/Si (p-type) interface on p-type silicon taken over a range of 60 degrees Celsius. Current response increases slightly for higher temperatures, and rectification is observed for all temperatures.

map represent threshold values near the -2.20 eV range. $\phi_b$ is the fit to the average of a few thousand spectra, while $\phi_t$ is the average of each individual fit. Finally the standard deviation is shown as $\sigma$.

The second threshold map also shows two distinct concentrations of threshold values, this time centered around -0.45 eV and -1.25 eV. The first peak region is consistent with the fit to the average spectra in Fig. 4.5, and the built-in potential extracted from ex-situ CV spectroscopy. The second peak region is consistent with thresholds from the first region. The inset map shows a strong boundary between threshold values in each peak such that higher thresholds exist exclusively on the right 20 nm of the map.

Three distinct average BHEM spectra for the hafnia samples are created out of the 10000 total spectra by averaging spectra within three specific threshold ranges
<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>SBH: IV (eV)</th>
<th>n</th>
<th>SBH: CV (eV)</th>
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<td>5.7</td>
<td>0.43</td>
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<td>0.43</td>
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<td>0.34</td>
<td>4.3</td>
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<td>0.35</td>
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<tr>
<td>85</td>
<td>0.38</td>
<td>3.6</td>
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Table 4.1: Barrier height calculations taken from temperature-dependent IV and CV measurements. Barrier heights trend to higher energies at higher temperatures, and a much higher barrier is found for CV measurements at high temperature (> 70° C)

(-2.5 to -1.8, -1.7 to -1.0, and -0.6 to 0.0 eV) and are displayed in Fig. 4.7. For comparison, spectra taken from separate Au/Si(001) and Au/Native SiO$_2$/Si(001) p-type samples are included. Averaged spectra from the lowest barrier height ranges of the hafnia samples match closely with spectra from the two included reference interfaces indicating the presence of native SiO$_2$/Si at 1.25 eV and Au/Si at 0.33 eV [24, 122].

4.0.2 Discussion

Previous studies of hafnium oxide on p-type Si have found a valence band offset of around 2.2 eV [123, 124]. The first BEEM region discussed in the Results section shows threshold values centered around -2.2 eV and are attributed to the HfO$_2$ band offset. This same sample region, however, is dominated by threshold values of lower energy, around 1.4 eV. These thresholds are attributed to the valence band offset for a native SiO$_2$. While thermally grown silicon oxide films typically have a much higher barrier height seen in both BEEM and photoemission studies, it is believed that the sub-nanometer thick SiO$_2$ layer such as a native oxide seen here is exhibiting the barrier lowering effect observed for ultrathin (~1-nm-thick) films when compared to thermally grown, ~3-nm and thicker oxide [24, 6, 125]. This ultrathin silica is the by-product of the ALD process and results after a few cycles to allow nucleation of the HfO$_2$ film. This oxide is seen in both BEEM regions suggesting uniformity across the wafer, however local non-uniformity may occur as suggested by the varying
Figure 4.4: XPS spectra for the Silicon 2p peak on a Au/HfO$_2$/SiO$_2$/Si interface. Peak "B" represents the bulk silicon substrate, while peak "A" is a component of the native oxide.

quantities of thresholds corresponding to the SiO$_2$/Si barrier. In addition, any non-uniform hafnia deposition that left the H-terminated Si untouched would result in native oxide formation during the transfer from ALD to the thermal evaporation UHV system.

While the two previously discussed threshold regions relate well to the assumed material stack, a large distribution of barrier heights centered at -0.45 eV dominate region two of this study. This peak distribution is broad and does include -0.33 eV - the known barrier height for Au/Si $p$-type, however a majority of the threshold values are closer to -0.45 eV [122]. In addition, threshold distributions for metal semiconductor interfaces formed by thermal evaporation and sputter-deposition are typically narrower [107, 40]. Peak distribution broadening is shown to occur due to elastic scattering which deflects electrons injected from the STM tip, increasing their parallel momentum $k_{\parallel}$ and requiring greater initial energy to surpass the electrostatic barrier. This skewing effect produces a characteristic histogram shape including a broad central distribution followed by a trailing shoulder region and large standard deviation shown in Fig. 2.7 [39, 107] Elastic scattering can be caused by surface roughness, material interfaces, and defects. The broad peaks from Region 1 are likely
Figure 4.5: An averaged BEEM spectra with inset linearized fit.

the result of elastic scattering in the oxide.

It is unlikely that any Au is in contact with the Si substrate, since both the hafnia ALD process and transfer of wafers in atmosphere would passivate any bare Si with an ultrathin oxide. This should provide a diffusion barrier for metal / semiconductor contact and also produce BEEM spectra like is shown in Fig. 2.7. An initial theory for this barrier was inspired by work done on metal / graphene / semiconductor interfaces which found that a graphene interlayer was capable of preventing metal diffusion into the semiconductor substrate without changing the electrostatic barrier height [126]. STM-injected electrons are able to travel ballistically through this diffusion barrier while not impacting the observed barrier height. Kinetic Monte Carlo modeling work described by Nolting et al. was performed for Region 2 to better understand the origin of the unknown barrier region [107]. The best fit found by the model had a -0.45 eV barrier height with 45 meV standard deviation and a 31 % elastic scattering rate, and was unable to produce a fit centered at -0.33 eV for the barrier height. This suggests that the Au/Si $p$-type barrier is not being observed.

An alternate theory is employed to diagnose the cause of this barrier height distribution. In describing the native oxide barrier height a distinction was made between thick, thermally grown oxide and ultrathin, native oxide. Thin oxides are
Figure 4.6: Histograms and inset Schottky barrier maps for two regions of a Au/HfO$_2$/SiO$_2$/Si interface. In Region 1 (left), two broad peaks are observed in the histogram, and the peaks seem to be distributed randomly throughout the spatial map. In Region 2 (right), one broad and one sharp peak is observed in the histogram, and the peaks seem to be distributed randomly throughout the spatial map and the inset map shows a clear divide between spatial distributions of high and low barrier heights.
Figure 4.7: Nonlinear spectra fits for both hafnia samples, as well as spectra from Au/Si-\(p\) and Au/SiO\(_2\)/Si-\(p\) samples for comparison. Spectra from the hafnia samples correspond with the native oxide comparison spectra and the known barrier height of hafnium oxide, however a new barrier is also observed at 0.45 eV that doesn’t correspond with the Au/Si interface. The -0.45 eV barrier is thus attributed to an ultrathin (0.3 – 0.9 nm) HfO\(_2\) which is locally thin compared to the average thickness grown by ALD. This explains why the expected barrier for hafnia on \(p\)-type Si is also found, however it suggests that local non-uniformity of hafnia thickness is more probable given the abundance of -0.45 eV thresholds. A representation of the sample is shown in Fig. 4.8, including regions of sufficiently thick HfO\(_2\) to observe the known barrier, locally thin regions which yield barrier-lowering values, and regions of no hafnia where the native silicon oxide barrier is observed.

The power of Schottky barrier visualization shown in Fig. 4.6 is that the transition between barrier heights can be locally witnessed across a broad 30 × 50 nm area consistent with a physical change to the sample surface such as a change in thickness. Fluctuations in the threshold histograms caused by effects like electron scattering are visually observable on the maps. This is especially useful for observing structural disorder due to silicide formation and other defects which change interface charge
density [127, 128]. Perhaps most importantly, it can reveal non-uniformity where spatially averaged techniques like IV and CV are unable. The CV spectra taken for Region 2 revealed only the lower energy barrier, and both techniques are incapable of showing nanometer spatial resolution. A uniform deposition process like ALD may be shown to have reasonably good wafer coverage, but nanometer-scale fluctuations may result in unexpected electrostatic behavior changes which have implications for device performance.

### 4.0.3 BEEM Measurement Resolution

While BEEM has exceptional lateral resolution due to the STM platform, the energetic sensitivity of the measurement technique must be defined. Differences in band structure between Si(001) and Si(001) as well as $k_\parallel$ conservation of the carriers are responsible for small shifts in barrier heights for non-epitaxial metal/semiconductor interfaces [129, 31]. The Si(111) interface lacks $k_\parallel = 0$ states and reflects forward focused electrons with energy equal to the barrier. Therefore,
carriers attempting to surmount the barrier must have enough forward momentum, $k_\perp$ to overcome the barrier which only occurs at higher total energy $E = \frac{\hbar}{2m} (k_\perp^2 + k_\parallel^2)$. Momentum randomization through scattering events is believed to suppress this effect [31]; only small differences in barrier height between Si(111) and Si(001) are observed, and only at cryogenic temperatures. Metal film thickness also plays a role in the effect [129].

![Figure 4.9: Comparison of measured barrier heights for Au/Si interfaces with varying Au thickness and Si substrate orientation. For thinner Au, the BHs overlap and become indistinguishable.](image)

Gold is chosen as the metal layer for its properties as a diffusion barrier, its inability to form a silicide, and to compare with previous results taken by this experimental setup. Histograms for Au/Si(111) and Au/Si(001) $n$-type interfaces are shown in Fig. 4.10. A summary of thickness dependence for each substrate is plotted in Fig. 4.9. They show that the divergence of barrier heights between Si(111) and Si(001) increases for thicker metal films, and for films smaller than 10 nm thick Au the barrier heights converge. For thinner metal films, carriers are able to make multiple attempts to surmount the barrier by reflecting off the vacuum/metal and metal/semiconductor interfaces.

These results enable a determination of the ultimate energetic resolution of this measurement setup by way of the Rayleigh criterion. Fig. 4.9 shows the minimum resolvable energetic separation between Si(111) and Si(001) occurs for 10 nm thick film based on the statistical standard deviation of each measurement. This is analogous to the minimum resolvable separation between spots in an optical microscope.

50
The minimum of one histogram occurs at the peak of the other, and a distinct saddle point occurs in the middle. The Rayleigh criterion for different values of peak separation are shown in Fig. 4.11 By taking half the distance between the peaks to be resolution, an ultimate resolution of approximately 10 meV is determined. The factors which influence this minimum detectable splitting include temperature, total number of spectra collected, and resolution of the STM tip bias used in collecting each spectra. Thermal spreading of the electron distribution at liquid nitrogen temperatures \(k_B T\) is 7 meV, and by lowering this value the resolution could be improved. However, it has been shown that carriers are frozen out at temperatures below 77 K, having a detrimental effect to BEEM measurements [130]. Constraints on the tip bias resolution (9 meV) include liquid nitrogen hold time in the STM cryostat (\(\sim 36 \text{ h}\)), data acquisition time per spectra (10–20 s), and the tip bias voltage range.
Figure 4.11: Rayleigh criterion for two sinusoidal peaks. For separation values less than 0.5, the peaks are unresolvable. Peaks can be resolved for $s > 0.5$. 
CHAPTER 5
THIN FILM HIGH-K SELECTIVE DEPOSITION VIA SELF-ASSEMBLED MONOLAYER BLOCKING LAYERS

5.1 High-k Selective Deposition

5.1.1 Results

Dodecanethiol (DDT) SAM is deposited onto blanket copper and low-k wafers. Ellipsometry shows an average thickness of approximately 4 nm of SAM, and WCA measurements confirm SAM adhesion as angles collected from DDT samples increase in relation to blanket Cu wafers. A table showing the peak areas for C 1s, Si 2p, Cu 2p, and S 2p is displayed in Table 5.1.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>C 1s</th>
<th>Si 2p</th>
<th>Cu 2p</th>
<th>S 2p</th>
<th>Al 2s</th>
</tr>
</thead>
<tbody>
<tr>
<td>No SAM Blkt Cu</td>
<td>218,265</td>
<td>0</td>
<td>16,564,000</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>No SAM Blkt BD3</td>
<td>878,841</td>
<td>959,738</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>DDT + Blkt Cu</td>
<td>1,799,825</td>
<td>0</td>
<td>5,656,679</td>
<td>295,031</td>
<td>0</td>
</tr>
<tr>
<td>DDT + Blkt BD3</td>
<td>899,760</td>
<td>1,052,248</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>High-k + Blkt Cu</td>
<td>590,966</td>
<td>0</td>
<td>5,699,469</td>
<td>111,025</td>
<td>218,763</td>
</tr>
<tr>
<td>High-k + Blkt BD3</td>
<td>273,308</td>
<td>224,181</td>
<td>0</td>
<td>0</td>
<td>1,263,263</td>
</tr>
</tbody>
</table>

Table 5.1: Thiol SAM on blanket wafer results. SAM concentration is 5mM. High-k deposition results indicate base substrate, however in both cases SAM was also present.

Selectivity ratios of 0.052 for DDT on Cu, 0.038 for Al on Cu, and 5.64 for Al on low-k are obtained from Eq. 2.29. These reference ratios are used to calculate the overall selectivity of measurements on pattern wafers. XPS spectra for the S 2p peak of 5mM DDT is shown in Fig. 5.1. The lower energy, larger peak represents bound thiolate, or sulfur atoms bound to the metal atoms at the interface of copper / DDT. The higher energy peaks represent unbound sulfur atoms that are associated with oxygen bonding such as in a sulfate group. The total counts for each deconvolved component are shown in the top left of the plot. A comparison of S 2p peaks for different thicknesses of DDT is also displayed in Fig. 5.1. Sulfur counts are highest
for higher concentrations of SAM. All XPS spectra are collected with a high resolution recipe for peak comparison.

Data from measurements taken on patterned wafers are also reported in Table 5.2. A nearly 5 nm film of Al₂O₃ is deposited via ALD onto patterned wafers post DDT application. Four different linespace regions are measured, as well as a field region that is comprised entirely of low-k material. The measured amounts of C 1s and S 2p peaks corresponding to DDT SAM are nearly identical in the linespace regions, and the Al 2s peak counts increase with increasing linespace size. Using Eq. 2.29 a measure of selectivity for aluminum in the linespace regions and field is obtained: The ratio of aluminum over copper is > 1 for all linespace regions except 42 nm. Additionally, the ratio of aluminum over low-k is nearly 1 in the field and approximately 0.06 in the linespace regions. Al 2s spectra are plotted for this sample and shown in Fig 5.2. Due to an overlap with the Cu 3s signal, the spectra for the linespace regions have a double peak. Only the component due to aluminum is reported in the peak area.

An identical procedure was done for samples using octodecanethiol (ODT) SAM chemistry. The data are presented in Table 5.3. Selectivity ratios were calculated for these data: selectivity of aluminum on copper is much greater than 1 for the linespace regions, and aluminum selectivity on low-k increases from 0.24 to 0.71 in the linespace regions and is identically 1 in the field.

<table>
<thead>
<tr>
<th></th>
<th>C 1s</th>
<th>Si 2p</th>
<th>Cu 2p</th>
<th>S 2p</th>
<th>Al 2s</th>
</tr>
</thead>
<tbody>
<tr>
<td>42nm</td>
<td>1,344,705</td>
<td>235,861</td>
<td>2,783,921</td>
<td>197,059</td>
<td>94,263</td>
</tr>
<tr>
<td>64nm</td>
<td>1,340,109</td>
<td>289,443</td>
<td>2,630,735</td>
<td>202,412</td>
<td>108,554</td>
</tr>
<tr>
<td>100nm</td>
<td>1,313,324</td>
<td>313,299</td>
<td>2,199,597</td>
<td>187,248</td>
<td>148,985</td>
</tr>
<tr>
<td>500nm</td>
<td>1,270,521</td>
<td>316,684</td>
<td>1,973,115</td>
<td>199,902</td>
<td>122,801</td>
</tr>
<tr>
<td>Field</td>
<td>325,699</td>
<td>245,277</td>
<td>0</td>
<td>0</td>
<td>1,114,311</td>
</tr>
</tbody>
</table>

**Table 5.2:** DDT Thiol SAM on pattern wafer results. SAM concentration is 5mM. 4 linespace regions in the wafer are measured and presented - 42nm, 64nm, 100nm, 500nm - as well as a low-k field region.

Hafnium oxide is investigated on pattern wafers using ODT and another hydro-
Figure 5.1: XPS spectra for the S 2p peak. There are two peaks representing bound S-Me bonds at the interface, and unbound thiolate. Thickness-dependent measurements of the S 2p peak for 3 concentrations of DDT SAM are also shown. Higher concentration of SAM directly correlates with deposited thickness.
Figure 5.2: Al 2s peaks for different regions on a patterned wafer with 5mM DDT. Al is most present on the field region, where DDT deposition is minimal.

carbon chain SAM. For the ODT SAM wafer, hafnia peak counts averaging 2.5 million are found in the linespace regions, while a signal of 5.7 million is found in the field, as shown in Fig. 5.3. The smallest pitch linespace region has a significant amount more hafnia than the other linespace regions. A selectivity ratio of 1 is obtained for hafnia in the field region, while the 100 nm and 500 nm linespace regions have selectivity ratios of 0.24 and 0.63. For the other SAM wafer, the amount of hafnia in the field region is consistent with approximately 4 nm of film thickness, and a selectivity ratio in the linespace regions is calculated to be about 0.40. TEM data for the ODT wafer is shown in Fig. 5.6.

5.1.2 Discussion

Blanket wafers are useful for characterizing the behavior of both SAMs and ALD high-k films. Tools like XPS have relatively large spot sizes (tens of microns) that are incapable of obtaining detailed information about localized changes to a film with nanometer spatial resolution. For finer pattern features like linespace pairs, a baseline knowledge of material behavior on blanket substrates can help determine overall behavior across hundreds of linespace pairs. DDT is a SAM that is known to adhere to metallic surfaces such as copper, while not adhering to oxidized or low-k
Figure 5.3: Hf 4f peaks for different regions on a patterned wafer with 5mM ODT. Hf is most present on the field region, where ODT deposition is minimal. Peak counts are high in the smallest pitch region, indicating poor selectivity, however the other pitch features appear to have good selectivity.

surfaces [75]. The results in this work shown in Table 5.1 corroborate literature results - evidence of SAM adhesion with the C 1s and S 2p peaks occurs only on blanket copper wafers. Additionally, after depositing ALD Al₂O₃, a significant Al 2s peak is observed for the blanket low-k wafer while a peak six times smaller is found on the copper wafer. This is evidence for the effectiveness of DDT in blocking aluminum oxide nucleation on the copper, however it also shows that there is a limit to how long the SAM behaves as a growth inhibitor in the ALD chamber. The technique may not be acceptable for dielectric-on-dielectric processes requiring thicker high-k films, where aluminum nucleation would begin to occur in undesired growth regions.

For patterned wafers, analysis of the deposition selectivity requires more effort. Fig. 5.2 shows the Al 2s peaks for four linespace regions and a low-k field region on the patterned wafer. This binding energy range contains information about the Al 2s transition as well as the Cu 3s transition, and due to the presence of copper in the sample a double peak is observed for the spectra taken from linespace regions. After deconvolving the peaks by modeling an aluminum and copper component, the aluminum signal can be extracted and compared to the pure aluminum signal found in
the field region. By looking at the selectivity equation, and using the reference values obtained for blanket wafers, it is determined that the aluminum selectivity in the field is approximately 1. This increases confidence that the desired thickness of aluminum has been successfully grown in the field. However, selectivity values for aluminum in the linespace regions tell a different story; namely, selectivity ratios bigger than 1 for copper and much less than 1 for low-k suggests both that aluminum is covering regions blocked by DDT and also not covering the low-k lines with equal thickness to the field. Qualitatively, this result can be inferred by the ratio of peak area in the linespaces and field - no more than 10% of the aluminum signal in the field is found in any of the linespace regions. It may be the case that for thin spacings, DDT is too effective at screening aluminum deposition, since results using other SAM materials have yielded aluminum signals at nearly 5 times the level shown here. Examples of selective and nonselective deposition are shown in Fig. 5.6.

**Figure 5.4:** Al 2s peaks for different regions on a patterned wafer with 5mM ODT. Al is most present on the field region, where DDT deposition is minimal. Selectivity of the aluminum appears better than for the DDT wafer.

For comparison, the longer hydrocarbon chain SAM ODT is used for the same ALD process and wafer conditions. Chain length is known to impact properties such as adhesion [131] and may impact the chemical blocking rate for ALD films, however both ODT and DDT have been shown to work in area-selective ALD of high-k films [9].
Table 5.3: ODT Thiol SAM on pattern wafer results. SAM concentration is 5mM. 4 linespace regions in the wafer are measured and presented - 42nm, 64nm, 100nm, 500nm - as well as a low-k field region.

<table>
<thead>
<tr>
<th></th>
<th>C 1s</th>
<th>Si 2p</th>
<th>Cu 2p</th>
<th>S 2p</th>
<th>Al 2s</th>
</tr>
</thead>
<tbody>
<tr>
<td>42nm</td>
<td>1,665,647</td>
<td>220,604</td>
<td>1,430,371</td>
<td>165,614</td>
<td>294,123</td>
</tr>
<tr>
<td>64nm</td>
<td>1,622,736</td>
<td>256,597</td>
<td>1,256,828</td>
<td>136,354</td>
<td>152,810</td>
</tr>
<tr>
<td>100nm</td>
<td>1,411,715</td>
<td>204,222</td>
<td>1,097,796</td>
<td>147,457</td>
<td>448,723</td>
</tr>
<tr>
<td>500nm</td>
<td>1,402,509</td>
<td>131,443</td>
<td>971,248</td>
<td>143,136</td>
<td>525,026</td>
</tr>
<tr>
<td>Field</td>
<td>266,797</td>
<td>189,870</td>
<td>0</td>
<td>0</td>
<td>1,136,551</td>
</tr>
</tbody>
</table>

Fig. 5.4 shows the aluminum peaks for a patterned wafer, and the differences between ODT and DDT are immediately apparent; aluminum signals in the linespace regions are significantly higher for ODT. For the 100 nm and 500 nm linespace regions, the aluminum peaks represent about 50% of the field signal. Since the linespace regions are comprised of equal parts copper and low-k, it makes sense that the aluminum signal in the linespace would be half the signal in the field, which is entirely made up of low-k. In terms of quantitative selectivity, a selectivity value of 1 is obtained for the field region and 0.39 and 0.71 for the 100 nm and 500 nm linespace regions, respectively. Clearly, better selectivity is achieved for the patterned wafer treated with ODT, and it appears that ideal behavior occurs for pattern dimensions between 100 and 500 nm. For this technique to offer a competitive edge over multiple patterning lithography, improvements will need to be made in order to achieve selectivity at the lower linespace pitches.

Additional analysis of both DDT and ODT SAM layers is conducted on patterned wafers by varying the concentration of the applied SAM. Fig 5.5 shows aluminum peak results for 1.25 mM ODT and 2.5 mM DDT concentrations. In each case, the peak height in the field is largely unchanged from the 5 mM trials. This is expected as SAM is not believed to adhere to the field region. In the linespace regions, however, the peak counts for aluminum increase categorically with decreasing concentration of both types of SAM.

At a naive first glance, it appears that 2.5 mM DDT has much better selective behav-
Figure 5.5: Aluminum 2s XPS spectra for 1.25 mM ODT and 2.5 mM DDT patterned wafer samples are plotted together to show the impact of reducing SAM concentration. Selectivity is negatively impacted by 1.25 mM for ODT, where Al is deposited largely uniformly across the different pattern features. 2.5 mM DDT looks more reasonable, and actually performs better with selectivity in the lower pitch regions.
ior at the smaller pitch regions. Indeed, calculated selectivity ratios for the linespace regions reveal nearly 0.50 selectivity for the 42 and 64 nm regions, while the larger pitches increase to approximately 1. Since we expect half of selectivity in the linespace as the field, it appears that decreasing the concentration of DDT by half significantly improves aluminum selectivity in the target small pitch regions, while leading to more than desired aluminum growth in the larger linespace regions. This effect is pronounced at 1.25 mM for ODT, as aluminum selectivity values greater than 1 are calculated for each linespace region. Aluminum is being deposited over both the desired low-k lines and undesired copper lines, resulting in a uniform film. By reducing the concentration of the SAM, it appears the effectiveness of aluminum screening is reduced. Any nonuniform SAM deposition would result in exposed copper lines which would be subject to aluminum oxide nucleation, which is the likely explanation for reduced ALD screening.

Work was also done with ALD HfO$_2$ as shown in Fig. 5.3. Interestingly, an over abundance of hafnia is found in the 42 nm linespace region, indicating poor SAM blockage. This can be attributed to defect formation during SAM coating which allowed hafnia deposition to occur over copper and low-k. The other linespace regions show qualitative selectivity, and for the 100 and 500 nm regions quantitative selectivity values of 0.25 and 0.63 are calculated. As with the aluminum samples, for 5 mM SAM the ideal selectivity occurs for pattern features between 100 and 500 nm. A different measurement using ODT SAM was measured using TEM shown in Fig. 5.7, which confirms excellent selectivity for the 100 nm region.
Figure 5.6: TEM images of selective and nonselective deposition of $\text{Al}_2\text{O}_3$ on a patterned wafer.
Figure 5.7: TEM image showing selective hafnia deposition on a 100 nm pitch linespace.
6.1 Conclusions

Ultrathin hafnia has been characterized to nanoscale dimensions using a high spatial resolution barrier height mapping technique which takes into account interface scattering and local nonuniformity. Determination of multiple barriers across a square micron of metal / oxide / semiconductor interface is possible due to the resolution of BEEM which is not otherwise possible using conventional IV or CV measurements that provide a spatially averaged measurement of the barrier.

Typically uniform ALD hafnia has been deposited at approximately 1.4 nm across a p-type Si substrate, with a 20 nm cap layer of Au. I-V and C-V measurements show an averaged barrier height consistent with a metal / semiconductor interface, indicating non bulk behavior of the hafnia film. BEEM analysis indicates the presence of a low energy barrier as well as two barriers higher than 1.0 eV, typically associated with insulators. Literature reported values of the hafnia and native oxide valence band offsets match with the higher energy barrier heights. However, the lower energy barrier does not match with reported values for Au/Si, and this new result is attributed to locally thin hafnia which has a lowered barrier in relation to the bulk value. This is seen for native silicon oxide when compared to thermally grown SiO$_2$ [24].

The barrier height visualization technique described in this report is capable of resolving electrostatic barriers to within 10 meV. This is facilitated by the natural discrepancy between Si(111) and Si(001) caused by a lack of $k_{||} = 0$ states in the former. In accordance with momentum conservation, scattering events result in a 10 meV separation between barrier heights for the two substrates with a 10 nm gold capping layer, and the Rayleigh criterion is employed to determine that the BH distributions for both substrates are resolvable. Having a known resolution limit allows for post hoc confirmation of peak identities from previous studies while also informing the analysis of future work using this experimental setup.

This work has also shown SAMs can be used to selectively grow thin high-k
oxide films to tens of nanometers. By depositing DDT and ODT SAMs onto metal substrates, ALD grown oxides nucleate on adjacent dielectric substrate while being blocked from the metal substrate. Multiple thicknesses of SAM are tested, revealing better $\text{Al}_2\text{O}_3$ selectivity in the smaller pitch regions for 2.5 mM DDT compared to 5 mM. Further diminishing the concentration to 1.25 mM with ODT SAM results in nonselective deposition across all linespace regions. By finding an optimal SAM concentration, the desired pitch can be selectively coated. The best reliable selectivity is achieved for a linespace pitch as small as 100 nm.

6.2 Future Studies
6.2.1 Ultra-thin Oxides

Samples of hafnia at 1.4 and 4 nm have been tested with BEEM, with the latter being too thick to recover BEEM current [41]. A series of thickness varying measurements could be conducted to ascertain the thickness of hafnia required to see only the bulk valance band maximum while also not being too thick to fully attenuate the ballistic electrons. Similarly, a thinner film can be grown in an attempt to see ballistically transparent behavior such as reported by Wong et al. with interstitial graphene [126]. Tuning the thickness of the gate oxide has implications both for the feasibility of uniform ALD and also of leakage current, so a comprehensive understanding of the electrostatic properties of a common gate oxide material may be useful in the development of next generation field effect transistors.

$\text{Al}_2\text{O}_3$ is another commonly used high-k dielectric in the semiconductor industry, functioning particularly well as a barrier layer in tunnel junctions. Ultrathin aluminum oxide (0.6 to 1.5 nm) has been shown to exhibit a barrier height of 1.2 eV on $n$-type Si [132]. A study on $p$-type Si may allow better comparison to the hafnia samples reported here, as would a study of hafnia on $n$-type Si. Additionally, since for metal / semiconductor Schottky barriers the sum of the $p$ and $n$-type barriers is equal to the bandgap of the semiconductor substrate, it would be interesting to see if this holds for metal / oxide / semiconductor interfaces in terms of the bandgap of the oxide. Thermally grown $\text{SiO}_2$ is shown to produce barrier heights on both $p$ and $n$-type substrates that sum to the bandgap of silicon dioxide ($\sim 9$ eV) [125, 24], however the barrier lowering seen on native and ultrathin oxides may result in a much
lower summation of barrier heights than predicted by the oxide bandgap.

6.2.2 SAM Optimization

Thickness studies of DDT and ODT were conducted for selective deposition of aluminum oxide, but not hafnium oxide. HfO$_2$ was shown to exhibit comparable selectivity with 5 mM ODT blocking material, and may benefit from reducing SAM concentration in the lower pitch regions. Clearly, some optimization of both SAM material and ALD needs to occur for selectivity past the 100 nm pitch - a requirement if selective deposition using SAMs is to replace photolithography in printing small feature sizes.

Similar pattern dimensions are successfully utilized for AS-ALD by Liu and Bent, who investigate the metal-oxide blocking capabilities of octadecylphosphonic acid (ODPA) [133]. While the scope of this work involved dielectric-on-dielectric selective deposition, in principle dielectric-on-metal or metal-on-metal deposition can be achieved using SAMs such as ODPA; the latter type of deposition could be useful for vias connecting metallization lines.
LITERATURE CITED


