Investigation of the threshold voltage shift effect of LA2O3 on tin/HFO2/LA2O3/SIO2/SI stacks

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INVESTIGATION OF THE THRESHOLD VOLTAGE SHIFT
EFFECT OF LA$_2$O$_3$ ON TIN/HFO$_2$/LA$_2$O$_3$/SIO$_2$/SI STACKS

By

Ming Di

A Dissertation
Submitted to the University at Albany, State University of New York
in Partial Fulfillment of
the Requirements of the Degree of
Doctor of Philosophy

College of Nanoscale Science and Engineering

2010
INVESTIGATION OF THE THRESHOLD VOLTAGE SHIFT
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Abstract

The semiconductor industry continues to scale (shrink) transistor dimensions to both increase the number of transistors per integrated circuit and their speed. One important aspect of scaling is the need to decrease the equivalent oxide thickness of the transistor gate dielectric while minimizing leakage current. Traditional thin layer SiO$_2$ or SiO$_x$N$_y$ films have been replaced by higher dielectric constant film stacks. Here we study one example, the HfO$_2$/La$_2$O$_3$/SiO$_2$ stack. This dissertation describes an investigation of the use of La$_2$O$_3$ to reduce the threshold voltage of TiN/HfO$_2$/SiO$_2$/Si stacks (high-$\kappa$/metal gate stacks). A significant aspect of this study is the determination of band alignment for a series of high-$\kappa$/metal gate stacks that explore the effect of placement and thickness of the Lanthanum oxide layer. In order to achieve this goal, a number of film stack properties were determined including film thicknesses, band gap of the high-$\kappa$ oxides, the flat band voltages, Si band bending, and the valence band and conduction band offsets.

The first part of this work was measurement of individual layer thickness in the multi-layer film stacks using spectroscopic ellipsometry (SE) and other complementary techniques. In order to more completely understand the SE measurements, complementary techniques were used. These techniques include angle resolved X-ray photoelectron spectroscopy (ARXPS), X-ray reflectivity (XRR), transmission electron microscopy (TEM), and Rutherford backscattering spectroscopy (RBS). In this dissertation, we show that SE can simultaneously measure HfO$_2$ and SiO$_2$ thicknesses in HfO$_2$/SiO$_2$/Si stacks. We discuss the difficulties in simultaneous measurement of all films in the La oxide Hf oxide film stack.
The second part of this dissertation is the measurement of the band gap of high-\(\kappa\) films. The band gap of a high-\(\kappa\) film is an important parameter because it affects the conduction band offset (CBO) between high-\(\kappa\) and Si substrate. The CBO affects the gate leakage current of the transistor. The band gap of high-\(\kappa\) films was determined from the complex refractive index using several different methods. Comparisons of plots of the extinction coefficient (\(k\)), absorption coefficient (\(\alpha\)), and optical models for imaginary part of the dielectric function (\(\varepsilon_2\)) show that each method gives slightly different values for the band gap. The Cody Lorentz model for the dielectric function provides a useful model for the defect induced sub-band gap absorption. We show the impact of the sub-band gap absorption on band gap extrapolation. Because the existence of sub band gap states is well documented in the literature, we use the Cody Lorentz model to determine the band gap.

The next step was to determine band alignment of the valence and conduction bands the layers in the film stack. X-Ray photoelectron spectroscopy (XPS) measurements were used to determine the valence band offset (VBO) and silicon band bending. The conduction band levels were determined from the valence band energy levels and the band gap. The CBO we measured (1.77eV) is well above the specified minimum CBO for Hf oxide (1.0eV). We developed a band alignment model to account for the trends that we observed. Our data is consistent with the presence of a dipole at the high-\(\kappa\)/SiO\(_2\) interface. According to this model, the change in VBO is a direct measure of the change in the interface dipole moment.

Because the combination of capacitance – voltage (C-V) and XPS to measure the flat band voltage and Si band bending, respectively, has rarely been used, relationship
between these two quantities has not been discussed in the literature. The agreement between an empirical, theoretical relationship between flat band voltage vs. Si band and our data suggests that XPS can be a useful tool for examining $V_T$ shift layers in high-κ gate stacks.

We also investigated the effect of the SiO$_2$ thickness and growth method on the flat band voltage of TiN/HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stacks. We observed no change in flat band voltage for stacks with nominally 12, 20, and 30 Å thermally grown SiO$_2$ layers. The stack with the nominally 8 Å chemically grown SiO$_2$ layer, however, showed a flat band voltage that was significantly more negative. This difference in flat band voltage may be due to an increase in sub-oxide concentration in the 8 Å chemically grown SiO$_2$ layer which could affect the chemistry at the La$_2$O$_3$/SiO$_2$ interface and thus the interface dipole.
Acknowledgements

There are many people that I would like to thank that helped me to complete this dissertation. The first person that I would like to thank is my advisor, Professor Alain C. Diebold. Professor Diebold has been an excellent advisor during my graduate career. He provided me with challenging projects and guided me every step of the way. I have also learned a lot from Prof. Diebold besides academic information. He taught me how to do research, how to be professional, and to share knowledge with others.

I would also like to thank my committee members, Professor Fatemeh Shahedipour-Sandvik, Professor Kathleen Dunn, Professor Robert Geer, Dr. Gert Leusink, and Professor Alain Diebold. They have offered very valuable input towards the major direction of my research.

I also would like to thank my group members, especially Dr. Eric Bersch. He trained me to operate and understand X-ray photoelectron spectroscopy. He offered constructive suggestions to this project. Besides the work, he also influenced me on how to be a better person on a personal level. I am grateful to have had him as a mentor during my Ph.D career.

I would also like to thank our industry collaborators, Dr. Steven Consiglio, Dr. Robert Clark, and Dr. Gert Leusink from Tokyo Electron Limited (TEL). It was a very pleasant experience working with the folks from TEL. They are intelligent, professional, and insightful.

I would also like to thank Barry Karlin, Dr. Dan Fischer, and Dr. Joe Woicik from Brookhaven National Lab. They have assisted us to use the synchrotron XPS system at national synchrotron light source (NSLS). I would also like to thank Dr. Richard Moore
from the College of Nanoscale Science and Engineering (CNSE) for all his assistance on
the XPS system on site.

I would also like to thank the folks from KLA-Tencor, especially Torsten Kaack
for the support on the Aleris\textsuperscript{TM} tool. I would also like to thank the folks from J. A.
Woollam for their support on the Woollam VUV VASE\textsuperscript{TM} system.

I would like to thank my friends during my study at CNSE. They made my Ph.D
study more enjoyable. Last, I would like to thank my family, especially my parents and
my wife. Although my parents are half a globe away, the distance does not reduce the
support I receive from them at all. My wife Sheri went through all of my ups and downs
with me. Her support and encouragement was essential to my dissertation.
List of Acronyms

MOSFET: metal oxide semiconductor field effect transistor
CMOS: complementary metal oxide semiconductor
FET: field effect transistor
IC: integrated circuit
SE: spectroscopic ellipsometry
XPS: X-ray photoelectron spectroscopy
ARXPS: angle-resolved X-ray photoelectron spectroscopy
XRR: X-ray reflectivity
C-V: capacitance -voltage
TEM: transmission electron microscopy
STEM: scanning transmission electron microscopy
RBS: Rutherford backscattering spectroscopy
VBO: valence band offset
CBO: conduction band offset
UPS: ultraviolet photoelectron spectroscopy
IPS: inverse photoemission spectroscopy
FB: flat band
BEMA: Bruggeman effective media approximation
EELS: electron energy loss spectroscopy
PC: photo conductivity
LEIS: low energy ion scattering spectroscopy
EOT: effective oxide thickness
La$_2$O$_3$: lanthanum oxide
HfO$_2$: hafnium oxide
SiO$_2$: silicon di-oxide
TiN: titanium nitride
SiO$_x$N$_y$: Silicon oxynitride
HfSi$_x$O$_y$: hafnium silicate
HfSi$_x$O$_y$N$_z$: hafnium silicon oxynitride
List of Symbols

$E_c$: conduction band edge

$E_v$: valence band edge

$E_f$: Fermi level

$E_{Vac}$: vacuum level

$E_g$: band gap

$E_i$: intrinsic level

$n_i$: intrinsic density of electrons

$p_0$: hole density in Si

$n_0$: electron density in Si

$c$: speed of light

$h$: Plank constant

$n$: refractive index

$k$: extinction coefficient

$N$: complex refractive index ($N=n+ik$)

$\alpha$: absorption coefficient

$\varepsilon$: dielectric function ($\varepsilon=\varepsilon_1+\varepsilon_2$)

$\varepsilon_1$: real part of the dielectric function

$\varepsilon_2$: imaginary part of the dielectric function

$C$: capacitance

$t$: thickness

$K$: relative permittivity

$A$: area of a capacitor
$\beta$: phase factor
Contents

List of Acronyms ......................................................................................................... viii
List of Symbols ............................................................................................................... x
List of Figures ............................................................................................................... xv
List of Tables ............................................................................................................... xxi

Chapter 1 : Background.................................................................1
  1.1 High-κ MOSFET introduction .............................................................. 1
  1.2 Band diagram of a MOSFET gate structure .............................................. 6
  1.3 High-κ stack thickness characterization ................................................... 8
  1.4 Band gap, VBO, and CBO characterization of HfO$_2$/SiO$_2$/Si stacks ........... 9
  1.5 Effect of La$_2$O$_3$ on the threshold voltage of the high-κ/metal gate stack ...... 11
      1.5.1 MOSFET function ................................................................................. 11
      1.5.2 Capacitance-voltage (C-V) measurement .............................................. 15
  1.6 Dissertation outline ...................................................................................... 18
  1.7 References ..................................................................................................... 19

Chapter 2 : Experimental techniques .............................................22
  2.1 Spectroscopic ellipsometry ......................................................................... 22
      2.1.1 Introduction of spectroscopic ellipsometry ............................................. 22
      2.1.2 Reflection for p light and s light .............................................................. 23
      2.1.3 Spectroscopic ellipsometry measurement of thin film thickness .......... 26
  2.2 X-ray reflectivity ........................................................................................... 28
  2.3 X-ray photoelectron spectroscopy (XPS) and angle resolved XPS (ARXPS) ... 32
      2.3.1 Introduction of XPS ............................................................................... 32
      2.3.2 ARXPS and elemental depth profile ...................................................... 40
      2.3.3 Valence band edge maximum (VBM) measurement by XPS .................. 44
  2.4 Rutherford backscattering spectroscopy (RBS) .............................................. 46
  2.5 Atomic layer deposition (ALD) ..................................................................... 47
  2.6 References ..................................................................................................... 49

Chapter 3 : Film thickness characterization of HfO$_2$ stacks ...............54
  3.1 Background .................................................................................................... 54
  3.2 Experimental methods and current challenge for SE .................................. 55
  3.3 Experimental design and results ................................................................. 57
      3.3.1 SE characterization of HfO$_2$/SiO$_2$/Si stacks ....................................... 57
      3.3.2 XRR characterization of HfO$_2$/SiO$_2$/Si stacks .................................... 61
      3.3.3 ARXPS characterization of HfO$_2$/SiO$_2$/Si stacks ................................. 62
  3.4 Comparison between SE and Scanning transmission electron microscopy (STEM) characterization of HfO$_2$ stack ......................................................... 64
  3.5 Discussion ..................................................................................................... 66
      3.4.1 VUV is the key to measure HfO$_2$ stacks ................................................ 66
      3.4.2 Optical modeling of amorphous HfO$_2$ films .......................................... 66
  3.6 References ..................................................................................................... 73

Chapter 4 : Spectroscopic ellipsometry thickness characterization of high-κ gate stacks with La$_2$O$_3$ $V_t$ shift layers .................................76
Chapter 5: Band gap measurement of HfO₂ stack by spectroscopic ellipsometry

5.1 Introduction ........................................................................................................... 102
5.2 SE band gap measurement of HfO₂ films .......................................................... 104
5.2.1 Band gap extrapolation from experimental data ............................................ 106
5.2.2 Band gap measurement from Tauc Lorentz model and Cody Lorentz model .... 112
5.2.3 Conclusion of SE band gap measurement of HfO₂ films ................................. 117
5.3 Dependence of band gap on the silicate percentage and nitrogen content .......... 118
5.4 VBO and CBO measurement of HfO₂ stack ....................................................... 120
5.5 Summary ............................................................................................................. 125
5.6 References .......................................................................................................... 126

Chapter 6: The effect of La₂O₃ on the flat band voltage of TiN/HfO₂/SiO₂/Si stacks and band alignment of TiN/HfO₂/La₂O₃/SiO₂/Si stacks

6.1 Introduction: V_T shift layers ............................................................................. 129
6.2 Outline of the research ....................................................................................... 137
6.3 Experimental details ......................................................................................... 139
6.3.1 Experimental design .................................................................................... 139
6.3.2 Fabrication of samples ................................................................................. 140
6.3.3 Characterization of samples ......................................................................... 141
6.4 Experimental results .......................................................................................... 142
6.4.1 Spectroscopic ellipsometry (SE) characterization ......................................... 142
6.4.2 Increasing the amount of bottom La₂O₃ ......................................................... 143
6.4.2.1 Flat band measurement of using C-V characterization ............................... 144
6.4.2.2 Si band bending using XPS characterization ............................................ 145
6.4.3 Varying the amount of bottom HfO₂ ............................................................. 150
6.4.3.1 C-V characterization of bottom HfO₂ samples ....................................... 151
6.4.3.2 XPS characterization of bottom HfO₂ samples ....................................... 151
6.4.4 Valence band offset (VBO) characterization ................................................ 154
6.5 Results and discussion ...................................................................................... 158
6.5.1 Band alignment of high-k stacks and cause of different band bending .......... 159
6.5.2 Relationship between flat band voltage and Si band bending ....................... 163
6.5.3 Optimum La₂O₃ V_T shift layer ..................................................................... 170
6.6 Charge density change for corresponding interface dipole moment change .... 171
6.7 Summary ........................................................................................................... 177
## List of Figures

Figure 1-1: Schematic diagram of a metal oxide semiconductor field effect transistor (MOSFET) .......................................................................................................................... 2
Figure 1-2: Band diagram of a TiN/HfO$_2$/SiO$_2$/Si stack before TiN deposition (thk: thickness) ............................................................................................................................ 7
Figure 1-3: Band diagram of a TiN/HfO$_2$/SiO$_2$/Si stack after TiN deposition before applying any gate voltage ................................................................. 7
Figure 1-4: Gate leakage current mechanisms (a) Fowler Nordheim, (b) direct, (c) Poole Frenkel, (d) Schottky emission ......................................................................................... 10
Figure 1-5: Accumulation, depletion, and inversion conditions of MOS structures \(^{30}\) (Image is from: Y. Taur and T. H. Ning, "Fundamentals of Modern VLSI Devices," (1998))............................................................................................................................... 14
Figure 1-6: charge in Si channel as a function of band bending \(^{31}\) (Image is from: K. Kano, "Semiconductor Devices," (1998)) .......................................................................................................................... 15
Figure 1-7: A typical C-V curve for an ideal NMOS device \(^{32}\) (Image is from: A. C. Diebold, "Class note of Semiconductor Metrology at College of Nanoscale Science & Engineering.")................................................................................................................... 17
Figure 2-1: Reflection of p and s light .............................................................................. 24
Figure 2-2: Reflection for an ambient/film/substrate system \(^{35}\) (Image is from: H. Fujiwara, *Spectroscopic ellipsometry principles and applications*. (WILEY, 2003)) .... 26
Figure 2-3: Measurement flow of SE........................................................................... 28
Figure 2-4: XRR measurement set up using specular beam ........................................ 29
Figure 2-5: XRR for an air/film/substrate measurement .............................................. 30
Figure 2-6: XRR spectrum from 4nm HfO$_2$/3nmSiO$_2$/Si stack ........................................ 31
Figure 2-7: Photoelectron generated by incoming X-ray ........................................ 33
Figure 2-8: XPS spectra from a SiO$_2$/Si stack (data taken from Thermo-fisher theta probe at CNSE) .......................................................................................................................... 34
Figure 2-9: Si 2p XPS spectra from a 12ÅSiO$_2$/Si sample (measured at X-24A, NSLS) 35
Figure 2-10: Fitting of the experimental spectra in figure 2-9 (measured at X-24A, NSLS) .................................................................................................................. 35
Figure 2-11: Si 2s XPS spectra from a 12ÅSiO$_2$/Si sample (measured at X-24A, NSLS) 36
Figure 2-12: Fitting of Si 2s XPS experimental spectra from a 12ÅSiO$_2$/Si sample (measured at X-24A, NSLS) .................................................................................................................. 36
Figure 2-13: Si valence band XPS spectra from a hydrogen terminated Si (measured at X-24A, NSLS) .................................................................................................................. 37
Figure 2-14: XPS spectra of Au from 0 to 1 keV binding energy (measured at CNSE). 38
Figure 2-15: Valence band of Au (measured at CNSE) .............................................. 38
Figure 2-16: Theoretical Fermi-Dirac distribution (E$_f$=0eV) ........................................ 39
Figure 2-17: Determination of Au Fermi level from figure 2-15 .................................. 40
Figure 2-18: XPS spectrum of Au 4f peaks (measured at CNSE) .................................. 40
Figure 2-19: Take off angle of Photoelectron ............................................................. 41
Figure 2-20: Sensitivity of surface vs. bulk with respect to emission angle ............ 42
Figure 2-21: SiO$_2$ film (A) on Si substrate (B) ......................................................... 42
Figure 2-22: ARXPS signal as a function of emission angle \( \text{55} \) (Image is from: J. Wolstenholme, "Application Note," ThermoFisher SCIENTIFIC) ........................................ 43
Figure 2-23: ARXPS depth profile of a HfO\(_2\) stack ....................................................... 44
Figure 2-24: Binding energy difference (\( \Delta \)) between Si 2p and Si VBM ......................... 45
Figure 2-25: Ion repulsion in a RBS measurement ............................................................. 46
Figure 2-26: Areal density and film thickness measurement from RBS spectrum .......... 47
Figure 2-27: HfO\(_2\) ALD flow by TEL \( ^{14} \) (Image is from: R. Clark and e. al, Fall 2007 ECS Meeting, Washing D. C. (2007).) ................................................................. 49
Figure 2-28: Counter flow ALD set up by TEL \( ^{13} \) (Image is from: R. D. Clark, S. Consiglio, C. S. Wajda, G. J. Leusink, T. Sugawara, H. Nakabayashi, H. Jagannathan, L. F. Edge, P. Jamison, V. K. Paruchuri, R. Iijima, M. Takayanagi, B. P. Linder, J. Brukey, M. Copel, and V. Narayanan, "High-K Gate Dielectric Structures by Atomic Layer Deposition for the 32nm and Beyond Nodes," ECS Transactions 16 (4), 291-305 (2008).) ................................................................. 49

Figure 3-1: Complex refractive index of single crystal silicon \( \text{71} \) .................................... 56
Figure 3-2: Refractive index of Si\(_2\)O\(_3\) between 240 and 800 nm wavelength .................. 57
Figure 3-3: Refractive index of HfO\(_2\) between 240 and 800 nm wavelength .................. 57
Figure 3-4: Thickness of HfO\(_2\) & Si\(_2\)O\(_3\) across a diameter of a wafer .......................... 60
Figure 3-5: Uniqueness for a HfO\(_2\)/Si\(_2\)O\(_3\)/Si stack .................................................. 61
Figure 3-6: TEM characterization of 60 Å unannealed HfO\(_2\) stacks ............................... 64
Figure 3-7: Si\(_2\)O\(_3\) thickness from TEM cross section measurement ............................... 65
Figure 3-8: HfO\(_2\) thickness from TEM cross section measurement ............................... 65
Figure 3-9: Complex refractive index of HfO\(_2\) and Si\(_2\)O\(_3\) from 150nm to 1000nm ....... 66
Figure 3-10: Typical optical dispersion of a Tauc Lorentz model for HfO\(_2\) ......................... 68
Figure 3-11: Parameter of a Cody Lorentz model ......................................................... 70
Figure 3-12: Effect of \( E_t \) to the extinction coefficient \( k \) of HfO\(_2\) ................................. 71
Figure 3-13: Effect of \( E_u \) on extinction coefficient \( k \) .................................................. 72
Figure 3-14: \( E_p \) effect on band gap ............................................................................ 73

Figure 4-1: The Si 2s spectra from various samples show that the Si\(_2\)O\(_3\) layer is not strongly altered by the deposition of the HfO\(_2\) and La\(_2\)O\(_3\) layers ........................................ 80
Figure 4-2: Si 2p peaks of Si substrate and Si\(_2\)O\(_3\) as a function of emission angle .......... 82
Figure 4-3: ARXPS determination of the Si\(_2\)O\(_3\) thickness in Si\(_2\)O\(_3\)/Si ...................... 82
Figure 4-4: Index of refraction (\( n \)) and extinction coefficient (\( k \)) as a function of photon energy for HfO\(_2\) and La\(_2\)O\(_3\) ............................................................. 83
Figure 4-5: Extinction coefficient of La\(_2\)O\(_3\) and HfO\(_2\) from point-by-point fit ................. 84
Figure 4-6: XRR experimental and model spectra from HfO\(_2\)/Si\(_2\)O\(_3\)/Si ....................... 85
Figure 4-7: XRR of Si\(_2\)O\(_3\)/Si and La\(_2\)O\(_3\)/Si\(_2\)O\(_3\)/Si stacks (cyc: ALD cycle number) ........ 86
Figure 4-8: RBS spectra of 15 and 40 cycle La\(_2\)O\(_3\)/Si\(_2\)O\(_3\)/Si ........................................ 87
Figure 4-9: SE data (\( \psi \)) for Si\(_2\)O\(_3\)/Si, La\(_2\)O\(_3\)/Si\(_2\)O\(_3\)/Si, and HfO\(_2\)/La\(_2\)O\(_3\)/Si\(_2\)O\(_3\)/Si stacks .......... 88
Figure 4-10: SE data (\( \Delta \)) for Si\(_2\)O\(_3\)/Si, La\(_2\)O\(_3\)/Si\(_2\)O\(_3\)/Si, and HfO\(_2\)/La\(_2\)O\(_3\)/Si\(_2\)O\(_3\)/Si stacks ... 89
Figure 4-11: RBS spectra from HfO\(_2\)/Si\(_2\)O\(_3\)/Si, La\(_2\)O\(_3\)/Si\(_2\)O\(_3\)/Si, HfO\(_2\)/La\(_2\)O\(_3\)/Si\(_2\)O\(_3\)/Si and La\(_2\)O\(_3\)/HfO\(_2\)/Si\(_2\)O\(_3\)/Si stacks ............................................................. 91
Figure 4-12: SE data (\( \psi \)) for Si\(_2\)O\(_3\)/Si, HfO\(_2\)/Si\(_2\)O\(_3\)/Si, La\(_2\)O\(_3\)/HfO\(_2\)/Si\(_2\)O\(_3\)/Si ................. 92
Figure 4-13: SE data (\( \Delta \)) for Si\(_2\)O\(_3\)/Si, HfO\(_2\)/Si\(_2\)O\(_3\)/Si, La\(_2\)O\(_3\)/HfO\(_2\)/Si\(_2\)O\(_3\)/Si ........................................ 92
Figure 4-14: SE data (Cos(Del)) for Si\(_2\)O\(_3\)/Si and 5, 10 and 15 cycle La\(_2\)O\(_3\)/Si\(_2\)O\(_3\)/Si ...... 95
Figure 4-15: SE data (Cos (Del) difference) for 5, 10 and 15 cycle La$_2$O$_3$/SiO$_2$/Si compared to SiO$_2$/Si ................................................................. 95
Figure 4-16: RBS data for 40 cycle HfO$_2$/x cycle La$_2$O$_3$/SiO$_2$/Si stacks (x=0, 5, 10, 15) 96
Figure 4-17: XRR spectra of a 30 Å TiN/12 Å SiO$_2$/Si stack ........................................ 97
Figure 4-18: SE spectra $\Psi$ of a 30 Å TiN/12 Å SiO$_2$/Si stack .................................... 98
Figure 4-19: SE spectra $\Delta$ of a 30 Å TiN/12 Å SiO$_2$/Si stack .................................... 98
Figure 4-20: Complex refractive index of TiN ................................................................. 99
Figure 5-1: Band diagram of a HfO$_2$/SiO$_2$/Si stack ...................................................... 102
Figure 5-2: Transition metal band gap 91 (Image is from: S.-G. Lim, S. Kriventsov, T. N. Jackson, J. H. Haeni, D. G. Schlom, A. M. Balbashov, R. Uecker, P. Reiche, J. L. Freeouf, and G. Lucovsky, "Dielectric functions and optical bandgaps of high-$\kappa$ dielectrics for metal-oxide-semiconductor field-effect transistors by far ultraviolet spectroscopic ellipsometry," JOURNAL OF APPLIED PHYSICS 91 (7), 4500-4505 (2002).)......................................................... 103
Figure 5-3: Extinction coefficient of unannealed HfO$_2$ .................................................... 106
Figure 5-4: Extinction coefficient of annealed HfO$_2$ ...................................................... 106
Figure 5-5: Band gap extrapolation from extinction coefficient $k(E)$ ($E_g$=5.94eV) ....... 109
Figure 5-6: Band gap extrapolation from imaginary part of dielectric function ($E_g$=5.91eV) ................................................................. 109
Figure 5-7: Band gap extrapolation from absorption coefficient ($E_g$=6.04eV) ............ 110
Figure 5-8: Band gap extrapolation from Tauc method using the whole band edge absorption for the extrapolation ($E_g$=5.48eV) ........................................ 110
Figure 5-9: Band gap extrapolation from Cody method ($E_g$=5.36eV) ......................... 111
Figure 5-10: Normalized values from each method ......................................................... 112
Figure 5-11: Comparison between Cody Lorentz model, Tauc Lorentz model and point-by-point fitting ......................................................... 114
Figure 5-12: Extinction coefficient of unannealed HfO$_2$ films ...................................... 116
Figure 5-13: Extinction coefficient of high-$\kappa$ films with different silicate concentration ................................................................. 118
Figure 5-14: Extinction coefficient of Hf$_{0.7}$Si$_{0.3}$O$_2$ with no, low, and high N dose ...... 119
Figure 5-15: Extinction coefficient of Hf$_x$Si$_{1-x}$O$_2$ with high N dose .......................... 119
Figure 5-16: VBO measurement from XPS 29 (Image is from: E. Bersch, M. Di, S. Consiglio, R. D. Clark, G. J. Leusink, and A. C. Diebold, "Complete band offset characterization of the HfO$_2$/SiO$_2$/Si stack using charge corrected x-ray photoelectron spectroscopy," J. Appl. Phys. 107, 043702 (2010).)......................................................... 121
Figure 5-17: Si 2p and Si valence band maximum of a hydrogen terminated Si sample (measured at CNSE) 29 (Image is from: E. Bersch, M. Di, S. Consiglio, R. D. Clark, G. J. Leusink, and A. C. Diebold, "Complete band offset characterization of the HfO$_2$/SiO$_2$/Si stack using charge corrected x-ray photoelectron spectroscopy," Jour. Appl. Phys. 107, 043702 (2010).)......................................................... 122
Figure 5-18: Si 2p from SiO$_2$ and the VBM of SiO$_2$ from a 12 Å SiO$_2$/Si sample 29 (Image is from: E. Bersch, M. Di, S. Consiglio, R. D. Clark, G. J. Leusink, and A. C. Diebold, "Complete band offset characterization of the HfO$_2$/SiO$_2$/Si stack using charge corrected x-ray photoelectron spectroscopy," Jour. Appl. Phys. 107, 043702 (2010).)...................... 123
Figure 5-19: Valence band maximum of HfO$_2$ from a 20Å HfO$_2$/SiO$_2$/Si stack 29 (Image is from: E. Bersch, M. Di, S. Consiglio, R. D. Clark, G. J. Leusink, and A. C. Diebold,
Figure 5-20: Band gap of 20 Å unannealed HfO$_2$ film (Image is from: E. Bersch, M. Di, S. Consiglio, R. D. Clark, G. J. Leusink, and A. C. Diebold, "Complete band offset characterization of the HfO$_2$/SiO$_2$/Si stack using charge corrected x-ray photoelectron spectroscopy," Jour. Appl. Phys. 107, 043702 (2010).) ................................................. 124
Figure 5-21: Complete band alignment of a 20Å HfO$_2$/SiO$_2$/Si stack using combination of SE and XPS ..................................................................................................................... 125
Figure 6-1: Fabrication process for MgO and Al$_2$O$_3$ capping layers (Image is from: H. Jagannathan, V. Narayanan, and S. Brown, "Engineering High Dielectric Constant Materials for Band-Edge CMOS Applications," ECS Trans. 16 (5), 19-26 (2008).) .................................................. 130
Figure 6-2: C-V curve shift due to MgO & Al$_2$O$_3$ (Image is from: H. Jagannathan, V. Narayanan, and S. Brown, "Engineering High Dielectric Constant Materials for Band-Edge CMOS Applications," ECS Trans. 16 (5), 19-26 (2008).) .................................................. 131
Figure 6-3: Comparison between C-V curves from stacks with Al$_2$O$_3$ capping layers (Image is from: H. Jagannathan, V. Narayanan, and S. Brown, "Engineering High Dielectric Constant Materials for Band-Edge CMOS Applications," ECS Trans. 16 (5), 19-26 (2008).) ................................................................................................................. 132
Figure 6-4: Comparison between C-V curves from stacks with MgO capping (Image is from: H. Jagannathan, V. Narayanan, and S. Brown, "Engineering High Dielectric Constant Materials for Band-Edge CMOS Applications," ECS Trans. 16 (5), 19-26 (2008).) ............................................................................................................................ 132
Figure 6-5: Flat band voltage ($V_{FB}$) vs. (a) top and (b) bottom high-$\kappa$ thickness (Image is from: K. Iwamoto, Y. Kamimuta, A. Ogawa, Y. Watanabe, S. Migita, W. Mizubayashi, Y. Morita, M. Takahashi, H. Ota, T. Nabatame, and A. Toriumi, "Experimental evidence for the flatband voltage shift of high-$\kappa$ metal-oxide-semiconductor devices due to the dipole formation at the high-$\kappa$/SiO$_2$ interface," Applied Physics Letters 92, 132907 (2008).) ............................................................................................................................ 134
Figure 6-6: Flat band voltage vs. HfO$_2$ and Al$_2$O$_3$ thicknesses (Image is from: K. Iwamoto, Y. Kamimuta, A. Ogawa, Y. Watanabe, S. Migita, W. Mizubayashi, Y. Morita, M. Takahashi, H. Ota, T. Nabatame, and A. Toriumi, "Experimental evidence for the flatband voltage shift of high-$\kappa$ metal-oxide-semiconductor devices due to the dipole formation at the high-$\kappa$/SiO$_2$ interface," Applied Physics Letters 92, 132907 (2008).) ............................................................................................................................ 135
Figure 6-8: XPS measurements of high-$\kappa$ metal stacks with La$_2$O$_3$ (Image is from: K. Kakushima, K. Okamoto, M. Adachi, K. Tachi, J. Song, S. Sato, T. Kawanago, P. Ahmet, K. Tsutsui, N. Sugii, T. Hattori, and H. Iwai, "Band bending measurement of HfO$_2$/SiO$_2$/Si capacitor with ultra-thin La$_2$O$_3$ insertion by XPS," Appl. Surf. Sci. 254, 6106-6108 (2008).) ............................................................................................................................ 137
Figure 6-9: Two comparisons to study the effect of La$_2$O$_3$ on the flat band voltage change ......................................................................................................................................... 140
Figure 6-10: Geometry of XPS measurement at X-24A, NSLS, BNL ............................................................................................................................ 142
Figure 6-11: C-V curves at the center of each wafer for samples 1-4 in Table 6.1, where the amount of bottom La$_2$O$_3$ is being varied................................................................. 144
Figure 6-12: Flat band voltage vs. bottom La$_2$O$_3$ cycle number................................. 145
Figure 6-13: XPS spectra of the valence band of TiN films.............................................. 146
Figure 6-14: XPS spectra of Si 2p, SiO$_2$ 2p, and La 4d from BNL measurements ........... 148
Figure 6-15: XPS spectra of Si 2p, SiO$_2$ 2p, and La 4d from CNSE measurements...... 148
Figure 6-16: Si band bending calculation from XPS binding energy Si 2p 3/2 .......... 149
Figure 6-17: Si surface band bending and flat band voltage vs. bottom La$_2$O$_3$ ALD cycle numbers........................................................................................................... 150
Figure 6-18: C-V curves comparison between 0, 5, 10, and 40 cycles bottom HfO$_2$..... 151
Figure 6-19: XPS spectra of stacks with bottom HfO$_2$ from BNL............................... 152
Figure 6-20: XPS spectra of stacks with bottom HfO$_2$ from CNSE.............................. 153
Figure 6-21: Si band bending and flat band voltage of samples with bottom HfO$_2$..... 154
Figure 6-22: Illustration of band alignment of a high-κ/metal gate stack...................... 155
Figure 6-23: Valence band offset (VBO) between HfO$_2$ and Si..................................... 156
Figure 6-24: Hf 4f XPS spectrum from the 40 cycle HfO$_2$/ 12 Å SiO$_2$/Si stack........ 157
Figure 6-25: VBO between HfO$_2$ and Si vs. bottom La$_2$O$_3$ ALD cycle number........ 158
Figure 6-26: VBO between HfO$_2$ and Si vs. bottom HfO$_2$ ALD cycle number........ 158
Figure 6-27: Flat band voltage vs. Si band bending for the samples in Table 6.1 (Sample number is labled)........................................................................................................... 159
Figure 6-28: VBO for a HfO$_2$/SiO$_2$/Si stack with assumed continuous vacuum level at high-κ/SiO$_2$ interface ................................................................. 161
Figure 6-29: VBO for a HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stack with assumed non-continuous vacuum level at high-κ/SiO$_2$ interface................................................................. 161
Figure 6-30: Band alignment before applying any gate voltage of a TiN/HfO$_2$/SiO$_2$/Si stack ................................................................. 162
Figure 6-31: Band alignment before applying any gate voltage of a TiN/HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stack ................................................................. 163
Figure 6-32: Flat band voltage definition ................................................................. 164
Figure 6-33: Electric field as a function of Si band bending ........................................ 166
Figure 6-34: Voltage drop across 1nm SiO$_2$ and 3 nm high-κ as a function of Si surface band bending................................................................. 167
Figure 6-35: Experimental data compared to the theoretical model curve................. 168
Figure 6-36: Dependence of flat band voltage on SiO$_2$ thickness ......................... 169
Figure 6-37: Dependence of flat band voltage on HfO$_2$ thickness ......................... 170
Figure 6-38: Direct comparison of band alignment between TiN/HfO$_2$/SiO$_2$/Si and TiN/HfO$_2$/SiO$_2$/La$_2$O$_3$/Si stacks................................................................. 172
Figure 6-39: Interface dipole between SiO$_2$ and HfO$_2$ (Image is from Y. Yamamoto, K. Kita, K. Kyuno, and A. Toriumi, "Study of La-Induced Flat Band Voltage Shift in Metal/HfLaO$_3$/SiO$_2$/Si Capacitors," Japanese Journal of Applied Physics 46 (11), 7251-7255 (2007))................................................................. 173
Figure 6-40: Interface dipole model between SiO$_2$ and HfO$_2$ ................................ 174
Figure 6-41: Oxygen areal density by Kita et al. (Image is from K. Kita and A. Toriumi, "Origin of electric dipoles formed at high-κ/SiO$_2$ interface," Applied Physics Letters 94, 132902 (2009))................................................................. 174
Figure 6-42: correlation between $V_{FB}$ shift and normalized oxygen areal density. (Image is from K. Kita and A. Toriumi, "Origin of electric dipoles formed at high-k/SiO$_2$ interface," Applied Physics Letters 94, 132902 (2009))................................. 175

Figure 7-1: X24A XPS spectra for 30 Å TiN/40 cycle HfO$_2$/12 Å SiO$_2$/Si and 30 Å TiN/40 cycle HfO$_2$/8 Å SiO$_2$/Si................................................................. 184

Figure 7-2: CNSE XPS spectra for 30 Å TiN/40 cycle HfO$_2$/12 Å SiO$_2$/Si and 30 Å TiN/40 cycle HfO$_2$/8 Å SiO$_2$/Si ................................................................. 185

Figure 7-3: C-V curve for 30 Å TiN/40 cycle HfO$_2$/12 Å thermal SiO$_2$/Si and 30 Å TiN/40 cycle HfO$_2$/8 Å chemical SiO$_2$/Si stacks ........................................ 186

Figure 7-4: C-V curves from Ir/HfO$_2$/SiO$_2$/Si stack with various SiO$_2$ thicknesses. (Image is from Y. Abe and N. Miyata, "Dipole formation at direct-contact HfO$_2$/Si interface," Appl. Phys. Lett. 90, 172906 (2007)).................................................. 187

Figure 7-5: flat band voltage as a function of SiO$_2$ thickness. (Image is from N. Miyata, Y. Abe, and T. Yasuda, "Conductance spectroscopy study on interface electronic states of HfO$_2$/Si structures: comparison with interface dipole," Applied Physics Express 2, 035502 (2009))......................................................................................... 188

Figure 7-6: X-24A XPS spectra for 30 Å TiN/40 cycle HfO$_2$/15 cycle La$_2$O$_3$/12 Å SiO$_2$/Si and 30 Å TiN/40 cycle HfO$_2$/15 cycle La$_2$O$_3$/8 Å SiO$_2$/Si. ........................................ 190

Figure 7-7: X-24A XPS spectra for 30 Å TiN/40 cycle HfO$_2$/15 cycle La$_2$O$_3$/12 Å SiO$_2$/Si, 30 Å TiN/40 cycle HfO$_2$/5 cycle La$_2$O$_3$/8 Å SiO$_2$/Si, 30 Å TiN/40 cycle HfO$_2$/10 cycle La$_2$O$_3$/8 Å SiO$_2$/Si, and 30 Å TiN/40 cycle HfO$_2$/15 cycle La$_2$O$_3$/8 Å SiO$_2$/Si........................................ 191

Figure 7-8: C-V curves for samples 4 and 6 in table 7-1. ........................................ 191

Figure 7-9: C-V curves comparison of center point of each wafer from 500 Å TiN/40 cycle HfO$_2$/15 cycle La$_2$O$_3$/12 Å SiO$_2$/Si, 500 Å TiN/40 cycle HfO$_2$/15 cycle La$_2$O$_3$/20 Å SiO$_2$/Si, and 500 Å TiN/40 cycle HfO$_2$/15 cycle La$_2$O$_3$/30 Å SiO$_2$/Si samples ........ 193

Figure 7-10: EELS O K edge difference between interface SiO$_2$ and bulk SiO$_2$ at an atomic smooth interface. (Image is from D. A. Muller, T. Sorsch, S. Moccio, F. H. Baumann, K. Evans-Lutterodt, and G. Timp, "The electronic structure at the atomic scale of ultrathin gate oxides," Nature 399 (24), 758-761 (1999)).............................. 195

Figure 7-11: EELS spectra of ultra thin SiO$_2$. (Image is from D. A. Muller, T. Sorsch, S. Moccio, F. H. Baumann, K. Evans-Lutterodt, and G. Timp, "The electronic structure at the atomic scale of ultrathin gate oxides," Nature 399 (24), 758-761 (1999)).............. 195

Figure 7-12: Si 2p spectra of 8 Å SiO$_2$/Si, 12 Å SiO$_2$/Si, and hydrogen terminated Si. 196
List of Tables

Table 3-1: Comparison between Woollam VUV VASE™ and KLA-Tencor Aleris™ measurements on HfO₂ stacks with combination of various HfO₂ thicknesses and SiO₂ thicknesses ................................................................. 58
Table 3-2: HfO₂ thicknesses from XRR measurements ................................................................. 63
Table 3-3: ARXPS-derived thickness measurements of 20Å HfO₂ stacks................................. 63
Table 4-1: Film stacks measured in this study. (*: 12 Å thick thermally grown, +: 8 Å thick chemically grown) .................................................................................................................... 78
Table 4-2: SE determined La₂O₃ and HfO₂ thicknesses from La₂O₃/HfO₂/SiO₂/Si ............. 89
Table 4-3: HfO₂ and La₂O₃ thicknesses from La₂O₃/HfO₂/SiO₂/Si ........................................ 93
Table 5-1: Band gap values (eV) from different methods for unannealed HfO₂ films... 117
Table 6-1: Sample list for high-κ films on chemical SiO₂..................................................... 140
Table 6-2: SE thickness characterization of table 6-1 by the Aleris™................................. 143
Table 6-3: Group electro-negativities of various materials ¹⁸ (Table is from H. Jagannathan, V. Narayanan, and S. Brown, "Engineering High Dielectric Constant Materials for Band-Edge CMOS Applications," ECS Trans. 16 (5), 19-26 (2008)) ...... 177
Table 7-1: Sample sets to investigate how SiO₂ affects flat band voltage of high-κ metal gate stacks ..................................................................................................................................................... 182
Table 7-2: Flat band voltage values measured from C-V tests ............................................. 186
Chapter 1: Background

1.1 High-κ MOSFET introduction

In the semiconductor industry, metal oxide semiconductor field effect transistor (MOSFET) devices have been shrinking for the last four decades. Reduction of the transistor dimensions is one of the key steps that have enabled the semiconductor industry to maintain Moore’s law. The scaling of transistors is expected to continue until another switch replaces the transistor.

The basic structure of a Si based MOSFET is shown in figure 1-1. There are four key components in a MOSFET: the source, the drain, the gate and the channel. The film stack consisting of the gate, the gate dielectric and the Si substrate is called the gate stack. For the majority of the history of the MOSFET, the materials that have been used are highly doped poly Si, SiO₂, and single crystal Si as the gate, gate dielectric, and substrate, respectively. This system has been very effective largely because of the low defect density at the SiO₂/Si interface. As the lateral dimensions of the MOSFET were being shrunk to fit more transistors onto an IC chip, the vertical dimension was also reduced in order to increase the gate capacitance and for other device considerations. This increases the switching speed. The equation which describes the capacitance of the gate stack is the equation for a parallel plate capacitor:

\[ C = \frac{\varepsilon_0 K A}{t}. \]

In this equation, \( C \) is the capacitance, \( \varepsilon_0 \) is the vacuum permittivity, \( K \) is the relative permittivity (dielectric constant), \( A \) is the area of a capacitor, and \( t \) is the gate dielectric
physical thickness. As this equation shows, reducing the SiO$_2$ thickness increases the capacitance.

Figure 1-1: Schematic diagram of a metal oxide semiconductor field effect transistor (MOSFET)

As the SiO$_2$ gate dielectric was made thinner, the amount of leakage current across the gate dielectric increased. The leakage current of ultra-thin SiO$_2$ is significant and causes power loss and heat dissipation issues. It has been shown that the high gate leakage current for an under 1.4 nm thick SiO$_2$ exceeds 1 A/cm$^2$. Thus, MOSFETs with SiO$_2$ gate dielectric thinner than 1 nm will not work properly due to exceptionally high leakage current. In order to continue to downscale the MOSFETs, an alternative strategy must be used.

A strategy to reduce the leakage current while maintaining the high capacitance is to use the high-$\kappa$ material. This material can be made thicker and still give a high capacitance as can be seen in the parallel capacitor capacitance equation. A thicker gate dielectric will reduce the gate leakage current. An important figure of merit for a gate dielectric film or film stack is the equivalent oxide thickness (EOT). It is defined as:

$$EOT = \left(\frac{K_{SiO_2}}{K_{high-\kappa}}\right)_{high-\kappa},$$
where \( t_{\text{high}-\kappa} \) is the physical thickness of a high-\( \kappa \) layer. The EOT indicates how thick a SiO\(_2\) film would have to be to have the same capacitance as a high-\( \kappa \) film. The first high-\( \kappa \) dielectric was silicon oxynitride. This strategy has reached its limits.\(^{4-6}\)

Currently, amorphous hafnium oxide (HfO\(_2\)), hafnium silicate (HfSi\(_x\)O\(_y\)) and nitrided hafnium silicate (HfSi\(_x\)O\(_y\)N\(_z\)) are leading candidates for replacing SiO\(_2\)-based gate dielectrics in all complementary metal oxide semiconductor (CMOS) devices. These materials were selected due to their relatively large permittivity, thermal stability, and reasonable conduction band offset with respect to Si substrate.\(^7\) For example, amorphous HfO\(_2\) has a relative permittivity value (\( K \)) of approximately 20, compared to that of SiO\(_2\) (3.9).\(^7\) However, despite the advantages of hafnium oxide based high-\( \kappa \) films, there are several issues. The first issue is that if hafnium oxide-based high-\( \kappa \) films are directly deposited on Si substrate, the interface defect density is high. A defect density higher than \( 10^{12} \) cm\(^{-2}\) has been reported.\(^7\) In order to reduce the surface defect density between high-\( \kappa \) and Si, a layer of ultra thin SiO\(_2\) interfacial layer (IL) is deposited between high-\( \kappa \) and Si.\(^8\) The defect density between SiO\(_2\) and Si is typically \( 10^{10} \) cm\(^{-2}\) or less. This SiO\(_2\) layer increases the EOT of the dielectric film stack by adding to the EOT of the high-\( \kappa \) layer as given by:

\[
EOT_{\text{total}} = T_{\text{SiO}_2} + (K_{\text{SiO}_2}/K_{\text{high}-\kappa})T_{\text{high}-\kappa}.
\]

In this equation, \( T \) is the physical thickness of each layer and \( K \) is the dielectric constant of each layer. This equation shows that an increase in the thickness of the SiO\(_2\) IL layer adds to the total EOT more significantly than an equal increase in the thickness of the high-\( \kappa \) layer.
Another issue related to HfO$_2$ is that pure hafnium oxide has low crystallization temperature. HfO$_2$ tend to crystallize during high temperature processing to form polycrystalline films that have different dielectric properties than amorphous HfO$_2$. HfO$_2$ has four different crystal structures, and the polycrystalline HfO$_2$ has more surface boundary defects, which can result in higher leakage current.\textsuperscript{9,10} In order to increase the crystallization temperature, silicon is added to hafnium oxide films to form hafnium silicate films (HfSi$_x$O$_y$). Several concentrations of silicate are being considered. One issue with the HfSi$_x$O$_y$ films is that the permittivity (dielectric constant) is less than that of HfO$_2$. To solve this issue, SiN$_z$ component is added to the HfSi$_x$O$_y$ films to form HfSi$_x$O$_y$N$_z$ films.\textsuperscript{11} Another issue with HfSi$_x$O$_y$N$_z$ films is that the band gap is reduced, so the conduction band offset between high-\(\kappa\) and silicon is significantly smaller than other films, which can lead to more leakage current through the gate. Other issues for HfO$_2$ include oxygen vacancies and crystallization. This is the reason that Zirconium (Zr) doping of HfO$_2$ is also under consideration. Addition of Zr prevents certain phases of HfO$_2$ from forming.\textsuperscript{12} In summary, the optimization of hafnium oxide-based high-\(\kappa\) films is still ongoing and will continue in the near future. In this dissertation, HfO$_2$ will be mostly used.\textsuperscript{13,14}

Another improvement to traditional poly-Si/SiO$_2$/Si gate stacks is the replacement of the poly-Si gate by metal gate materials.\textsuperscript{15} Several advantages with the metal gate include increased gate conductivity, reduced gate depletion region, and desirable work function.\textsuperscript{16,17} The effective EOT is reduced by the use of metal gates because there is no charge depletion region. In this dissertation, titanium nitride (TiN) was used as the metal gate material.
Within the past several years, a critical issue that has arisen with hafnium-oxide based high-κ MOSFETs is the need for threshold voltage ($V_T$) reduction for both PMOS and NMOS. This issue has been addressed by including an extra ultra thin (~5Å) oxide layer within the gate stack, which has the effect of lowering the $V_T$. The most effective so called $V_T$ shift layers are aluminum oxide (Al$_2$O$_3$) for PMOS, and magnesium oxide (MgO) and lanthanum oxide (La$_2$O$_3$) for NMOS. Though it has been experimentally shown through capacitance-voltage (C-V) measurements that these $V_T$ shift layers can reduce the $V_T$ of the gate stacks, the mechanism of the $V_T$ shift is not well understood. An improved understanding of the mechanism of the $V_T$ shift may help to optimize the use of $V_T$ shift layers in high-κ gate stacks. Several groups have proposed a theory of a dipole at the high-κ/SiO$_2$ interface to explain these $V_T$ shifts, but quantitative demonstration of the interface dipole model based on experimental evidence has been lacking.

We have performed a study of the effect of La$_2$O$_3$ on the TiN/HfO$_2$/SiO$_2$/Si stack. In this study, we varied both the amount and position of La$_2$O$_3$ layer within the high-κ stack. These stacks were measured using C-V to determine the flat band voltage and XPS to determine Si band bending and HfO$_2$-Si valence band offset. We observed systematic results as the amount and position of La$_2$O$_3$ were varied which we accounted for using a band alignment model with a dipole at the high-κ/SiO$_2$ interface. Furthermore, using this model, we obtained a direct measure of the change in the dipole by the addition of La$_2$O$_3$ at the high-κ/SiO$_2$ interface. In addition, the relationship between the flat band voltage and Si band bending was investigated theoretically, and this theoretical relationship was
compared with the experimental results. The theoretical and experimental results agree with each other well.

Several aspects of the $V_T$ shifting layers need to be addressed, such as the location of the layer, and the amount of materials within this layer.

### 1.2 Band diagram of a MOSFET gate structure

The energy band diagram is central to describing the working mechanism of a MOS structure. Figure 1-2 shows a band diagram of TiN/HfO$_2$/SiO$_2$/Si stack before TiN deposition onto the high-$\kappa$ stack. In figure 1-2, $E_c$ is the conduction band edge, $E_v$ is the valence band edge, $E_F$ is the Fermi level, $E_{Vac}$ is the vacuum level, $E_g$ is the band gap, $thk$ is the thickness of HfO$_2$, and $\Phi$ is the work function. CBO is the conduction band offset between HfO$_2$ and Si, which is the energy difference between the conduction band edge of HfO$_2$ and that of Si. VBO is the valence band offset between HfO$_2$ and Si; which it is the energy difference between the valence band edge of HfO$_2$ and that of Si. Figure 1-3 shows the band diagram of the TiN/HfO$_2$/SiO$_2$/Si stack after TiN deposition and before applying any voltage on the gate. Due to the work function difference between the TiN metal gate and Si substrate, Si surface band bending may occur in the Si. The amount of Si surface band bending is defined as the energy difference of valence band edge between the Si surface and Si bulk as shown in figure 1-3.
In this dissertation, several of these parameters shown in figure 1-2 will be measured in order to fully characterize the gate stack band offsets and to investigate how La$_2$O$_3$ change the threshold voltage of NMOS devices. The parameters that will be measured are
the HfO₂ and SiO₂ thickness, the HfO₂; Si VBO and CBO, the HfO₂ band gap and the Si band bending.

1.3 High-κ stack thickness characterization

The first aspect of this research is the thickness measurement of the layers of high-κ stacks. Spectroscopic ellipsometry (SE) is one of the leading techniques for measuring the thickness of ultrathin films used in high-κ/metal gate stacks. Other techniques, including X-ray reflectivity (XRR), angle resolved X-ray photoelectron spectroscopy (ARXPS), Rutherford backscattering spectroscopy (RBS), and transmission electron microscopy (TEM) were also used to verify the thicknesses of the high-κ stacks in this dissertation. The reason that multiple metrology techniques are used is that the ultrathin films are challenging for each technique, and each technique has its own advantages and disadvantages. For example, XRR is effective at measuring the high-κ film thicknesses because of their relatively high electron densities with respect to that of Si, but cannot easily differentiate between the SiO₂ film and Si substrate due to similar electron densities. ARXPS can measure the thickness of SiO₂ and HfO₂ films well, but is limited to stacks where the film total thickness is ~ 50 Å or less due to the electron attenuation. RBS can measure areal density well, but the thickness measurements need careful calibration using the film density. TEM can not easily differentiate La₂O₃ and HfO₂ due to poor contrast between the two films. A combination of these techniques may be used to fully characterize the thicknesses of the high-κ gate stack.

For the HfO₂/SiO₂/Si stack, the challenge for SE is to accurately measure the thicknesses of both HfO₂ and SiO₂ simultaneously. For this dissertation, a set of samples that systematically vary the thickness of SiO₂ and HfO₂ thickness was measured. It will
be shown that SE with VUV (vacuum ultraviolet) capability was able to differentiate the HfO$_2$ and SiO$_2$ and measure the thicknesses of the two films accurately. The HfO$_2$ thickness measured by SE was confirmed by XRR, and the SiO$_2$ thickness measured by SE was confirmed by ARXPS. Also, STEM was performed on a high-κ sample, and the result is consistent with SE measurement. Details of this study will be discussed in Chapter 3.

Measuring the thicknesses of the oxide films in HfO$_2$/La$_2$O$_3$/SiO$_2$/Si and La$_2$O$_3$/HfO$_2$/SiO$_2$/Si stacks presents an even greater challenge for SE. A particular challenge for SE with these stacks is to measure the thickness of HfO$_2$ and La$_2$O$_3$ films accurately. In order to investigate the ability of SE to measure the thicknesses of the films in these three-film-stacks, a sample set was grown consisting of one film (SiO$_2$/Si), two film (HfO$_2$/SiO$_2$/Si) and three film (HfO$_2$/La$_2$O$_3$/SiO$_2$/Si and La$_2$O$_3$/HfO$_2$/SiO$_2$/Si) stacks. Different SE measurement modeling strategies were used and compared. One modeling method, which will be referred to as layer-by-layer method, was able to measure the HfO$_2$ and La$_2$O$_3$ films. These SE results were evaluated using XRR, ARXPS, and RBS. This study is described in detail in Chapter 4.

1.4 Band gap, VBO, and CBO characterization of HfO$_2$/SiO$_2$/Si stacks

Gate leakage current results from various mechanisms, such as Fowler Nordheim tunneling, direct tunneling, Poole Frenkel tunneling, and Schottky emission mechanisms are shown in figure 1-4. $^{25-28}$ In general, thicker gate dielectrics can reduce the leakage current, as tunneling currents decrease exponentially with increasing physical thickness. Besides the thickness of gate dielectric film, another parameter that determines the gate leakage current is the conduction band offset (CBO) between high-κ film and Si substrate.
Figure 1-4: Gate leakage current mechanisms (a) Fowler Nordheim, (b) direct, (c) Poole Frenkel, (d) Schottky emission

Historically, as the band gaps of high-κ films are smaller than that of SiO₂, the measurement of the high-κ/Si CBO was important to verify that it is large enough to limit electron leakage current in MOSFETs with high-κ dielectrics. For HfO₂, hafnium silicate, and nitridated hafnium silicate the CBOs with Si have been shown to be sufficiently large. However, there is still disagreement about the value of the HfO₂-Si CBO. Reported values range between 1.0 eV and 2.2 eV. An accurate value for the HfO₂-Si CBO as well as other band offsets in the HfO₂/SiO₂/Si stack would be useful for those who are attempting to calculate the electronic structure of this stack as well as those who are seeking to model the leakage current across this stack.

The HfO₂-Si CBO can be determined by first measuring the HfO₂-Si VBO using X-ray photoelectron spectroscopy (XPS). Determining the VBO between HfO₂ and Si requires the valence band maximum (VBM) measurement of HfO₂ and Si. Details of VBM measurement will be discussed in Chapter 2. CBO can be calculated from VBO once the band gap of high-κ is determined. The band gap of high-κ films can be measured using spectroscopic ellipsometry (SE). Various methods of using SE for measurement of band gap of HfO₂ exist and they systematically differ from each other. Extra care has to be taken when comparing the band gap values between different methods. In summary,
VBO, CBO, and band gap characterization of a HfO$_2$/SiO$_2$/Si stack will be discussed in Chapter 5 and a complete band alignment picture of this stack will be presented.

### 1.5 Effect of La$_2$O$_3$ on the threshold voltage of the high-κ/metal gate stack

The main goal of this dissertation is to investigate how the La$_2$O$_3$ shifts the threshold voltage of NMOS devices. In this dissertation, as will be discussed in Chapter 6, a set of samples in which the amount as well as the position of La$_2$O$_3$ within the high-κ stack were systematically varied, in order to investigate the effect of La$_2$O$_3$ on threshold voltage. These stacks were measured using C-V measurements. In a C-V measurement, the flat band voltage can be extracted. The change in flat band voltages between two samples is equal to the change in threshold voltage between these samples, as will be discussed in section 1.5.2. However, C-V measurement was not able to fully investigate the mechanism by which the flat band voltage is shifted by the La$_2$O$_3$ capping layer. In this regard, XPS was also used to measure the Si band bending, and the HfO$_2$-Si VBO, and to provide information about the chemical states of layers in the stacks. The HfO$_2$-Si VBO was central to revealing the mechanism of how the La$_2$O$_3$ change the flat band voltage, which is by changing the dipole that exists at the high-κ /Si interface. This change in the dipole changes the band alignment between Si and HfO$_2$, thus changes the Si band bending after TiN deposition, as well as the flat band voltage. The details of this study will be discussed in Chapter 6.

### 1.5.1 MOSFET function

A MOSFET transistor has four different conditions depending on the applied gate voltage. The four conditions are referred to as flat band, accumulation, depletion, and
inversion. Figure 1-5 shows the band diagrams for the four different MOSFET conditions for stacks with metal gates, SiO$_2$ gate dielectrics and both n-type and p-type Si substrates. In these diagrams, ideal MOSFETs are shown, where the work function of the metal equals the work function of the Si. Figures 1-5 (a)-(d) show n-type Si substrates, which are used in PMOS devices, and figures 1-5 (e)-(h) show p-type Si substrates, which are used in NMOS devices. Figure 1-5 (a) and (e) show the flat band condition. In this condition, there is no Si band bending and no band bending of gate oxide, due to the fact that the work function of metal and Si is the same. The accumulation condition is shown in figures 1-5 (b) and (f). For a p-type Si sample (NMOS), a negative voltage is applied to the gate; which attracts more holes to accumulate at the SiO$_2$/Si interface.

The density of holes ($P_0$) at SiO$_2$/Si interface is given by:

$$P_0 = n_i e^{(E_i - E_F) / kT},$$

where $n_i$ is the intrinsic density of electrons, which has a value of $10^{10}$ cm$^{-3}$, and $E_i$ is the intrinsic Fermi level. The intrinsic Fermi level is always mid-gap in a semiconductor, and it bends in the same way as the conduction and the valence band edges. For the hole accumulation, there is upward band bending and $E_i$ is raised. For the electron accumulation, there is downward band bending and $E_i$ is pushed lower in an energy band diagram.

For the depletion condition, a positive voltage is applied to the gate of the p-Si stack (NMOS). This voltage repels holes the SiO$_2$/Si interface and the Si band is bending downward. In this condition, the p-Si region near the SiO$_2$/Si interface, known as the channel, is still p-type. Figure 1-5 (c) and (g) show the depletion condition for a p-type Si and n-type Si stacks, respectively.
As the positive voltage is increased on the gate for the p-type Si stack, the electrons continue to build up at the SiO$_2$/Si interface, and eventually the number of electrons surpasses the number of holes. When this happens, the Si channel becomes n-type Si. This is called channel inversion, and it is shown figure 1-5 (d). The inversion condition of n-type Si, where the channel becomes p-type Si, is shown in figure 1-5 (h).

If the positive voltage on the gate of the p-Si stack is increased further, electrons will continue to build up in the channel. A quantity $\Phi_f$ is defined as the difference between the intrinsic Fermi level ($E_i$) and the Fermi level ($E_f$). For the ideal p-Si stack, $E_i$ is above $E_f$ where there is no applied gate voltage. Applying a positive gate voltage so that $E_i$ is bent downwards by 2 $\Phi_f$ is the condition where the MOSFET goes into strong inversion. At this point, there is a high density of electrons in the channel, and the device is on. The voltage needed to turn on the device on is called the threshold voltage ($V_T$). $V_T$ for an ideal MOSFET is given by the equation:

$$V_T = V_{Ox} + 2\Phi_F,$$

where $V_{Ox}$ is the voltage drop across the oxide layer.

Figure 1-6 shows the amount of electrical charge in Si channel as a function of Si surface band bending ($\Phi_s$) for an ideal MOS structure, which is a NMOS device with p-type Si substrate with doping level of $4 \times 10^{15}$ cm$^{-3}$. In figure 1-6, the negative gate voltage is the accumulation region, and the positive gate voltage is the depletion region, weak inversion region, and strong inversion region. Flat band condition is when the gate voltage is at zero because the work function of metal is the same with Si substrate for an ideal MOS structure. It should be noted that the transistor is off at the accumulation, flat
band, depletion and weak inversion conditions, and the transistor is on at the strong inversion region.

Figure 1-5: Accumulation, depletion, and inversion conditions of MOS structures. (Image is from: Y. Taur and T. H. Ning, "Fundamentals of Modern VLSI Devices," (1998))
For a non-ideal MOSFET, the work function of gate is different from that of Si. This work function difference is commonly used to reduce the threshold voltage. The threshold voltage of a non-ideal MOSFET is:

\[ V_T = \Phi_{MS} + V_{OX} + 2\Phi_F , \]

where \( \Phi_{MS} \) is the work function difference between metal and Si substrate. Fixed charge in the bulk of the oxide layer or at the oxide/Si interface can be included in the equation for the threshold voltage in a non-ideal MOSFET, but they will not be included in this dissertation.

1.5.2 Capacitance-voltage (C-V) measurement
We note that the C-V data is considered confidential information by Tokyo Electron Limited (TEL), USA. The flat band voltage ($V_{FB}$) was extracted and provided by TEL. Here we discuss C-V to illustrate the measuring of $V_{FB}$.

As the electrical charge stored in the Si channel changes with Si band bending, the capacitance of the MOS structure also changes accordingly. The capacitance-voltage measurement of the gate stack is an important measurement used to evaluate MOSFET devices. The capacitance ($C$) of a MOS structure is defined as:

$$C = \frac{dQ}{dV},$$

where the $Q$ is the charge in a capacitor and $V$ is the voltage across the capacitor, in this case the applied gate voltage. The total capacitance of a MOS structure has two components; one is the gate oxide, and the other component is the Si capacitance. The capacitance of a MOS structure is described as:

$$\frac{1}{C} = \frac{1}{C_{OX}} + \frac{1}{C_{Si}},$$

where $C$ is the total capacitance of MOS structure, $C_{ox}$ is the oxide capacitance, and $C_{si}$ is the capacitance of Si substrate. The $C_{ox}$ per unit area equals $\varepsilon_{ox}/t_{ox}$, where $\varepsilon_{ox}$ is the dielectric constant of gate oxide, and $t_{ox}$ is the gate oxide physical thickness. Figure 1-7 shows a capacitance-voltage curve of an ideal NMOS device.

When the gate voltage is sufficiently negative, the NMOS device is in the accumulation condition, and the capacitance is at the maximum. The maximum capacitance is equal to $C_{ox}$, because a high density of holes has accumulated in the channel. When the gate voltage is small and positive, the capacitance goes down because
holes are pushed out of the channel, and the capacitance of the Si contributes to the total capacitance.

Figure 1-7 shows that as the gate voltage is made more positive (inversion region), the curve goes up steeply when a low frequency (LF) voltage is applied. This is because a high density of electrons is occupying the channel. For a large enough LF positive voltage, the capacitance will return to the maximum value. For a high frequency (HF) voltage, the capacitance will remain low, because the inversion charge cannot respond quickly enough to the applied voltage. It should be noted that a high frequency C-V measurement was performed in this research.

The threshold voltage is shown in figure 1-7. It is the voltage where the capacitance of the LF C-V curve rises sharply. As the C-V curve in figure 1-7 is for an ideal NMOS device, the flat band voltage ($V_{fb}$) is 0. For a non-ideal NMOS device, a gate material with a low work function would be chosen. This would result in a negative $\Phi_{MS}$, and would shift the whole C-V curve negatively. In this case, the $V_{fb}$ would be negative and
the $V_T$ would be shifted lower by the same amount. Since the difference between $V_{fb}$ and $V_T$ is constant. Therefore, a change in $V_T$ can be measured by measuring a change in $V_{fb}$. This is typically done in research in MOSFET devices, and is the approach used in this dissertation.

1.6 Dissertation outline

In this dissertation, chapter 2 will describe the experimental techniques used to measure thickness, band gap, and band alignment of high-$\kappa$ stacks. These techniques include spectroscopic ellipsometry (SE), X-ray reflectivity (XRR), X-ray photoelectron spectroscopy (XPS), angle resolved XPS, and Rutherford backscattering spectroscopy (RBS). Chapter 3 discusses the thickness measurement of HfO$_2$/SiO$_2$/Si stacks and demonstrates that SE can accurately measure the SiO$_2$ and HfO$_2$ films simultaneously. In Chapter 4, the thickness characterization of HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stacks will be presented. The combination of using SE, XRR, and RBS to characterize the stack will be discussed in detail. Chapter 5 describes the band gap SE measurement of HfO$_2$ films, as well as the VBO and CBO measurements of the HfO$_2$/SiO$_2$/Si stack. In Chapter 6, the study of the effect of the La$_2$O$_3$ layer on the TiN/HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stacks is presented. In this, C-V is used to measure the flat band voltage and XPS is used to measure the Si band bending and the HfO$_2$-Si valence band offset. These results will be explained using a band alignment model containing an interface dipole. Chapter 7 will describe how differences in the SiO$_2$ films can alter the effect of the La$_2$O$_3$ film in the TiN/HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stacks. Chapter 8 contains a summary of the dissertation and future research directions.
1.7 References


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Chapter 2: Experimental techniques

2.1 Spectroscopic ellipsometry

2.1.1 Introduction of spectroscopic ellipsometry

Spectroscopic ellipsometry (SE) is a non-destructive optical metrology technique which characterizes the thickness and complex index of refraction of a sample. The sample can be a thin film (on a substrate), a substrate, or even a patterned structure. For a thin film, SE can measure properties such as thickness, roughness, composition through its optical properties. For thin dielectric films, SE can measure their thickness with sub-angstrom repeatability. SE has been applied in the semiconductor industry (IC industry) for decades. In the semiconductor industry, SE has been used to characterize a variety of different materials. The materials in the semiconductor industry can be dielectric, semiconductor, or thin conducting metal films. Dielectric films include different types of photo resist films, gate dielectrics, and low-k dielectrics materials. Semiconductor materials may be polysilicon, silicon germanium, and tantalum nitride. Metal films investigated by SE include titanium nitride and tantalum nitride. SE may also be used to measure the critical dimension (CD) of lithography structures through scatterometry technique.

SE measures the change in an elliptically polarized light after the light reflects from or transmits through a sample. Polarized light has two components, p and s. The electric field of p polarized light is in the plane of incidence, and the electric field of s polarized
light is normal to the plane of incidence. Elliptically polarized light is described by two values, $\Psi$ and $\Delta$, at each wavelength. $\tan(\Psi)$ is the amplitude ratio between $p$ and $s$ components, and $\Delta$ is the phase difference between the two components. In IC industry, a typical wavelength of a SE is from 240nm to 800nm. The reflection mode is typically used for a SE measurement, because silicon is typically the substrate material and it is mostly opaque in the wavelength range of SE.

### 2.1.2 Reflection for $p$ light and $s$ light

The working mechanism of ellipsometry is based on the fact that the reflection of a $p$ light and $s$ light is different. As shown in figure 2-1, the electric field of $p$ light oscillates in the plane of incidence and the electric field of $s$ light oscillates normal to the plane of incidence. The plane of incidence is defined as the plane made of the incoming beam and reflected beam. $p$ light and $s$ light reflect differently from an optical interface due to the different boundary conditions. In figure 2-1, $E_{ip}$, $E_{rp}$, and $E_{tp}$ are the electric fields of the $p$ component of incoming beam, reflective beam, and refracted beam, respectively. $E_{is}$, $E_{rs}$, and $E_{is}$ are the electric fields of the $s$ component of the incoming beam, refractive beam, and refractive beam, respectively. $\varphi_1$ is the angle of incidence for the incoming beam. $\Phi_2$ is the refracted beam angle, and $N_1$ and $N_2$ are the refractive index of medium 1 and 2, respectively.
The reflection coefficients of both p and s light can be described as the following equations:

\[
    r_p = \frac{N_1 \cos \varphi_1 - N_2 \sqrt{1 - (N_1/N_2)^2 \sin^2 \varphi_1}}{N_1 \cos \varphi_1 + N_2 \sqrt{1 - (N_1/N_2)^2 \sin^2 \varphi_1}},
\]

\[
    r_s = \frac{N_1 \cos \varphi_1 - \sqrt{N_2^2 - N_1^2 \sin^2 \varphi_1}}{N_1 \cos \varphi_1 + \sqrt{N_2^2 - N_1^2 \sin^2 \varphi_1}}.
\]

In general, since amplitudes and phases of both p light and s light change after reflection, reflections \(r_s\) and \(r_p\) can also be written as:

\[
    r_s = \tan \psi_s \exp(i \Delta_s),
\]

\[
    r_p = \tan \psi_p \exp(i \Delta_p),
\]

where the two parameters \(\psi\) and \(\Delta\) can be measured by SE.

For an ambient-film-substrate system as shown in figure 2-2, the reflection coefficients for both s light and p light change into a different form.

\[
    r_p = \frac{r_{01,p} + r_{12,p} \exp(-i2\beta)}{1 + r_{01,p} r_{12,p} \exp(-i2\beta)}.
\]
\[ r_s = \frac{r_{01,s} + r_{12,s} \exp(-i2\beta)}{1 + r_{01,s} r_{12,s} \exp(-i2\beta)} \]

In the equations above, \( r_{01} \) is the reflection coefficient at air-film interface; \( r_{12} \) is the reflection coefficient at film-substrate interface. \( \beta \) is called phase factor. The function form of \( \beta \) is as described by the following equation, where \( \lambda \) is the wavelength of the light:

\[ \beta = \frac{4\pi d N \cos \theta}{\lambda} \]

The functional forms for \( r_{12,s}, r_{12,p}, r_{01,s} \), and \( r_{01,p} \) are illustrated in the following equations:

\[ r_{12,p} = \frac{N_2 \cos \theta_1 - N_1 \cos \theta_2}{N_2 \cos \theta_1 + N_1 \cos \theta_2} \]
\[ r_{01,p} = \frac{N_1 \cos \theta_0 - N_0 \cos \theta_1}{N_1 \cos \theta_0 + N_0 \cos \theta_1} \]
\[ r_{12,s} = \frac{N_1 \cos \theta_1 - N_2 \cos \theta_2}{N_1 \cos \theta_1 + N_2 \cos \theta_2} \]
\[ r_{01,s} = \frac{N_0 \cos \theta_0 - N_1 \cos \theta_1}{N_0 \cos \theta_0 + N_1 \cos \theta_1} \]

In the equations above, \( N_0, N_1, \) and \( N_2 \) are the complex refractive index of ambient, film, and substrate. For a multiple film system, a similar fashion can be used to calculate the reflection coefficients for both \( p \) light and \( s \) light. The Jones matrix and the Mueller matrix are used for this type of calculation. 33
2.1.3 Spectroscopic ellipsometry measurement of thin film thickness

SE measures the change of polarization state of a light reflected back from a sample surface. Specifically, SE measures two parameters, $\psi$ and $\Delta$. $\psi$ and $\Delta$ are directly correlated to the reflection coefficient of $p$ light and $s$ light through the following equation:

$$\frac{r_s}{r_p} = \tan(\psi) e^{i\Delta}$$

In the equation above, $r_s$ and $r_p$ are correlated to the phase factor $\beta$ described in previous paragraphs, so the thickness of a film can be derived from $\psi$ and $\Delta$ measurement by ellipsometry. In order to measure a film’s thickness accurately, the refractive index of this film also must be accurate. For single wavelength ellipsometry (SWE), where the wavelength is typically 633 nm, only one set of $\psi$ and $\Delta$ is measured, so the refractive index ($N=n+ik$) of this material has to be known in order to calculate the thickness of this film. However, for SE, where $\psi$ and $\Delta$ over a range of wavelengths are measured, the
refractive index and a thin film’s thickness can be measured together. The refractive index of a film may be described by optical models mathematically, which typically consists of several parameters. SE measures hundreds or thousands of sets of $\psi$ and $\Delta$, and only one thickness and several parameters of an optical model need to be determined. Thus SE can determine the thickness and refractive index simultaneously.

Due to the complicated interaction between an elliptically polarized light and a sample, an analytical solution cannot be used to calculate the thickness of a film from measured $\psi$ and $\Delta$ in most cases. A regression method has to be used in order to measure film thickness and refractive index of a sample. A typical SE measurement flow is shown in figure 2-3. First, a measured spectrum is obtained by a SE tool, and then a set of theoretical $\psi$ and $\Delta$ curves is calculated by constructing the sample optically. The thickness and refractive index of the constructed sample are not necessarily accurate at this point. The next step is the minimization of the difference between experimental curves and theoretical curves by optimizing the thickness, refractive index, and even roughness of each layer in a sample. Once the agreement between the experimental curves and theoretical curves is optimized, then information such as thickness, refractive index, and roughness of each layer in a sample is determined.

During a regression analysis for a SE measurement, a figure of merit called mean-square error (MSE) is minimized through regression algorithms such as the gradient method, the inverse Hessian method, and the Levenberg-Marquardt algorithm. Details about these algorithms will not be discussed in this dissertation. The function form of the MSE is described in the equations below:
\[
MSE = \frac{1}{2N - M} \sum_{i=1}^{N} \left[ \left( \frac{\psi_i^{\text{mod}} - \psi_i^{\text{exp}}}{\sigma_{\psi,i}^{\text{exp}}} \right)^2 + \left( \frac{\Delta_i^{\text{mod}} - \Delta_i^{\text{exp}}}{\sigma_{\psi,i}^{\text{exp}}} \right)^2 \right],
\]

where \( N \) is the number of \( \psi \) and \( \Delta \) pairs, \( M \) is the number of variables from the SE modeling, and \( \sigma \) is the standard deviation of the each experimental data point.

![Diagram](image)

**Figure 2-3: Measurement flow of SE**

### 2.2 X-ray reflectivity

X-ray reflectivity (XRR) is another type of optical metrology technique used to measure thin film thickness.\(^{52}\) It has sub-nanometer repeatability and is non-destructive to samples.\(^{52}\) The intensity of X-rays reflected by thin film stacks varies as a function of grazing angle or the X-ray wavelength. Typically, except for a synchrotron x-ray source, the x-ray source for an XRR has a specific wavelength. For example, Cu K\(\alpha\) has a wavelength of 0.15nm. As a result, the reflectivity of an X-ray is measured as a function of grazing angle. For a typical XRR thickness measurement, only the specular beam is measured as shown in figure 2-4. Non-specular XRR can be used to characterize the pore
size of a low-κ dielectric film. In this research, only the specular XRR is used to characterize high-κ thickness, roughness, and density.

![XRR measurement setup](image)

**Figure 2-4: XRR measurement set up using specular beam**

In a XRR measurement, X-rays primarily interact with the electrons of atoms, rather than the nucleus of atoms in a material. The refractive index of a material for the X-ray wavelength can be written as:

\[ N = 1 - \frac{\lambda^2 r_0 \rho_e}{2\pi} - i \frac{\lambda u_x}{4\pi} = 1 - \delta - i\beta, \]

where \( \lambda \) is the wavelength of an X-ray, \( r_0 \) is the classical electron radius (2.818*10^{-15} m), \( \rho_e \) is electron density of a material, and \( u_x \) is the linear x-ray absorption coefficient. Typically, \( \beta \) is one to two orders of magnitude smaller than \( \delta \), so the x-ray absorption from a material (\( \beta \)) can typically be neglected. \( \delta \) is also a very small number; typically in the order of 10^{-6}. The refractive index of a material is very close to unity, but smaller than unity. There exists a critical angle when an X-ray reflects back from a sample surface. When the grazing angle is smaller than the critical angle, total reflection occurs. The
critical angle is equal to the refractive index when the absorption term is very close to zero and it is related to the electron density of a sample. The electron density can then be used to characterize the mass density of a film.

Figure 2-5 shows the X-ray reflection for an air/film/substrate system. There are two reflection interfaces; one is between the air and film, while the other is between film and substrate. The reflectivity from this system can be written as:

\[ R = \left| \frac{r_{01} + r_{12} e^{-2ikzd}}{1 + r_{01}r_{12} e^{-2ikzd}} \right|^2, \]

where \( r_{01} \) is the bottom interface reflection coefficient, and \( r_{12} \) is the top interface reflection coefficient; they can be calculated directly through the refractive index (N) of these materials in this system. \( k_z \) is the wave vector in the z direction of the film, and \( d \) is the film thickness. \( R \) is the total reflection. XRR is also capable of measuring multiple layers in a stack.

Figure 2-5: XRR for an air/film/substrate measurement

The reflected beams can interfere with each other constructively or destructively, and form an intensity oscillation as a function of grazing angle. This oscillation is called
Kiessig fringes as shown in figure 2-6, which shows the XRR spectrum from a 4nm HfO₂/3nmSiO₂/Si sample. In figure 2-6, the red curve is the theoretical fitting curve and the black curve is the experimental spectrum from an XRR measurement. The spacing of the Kiessig fringes in the angle space is directly related to the film thickness as shown by

$$\Delta \theta = \frac{\lambda}{2d^{37}}$$

XRR is also capable of measuring the roughness and density of a film as shown in figure 2-6. The density of a film is correlated to the critical angle, and the roughness of a film is correlated to how fast the intensity drops as a function of angle. A rougher surface scatters x-ray more significantly than a smooth surface, so the intensity drops faster. A MSE is minimized between the experimental data and theoretical modeling curve in order to measure the film thickness, roughness, and density. In this way, the regression of an XRR measurement fitting is very similar to that of an SE fitting.

Figure 2-6: XRR spectrum from 4nm HfO₂/3nmSiO₂/Si stack
2.3 X-ray photoelectron spectroscopy (XPS) and angle resolved XPS (ARXPS)

2.3.1 Introduction of XPS

XPS is a metrology technique that characterizes electronic states and the composition in the near surface region of a sample due to the limited escape depth (typically ~ 70-100 Å) of photoelectrons.\textsuperscript{53 54} XPS uses X-rays with energy typically between 1200 and 2000 eV to cause electrons to be emitted from a sample. These electrons are referred to as photoelectrons. Energy dispersive analysis is performed on these photoelectrons, in which their kinetic energy is measured. The kinetic energy (KE) of these photoelectrons is given by:

\[
\text{KE} = h\nu - \text{BE} - \psi,
\]

where \(h\nu\) is the energy of the incoming X-ray, \(\text{BE}\) is the binding energy of the electron, and \(\psi\) is the spectrometer work function. The binding energy of a photoelectron is the material property of a sample and it is defined as the energy difference between the Fermi level and a core level as shown in figure 2-7. \(\text{BE}\) is affected by factors such as the chemical element, chemical states, and overall energy level of a sample. Figure 2-7 shows the process of an X-ray generating a photoelectron. The intensity of all the photoelectrons will be a function of energy \(I(E)\), and this intensity is proportional to the density of the occupied electronic states \(N(E)\) multiplied by the photo absorption cross section \(\sigma_{\text{abs}}(E)\) as in the following equation:\textsuperscript{25}

\[
I(E) = N(E) \cdot \sigma_{\text{abs}}(E),
\]
where the photo absorption cross section may be calculated from Fermi golden rule.\textsuperscript{25} The Fermi golden rule describes the transition rate of an electron from an initial state to a final state when it is excited by the absorption of a photon. For photoemission, the initial state of an electron is its bound state within a solid, and the final state is a free electron state in the vacuum.

Figure 2-7: Photoelectron generated by incoming X-ray

Figure 2-8 shows the XPS spectra from a 12 Å SiO$_2$/Si stack. The spectrum was collected using Thermo fisher theta probe at College of Nanoscale Science and Engineering (CNSE), University at Albany. The X-ray source is Al k\textalpha with photon energy approximately 1.5 keV. The XPS spectrum was collected from 0 eV to 400 eV binding energy. The Si 2s and Si 2p peaks can be observed at approximately 150 eV and 100 eV, respectively. The small peak above 0 eV binding energy is the valence band of Si and SiO$_2$.

Figure 2-9 shows the Si 2p spectrum from a 12 Å SiO$_2$/Si sample. The two peaks around 100 eV binding energy are the Si 2p 1/2 and Si 2p 3/2 from Si substrate,
respectively. The peak around 104 eV is the combination of Si 2p 1/2 and Si 2p 3/2 from the SiO\textsubscript{2} layer. The 4 eV difference between the Si 2p from Si substrate and Si 2p from SiO\textsubscript{2} is due to the chemical state of Si. The exact value of binding energy is extracted by fitting the XPS peaks. Figure 2-10 shows fitting spectra compared to the raw experimental spectrum from figure 2-9. In figure 2-10, the black curve is the experimental spectrum collected at beam line X-24A, national synchrotron light source (NSLS), and Brookhaven national lab (BNL) where an X-ray with 2140 eV energy was used. The green peaks are the individual peaks for Si and SiO\textsubscript{2}, and the red curve is the sum of all the green peaks. It can be observed that the fitting curve agrees well with the experimental curve. The binding energy of Si 3/2, Si 1/2 and SiO\textsubscript{2} are 99.48, 100.05, and 103.80 eV, respectively. In this dissertation, the binding energy of Si 2p 3/2 was used to calculate the Si surface band bending; the details will be discussed in Chapter 6. It should also be noted that we performed a Shirley background subtraction for the data analysis in later chapters.

Figure 2-8: XPS spectra from a SiO\textsubscript{2}/Si stack (data taken from Thermo-fisher theta probe at CNSE)
Besides the Si 2p peaks, the Si 2s peaks were also collected during this research. The reason that Si 2s peaks were also investigated is that the Si 2p from SiO₂ overlap with La4d peaks for the high-κ stacks containing La₂O₃ and information from SiO₂ is impossible to extract from Si 2p peak. Instead, Si 2s are used to compare the amount of SiO₂ between samples. Details will be discussed in Chapter 4. Figures 2-11 and 2-12 show the experimental spectrum and fitted spectrum, respectively. In these two figures, the peak at 151 eV binding energy is Si 2s from Si substrate, and the peak at 155 eV
binding energy is the Si 2s peak from SiO$_2$. From figure 2-12, the exact fitting values are 150.93 eV and 154.86 eV, respectively.

Figure 2-11: Si 2s XPS spectra from a 12Å SiO$_2$/Si sample (measured at X-24A, NSLS)

Figure 2-12: Fitting of Si 2s XPS experimental spectra from a 12Å SiO$_2$/Si sample (measured at X-24A, NSLS)

Figure 2-13 shows the valence band structure of a hydrogen terminated Si sample. The XPS spectra of Si valence band may be used to find the valence band maximum by a linear fitting of the Si valence band edge, and take the value where the linear fit crosses at the x-axis. The valence band maximum may be used to calculate Si band bending and
valence band offset between Si substrate and HfO$_2$. Details will be discussed in Chapter 5 and Chapter 6.

![Figure 2-13: Si valence band XPS spectra from a hydrogen terminated Si (measured at X-24A, NSLS)](image)

In order to measure the accurate values of the binding energies of Si 2p and Si valence band edge, the XPS analyzer energy scale was calibrated with respect to the Au 4f and Au Fermi level. The Au does not oxidize and the Au 4f level and its Fermi level are stable. Figure 2-14 shows the Au XPS spectrum measured at CNSE. It can be observed that the peaks at 80 eV are Au 4f, and the peak above 0 eV is the Au valence band. Figure 2-15 shows the detailed profile of Au valence band. The Fermi level of may be determined from the valence band edge as shown in figure 2-17. Figure 2-18 shows the Au 4f 7/2 and 5/2 XPS spectra; the binding energies are determined to be 87.31 eV and 83.6 eV, respectively.
The valence electrons in the valence band of Au follow the Fermi-Dirac distribution. The function form of a Fermi-Dirac distribution is described as:

\[
N(E) = g(E) \frac{1}{e^{(E-E_F)/kT} + 1},
\]

Figure 2-14: XPS spectra of Au from 0 to 1 keV binding energy (measured at CNSE)

Figure 2-15: Valence band of Au (measured at CNSE)
where \( g \) is the density of state, \( E \) is energy, \( E_f \) is Fermi level, \( k \) is Boltzmann constant, and \( T \) is temperature. For a normalized ideal theoretical valence band Fermi-Dirac distribution, where the \( g(E) \) equals 1, the electron density is shown in figure 2-16. The Fermi level may be taken as the maximum value of the first derivative of electron density as a function of energy as shown in figure 2-16. The Fermi level in Au XPS valence band spectra shown in figure 2-15 may be taken in the same fashion, and the result is shown in figure 2-17. It can be observed from figure 2-17 that the measured Fermi level of Au is 0.5 eV, and this should be corrected to 0 eV. Figure 2-18 shows the Au 4f core level. The binding energy of Au 4f 7/2 is a stable value due to the fact that Au does not get oxidized. The Au 4f 7/2 binding energy is used to calibrate the binding energy of Si 2p in this research.

![Normalized Electron Density & dN/dE](image)

**Figure 2-16: Theoretical Fermi-Dirac distribution (\( E_f=0\) eV)**
2.3.2 ARXPS and elemental depth profile

Due to the strong interaction between photoelectrons and atoms in a sample, the photoelectrons usually travel a small distance before an inelastic scattering. The intensity
of the photoelectrons thus reduces due to the scattering in a sample. The intensity of the photoelectrons signal $I$ can be described as the following equation,

$$I = I_0 \exp(-d / \lambda \cos \theta),$$

where $I_0$ is the intensity per unit area at the surface, $\lambda$ is the escape depth of photoelectrons, $d$ is the depth where photoelectrons are generated, and $\theta$ is the collection angle of the emitted photoelectrons with respect to the surface normal as shown in figure 2-19. The escape depth of photoelectrons may be found on a tabulated list from the National Institute of Standards and Technology (NIST).

![Diagram of Photoelectron Emission](image)

**Figure 2-19: Take off angle of Photoelectron**

XPS signals may be collected from a range of different angles from surface normal to the grazing angle of the surface. The range of depth changes with this emission angle. Normal angle emission is more sensitive to the bulk property and, grazing angle emission is more sensitive to the surface property as shown in figure 2-20.
This angle sensitivity measurement can measure a film’s thickness quantitatively. As an example, a layer of SiO₂ (A), with thickness d on top of silicon substrate (B), as shown in figure 2-21, will be used to discuss the ARXPS measurement. The thickness of SiO₂ in figure 2-21 is d.

\[
I_A = I_{A0} \cos(\theta) \left[ 1 - \exp\left( -d / \lambda_{A,A} \cos \theta \right) \right],
\]

where \(I_A\) is the signal, \(I_{A0}\) is the signal from a thick sample of A, d is the film thickness, and \(\theta\) is the emission angle. \(\lambda_{A,A}\) is the attenuation length of signal A in material A. The photo electron signal from Si substrate (B) after travelling through film A may be written as:
\[ I_B = I_{B0} \cos(\theta) \exp\left(-d / \lambda_{B,A} \cos \theta \right), \]

where \( I_{B0} \) is the intensity from a thick substrate without SiO\(_2\) over-layer, \( d \) is the SiO\(_2\) thickness, and \( \lambda_{B,A} \) is the attenuation length of signal B in material A. The ratio of \( I_A \) over \( I_B \) may be written as:

\[
\frac{I_A}{I_B} = R = R_0 \left[ 1 - \exp\left(-d / \lambda_{A,A} \cos \theta \right) \right] / \exp\left(-d / \lambda_{B,A} \cos \theta \right).
\]

\[ R_0 = \frac{I_{A0}}{I_{B0}} \]

The equation above can be further simplified as:

\[
\ln \left[ 1 + \frac{R}{R_0} \right] = \frac{d}{\lambda_A \cos \theta},
\]

where the assumption is \( \lambda_{B,A} = \lambda_{A,A} = \lambda_A \).

For different thicknesses of SiO\(_2\) on Si, the equation above is illustrated in figure 2-22.

![Figure 2-22: ARXPS signal as a function of emission angle](Image is from: J. Wolstenholme, "Application Note," ThermoFisher SCIENTIFIC)

Besides the one-layer structure ARXPS measurement described in previous paragraphs, ARXPS may also be used to measure multi-overlayer structures using a
similar fashion. Also, by using an entropy maximum method, an elemental depth profile may be achieved. One example of such a profile is described in figure 2-23. Figure 2-23 is a 20 Å HfO₂ on 12 Å SiO₂ on Si sample. From the depth profile, the thickness of each layer may be calculated by the full width at half maximum (FWHM).

![ARXPS depth profile of a HfO₂ stack](image)

**2.3.3 Valence band edge maximum (VBM) measurement by XPS**

XPS may also be used to measure the valence band offset (VBO) and Si band bending. The details of VBO application in this dissertation will be discussed in Chapter 5, and the details of Si band bending measurement will be discussed in Chapter 6. The VBO and Si band bending measurement requires the valence band edge maximum (VBM) measurement. A brief description of valence band edge maximum (VBM) will be discussed herein.

When a sample is illuminated by an X-ray beam, photoelectrons are generated from all the occupied electron states, such as Si and Au, as shown in figures 2-8 and 2-14. Out of all of the photoelectrons, the photoelectrons with the highest kinetic energy are the
electrons with the lowest binding energy in a sample. For metal, it will be the Fermi level as shown in figure 2-17. For semiconductor and insulator materials, it will be the electrons at the top of the valence band of this material as shown in figure 2-13. A common method to extract a VBM value is by performing a linear fit to the valence band edge measured on hydrogen terminated Si samples.  

For a sample with over-layer on top of Si substrate, such as a HfO₂/SiO₂/Si stack, a direct measurement Si VBM is not possible because the valence band edge of Si is not clearly visible in the spectrum. The photoelectrons from the Si valence band edge are attenuated by the HfO₂ over-layer significantly, and only the valence band of HfO₂ can be measured. However, an indirect measurement of VBM is available. As shown in figure 2-24, the binding energy difference (Δ) between Si 2p 3/2 and Si VBM is a fixed value. Δ can be calculated on a hydrogen terminated Si sample because both the Si 2p 3/2 peak and the Si valence band edge are visible from an XPS spectrum. For a HfO₂/SiO₂/Si stack, only the binding energy of Si 2p 3/2 needs to be measured; the VBM of this sample can be calculated by subtracting the Δ.

![Figure 2-24: Binding energy difference (Δ) between Si 2p and Si VBM](image-url)
2.4 Rutherford backscattering spectroscopy (RBS)

Rutherford backscattering spectroscopy (RBS) is a metrology technique that characterizes the composition and depth profile of thin films. In an RBS measurement, ions are accelerated to energies typically around 2-4 MeV and directed into a sample. Some of the ions are repelled back due to the Coulomb repulsion between sample nuclei and ions. The repulsion of an ion by a nucleus is illustrated in figure 2-25, where $E_0$ is the energy of the incidence helium energy, $m$ is the mass of the ion, $M$ is the mass in the nucleus in the sample, $E_1$ is the energy after collision, and $\theta$ is the scattering angle. This collision can be described using the laws of the conservation of energy and the conservation of momentum. From this analysis it can be shown that the ratio of $E_1/E_0$ is dependent on the $m/M$ ratio. This ratio is the mechanism for RBS to differentiate different ion elements in samples.

Typically, two kinds of information may be obtained from an RBS measurement- the areal density of a particular element and the depth profile of this element. The counts per channel are directly proportional to the areal density of an element, and the depth profile depends on the width of the peak, as shown in figure 2-26.
The relationship between $E_1$ and $M$ is described by kinematic factor $K_M$ shown in the following equation, if the nuclear reaction between incoming ions and their targets is not considered:

$$K_M = \frac{E_1}{E_0} = \left[ \frac{(M^2 - m^2 \sin^2 \theta)^{1/2} + M \cos \theta}{M + m} \right]^2.$$ 

The sensitivity of heavy element areal density is in the range of $10^{13}$ atoms/cm$^2$. The sensitivity of light element areal density is significantly higher. The depth profile of elements depends on factors such as the ion energy, detector type, and film composition. There is software to simulate RBS spectra for a given film stack that can be compared with experimental spectra. This software is based on the conservation of energy and momentum analysis. Typically, the resolution for the depth profile is a few nanometers. We used RBS as a tool to compare samples. The ratios of the areas under the curves of the given peaks were used to extract film thickness ratios.

### 2.5 Atomic layer deposition (ALD)

Atomic layer deposition (ALD) is a vacuum thin film deposition technique with atomic layer precision. The thin films deposited by ALD are highly conformal. ALD
was invented by Suntola, and ALD has been applied to modern MOSFET devices. ALD is essentially a type of chemical vapor deposition (CVD) technique, but it has a fundamental difference. A traditional CVD process introduces different precursors together into a vacuum chamber. By varying parameters such as temperature, pressure, and the partial pressure and mass flow of carrier gases and precursor gases, different types of thin films can be deposited. ALD, on the other hand, introduces precursors in alternating steps, instead of introducing all the different chemical species into the chamber at the same time. Typically, two steps are used for an ALD process. ALD breaks a one step chemical reaction in a CVD process into two half reaction steps. These two half reactions are self limited. The advantage of ALD compared to CVD is that it has low temperature, more conformation film deposition, etc. The disadvantage of ALD is obvious, as it is a slow process compared to CVD process.

The high-κ films in this research are deposited on 300mm Si wafers (100) by Tokyo Electron Ltd (TEL) Technology Center America using ALD process. The ALD process detail of HfO₂ films is shown in figure 2-27. A counter flow is used for the introduction of precursors into the chambers of ALD as shown in figure 2-28.
Figure 2-27: HfO₂ ALD flow by TEL \(^{14}\) (Image is from: R. Clark and e. al, Fall 2007 ECS Meeting, Washing D. C. (2007).)

\[
\text{Hf(NEtMe)₄} + \text{O}_3 \rightarrow \text{HfO}_2 + x \text{HNEtMe} + y \text{CO}_2 + z \text{H}_2\text{O}
\]


2.6 References


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D. E. Aspnes and A. A. Studna, "Dielectric functions and optical parameters of Si, Ge, GaP, GaAs, GaSb, InP, InAs and InSb from 1.5 to 6.0eV," Physical Review B 27 (2), 985-1009 (1983).


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Chapter 3: Film thickness characterization of HfO$_2$ stacks

3.1 Background

SiO$_2$ based gate dielectrics have reached their fundamental physical limits due to significant gate leakage current. High-$\kappa$ films have been investigated for the purpose of using them as gate oxides in metal oxide semiconductor field effect transistors (MOSFETs) for over a decade.\textsuperscript{1,15,65-67} Hf-based oxides are the leading high-$\kappa$ candidates and have been successfully implemented in integrated circuits (IC) that are in production today.\textsuperscript{68} due to reasons such as high permittivity, good thermal stability, and reasonable conduction band offsets. High-$\kappa$ films (films with a low frequency dielectric constant greater than that of SiO$_2$ (3.9)) such as HfO$_2$ films provide the necessary capacitance with a greater physical thickness thus reducing leakage current.\textsuperscript{7,15,66,69} Incorporation of high-$\kappa$ into MOSFET devices requires films with uniform thickness and physical properties that produce the necessary electrical characteristics. In this light, metrology characterization of high-$\kappa$ dielectrics properties is critical during all steps of research, development, and manufacturing.\textsuperscript{70} Because the transistor’s electrical properties depend on the equivalent oxide thickness of the gate dielectric film stack, one of the most critical measurements is the thicknesses of both HfO$_2$ and SiO$_2$ films simultaneously and accurately. The equivalent oxide thickness is the thickness that the dielectric stack would be if it were SiO$_2$ with the same capacitance, and it is a result of the equivalent oxide thicknesses of both layers.\textsuperscript{7} The functional form of EOT is:

$$EOT = T_{SiO_2} + \frac{K_{SiO_2}}{K_{HfO_2}} T_{HfO_2},$$
where $T$ is the thickness and $K$ is the dielectric constant of each layer. The SiO$_2$ interface layer has to be thin in order to minimize the EOT and continue the scaling of MOSFET devices. Currently, the state of the art thin SiO$_2$ is nitrogen incorporated SiO$_x$N$_y$ films, with thickness approximately 1.2 nm. That is about 5 monolayers of SiO$_2$ molecules. The thickness measurement of this extremely thin SiO$_2$ is even more critical than HfO$_2$ because of the large contribution it makes to the total EOT. The dielectric constant of amorphous HfO$_2$ is approximately 20 compared to the 3.9 of SiO$_2$. The research challenge in this chapter is to measure the thickness of both HfO$_2$ and SiO$_2$ simultaneously and accurately.

### 3.2 Experimental methods and current challenge for SE

SE is an optical metrology technique used to measure film thickness, among other things. When applied to thin dielectric films it can have sub-Angstrom precision.\(^{36}\) The precision of Aleris™ SE measurements on SiO$_2$ and HfO$_2$ films is shown in appendix I. The standard deviation of SE measuring 13 Å SiO$_2$ is approximately 0.05 Å, and the standard deviation of SE measuring 40 Å HfO$_2$ is approximately 0.03 Å. It should be noted that the test structure size on an IC production wafer averages local non-uniformities and manufacturing capable systems are designed to achieve this level of precision. Because of the precision and the fact that the test structure can fit in between the die on a silicon wafer, SE has been used in the semiconductor industry as inline metrology tool for decades. It is one of the most precise measurement techniques when measuring SiO$_2$ on silicon substrate. The SiO$_2$/Si is an ideal sample for SE measurements because the optical dispersion of SiO$_2$ is significantly different from that of silicon, within the wavelength range of current inline ellipsometers, which is typically between
240nm and 1000nm. The optical properties of silicon are determined by its band structure. The optical properties of silicon ($\lambda=150$-1000nm) are shown in figure 3-1.

![Si optical dispersion](image)

**Figure 3-1: Complex refractive index of single crystal silicon**

Measurement of a dielectric film stack with two or more layers (films) presents a challenge for SE. The sensitivity of SE to the presence of each film depends on its thickness and dielectric function. Figures 3-2 and 3-3 show the refractive index of SiO$_2$ and HfO$_2$ from 240nm to 1000nm wavelength region, respectively. The extinction coefficients of both films in this wavelength region are zero, and thus we will only discuss the real part of the refractive index. Figures 3-2 and 3-3 show that the functional forms of the refractive index of the two films are similar within this wavelength region. Because of the similarity of optical dispersions, a correlation between the two films exists. A high correlation means that SE is not able to differentiate the two films, and the thicknesses of the two films are inter-exchangeable in an SE measurement. One SE with a wavelength range of 240nm to 800nm is not able to differentiate the two films.
3.3 Experimental design and results

3.3.1 SE characterization of HfO$_2$/SiO$_2$/Si stacks

In order to measure the thicknesses of both HfO$_2$ and SiO$_2$ simultaneously, we designed a set of samples with combinations of different thicknesses of both SiO$_2$ and HfO$_2$ films as shown in table 3-1. SiO$_2$ films were grown on 300mm Si wafers in oxygen atmosphere at 1050 °C. This is the so called thermal oxide interfacial layer. HfO$_2$ films were deposited on top of the SiO$_2$ films by TEL Technology Center America using
atomic layer deposition (ALD) technology, and then some of the HfO$_2$ films were annealed in nitrogen atmosphere. One HfO$_2$/SiO$_2$/Si structure is referred to as one HfO$_2$ stack.

<table>
<thead>
<tr>
<th>HfO$_2$ nominal thickness (Å)</th>
<th>SiO$_2$ nominal thickness (Å)</th>
<th>Woollam VUV VASE</th>
<th>Aleris</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>12</td>
<td>24.4</td>
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</tr>
<tr>
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<td>20.8</td>
</tr>
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<td>30</td>
<td>25.3</td>
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</tr>
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<td>12</td>
<td>34.5</td>
<td>13.6</td>
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<td>41.1</td>
<td>21.3</td>
</tr>
<tr>
<td>40 (annealed)</td>
<td>30</td>
<td>41.3</td>
<td>31.1</td>
</tr>
</tbody>
</table>

Table 3-1: Comparison between Woollam VUV VASE™ and KLA-Tencor Aleris™ measurements on HfO$_2$ stacks with combination of various HfO$_2$ thicknesses and SiO$_2$ thicknesses

Table 3-1 shows the SE measurements done on the Aleris™ and Woollam VUV VASE™. Half of the high-κ stacks were annealed. All measurements were made at a single point in the center of the wafer. To develop an optical model for the hafnium oxide, we first measured one 30 Å SiO$_2$ sample on Si substrate without any HfO$_2$ over layer. This 30 Å thermal oxide was fabricated using exactly the same process conditions as the 30 Å thermal SiO$_2$ in the HfO$_2$ film stack. We assume that the HfO$_2$ does not have
any effect on the thickness of the SiO$_2$ layer. We use the SiO$_2$-VUV model$^{72}$ for the SiO$_2$ layer.

It can be observed from table 3-1 that when the HfO$_2$ thickness (annealed and unannealed) is constant, SE was able to track the thickness change of SiO$_2$ film. Similarly, when the SiO$_2$ is constant, and the HfO$_2$ changes, the SE measurements notes the change in HfO$_2$ thickness. Thus, the SE measurements are sensitive to both the SiO$_2$ and HfO$_2$ thicknesses when they are fitted simultaneously. It should be noted that the accuracy of SiO$_2$ and HfO$_2$ thicknesses measured by SE were confirmed by ARXPS and XRR measurements, which will be discussed in section 3.3.3 and section 3.3.2, respectively.

In order to measure the precision of the ellipsometry measurement from the Aleris, a gauge study was also performed. The gauge study was a measurement of 36 sites on a $1\text{mm}^2$ area on high-$\kappa$ stacks. The standard deviation of the Aleris measurement on these HfO$_2$ stacks is 0.05 Å on average. This shows that the Aleris has very high repeatability. Details of the gauge study will be discussed in appendix I.

Using the Aleris$^{\text{TM}}$, we also measured 49 points across the diameter of a wafer along the notch direction as shown in figure 3-4. We observed that the HfO$_2$ thickness decreases from one side to the other side of the wafer monotonically by approximately 1 Å. Also, figure 3-4 shows that the SiO$_2$ interface layer has a symmetric bow structure. The trend of HfO$_2$ thickness is consistent with the counter flow set up of the ALD chamber,$^{73}$ while the bow of SiO$_2$ is due to the airborne molecular contamination layer (AMC) accumulation on a wafer. It is known that the edge of a wafer has more AMC accumulation than the center of a wafer due to the air flow in a front opening unified pod
(FOUP). The AMC has similar optical properties compared to those of SiO₂. SE contributes the AMC to SiO₂ thickness. From figure 3-4, it can be concluded that the thicknesses variations of HfO₂ and SiO₂ (SiO₂ plus AMC) are accurate based on the facts described above.

![Figure 3-4: Thickness of HfO₂ & SiO₂ across a diameter of a wafer](image)

For the Woollam VUV VASE™ measurement, a uniqueness fit was also performed. Figure 3-5 shows the uniqueness fit for a 30 Å annealed HfO₂ on 30 Å SiO₂ on Si substrate. A uniqueness fit is a function of mean square error (MSE) as a function of a fitting parameter; in this case, it is the HfO₂ thickness. In figure 3-5, the x-axis is the thickness of HfO₂ film and the y-axis the normalized MSE (mse0rel in graph). Normalized MSE means that the MSE values are normalized with respect to the lowest value of MSE. It can be observed that the normalized MSE is minimized at HfO₂ thickness of approximately 42Å. The normalized MSE increases significantly when the
HfO$_2$ thickness fitting parameter is increased or decreased. This indicates that the thickness value of HfO$_2$ is single and unique.

![Graph](image)

**Figure 3-5: Uniqueness for a HfO$_2$/SiO$_2$/Si stack**

### 3.3.2 XRR characterization of HfO$_2$/SiO$_2$/Si stacks

In order to confirm the SE results in table 3-1, all the samples in table 3-1 were measured by XRR using the BEDE Metrix-L$^\text{TM}$ system. Due to the similar electron density between SiO$_2$ and Si, SiO$_2$ thickness was not measured by the XRR measurements; only the HfO$_2$ thickness is reported. Appendix II shows the the XRR spectra from samples in table 3-1, where the red curves are the theoretical simulation XRR spectra and the black curves are the experimental raw spectra. Table 3-2 summarizes the thicknesses for all the HfO$_2$ samples measured by XRR.

A comparison of HfO$_2$ thicknesses between table 3-1 measured by SE and table 3-2 measured by XRR shows consistency between two techniques. For example, the nominal 20 Å unannealed HfO$_2$ thicknesses are between 24.4 to 25.3 Å measured by SE, and they are 20.4 and 20.7 Å from XRR measurements. Thus, XRR gives a slightly thinner thickness, but between tools this is reasonably good agreement.
3.3.3 ARXPS characterization of HfO$_2$/SiO$_2$/Si stacks

Since the XRR can not measure the thickness of SiO$_2$, ARXPS was also performed on certain high-$\kappa$ stacks, especially to measure the SiO$_2$ thickness. Since the oxide signal is attenuated significantly by the high-$\kappa$ over layer, only the stacks with 2nm thick HfO$_2$ over layer were measured by ARXPS. The ARXPS was performed using a Thermo Fisher Theta Probe$^\text{TM}$, which is equipped with a monochromatized Al K$\alpha$ X-ray source and a hemispherical sector analyzer detector. The detector collects photoelectrons over a range of emission angles from 24.875$^\circ$ – 81.125$^\circ$ in 3.75$^\circ$ increments in parallel. Table 3-3 shows the thicknesses of SiO$_2$ and HfO$_2$ from ARXPS measurements. The depth profiles of ARXPS from these samples are shown in appendix II.

The agreement between the measured SiO$_2$ and HfO$_2$ thicknesses and the target thicknesses is good evidence that ARXPS is sensitive to the thicknesses of both layers. A comparison between table 3-1 and table 3-3 shows the agreement between the thicknesses measured by SE and by ARXPS. For example, for the unannealed 20 Å/HfO$_2$/12 ÅSiO$_2$/Si sample, ARXPS measured an SiO$_2$ thickness of 10 Å, a HfO$_2$ thickness of 22 Å, and an AMC thickness of 4 Å. When the AMC thickness is added to the SiO$_2$ thickness, the ARXPS values agree well with the SE measurement of the SiO$_2$ thickness (13.8 Å) and the HfO$_2$ thickness (24.4Å).
<table>
<thead>
<tr>
<th>HfO$_2$ Nominal Thickness (Å)</th>
<th>Thickness from XRR (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 (unannealed)</td>
<td>20.45 ± 0.05</td>
</tr>
<tr>
<td>20 (unannealed)</td>
<td>20.70 ± 0.04</td>
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<td>20 (unannealed)</td>
<td>20.49 ± 0.06</td>
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<td>30 (unannealed)</td>
<td>30.67 ± 0.05</td>
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<td>40 (unannealed)</td>
<td>39.99 ± 0.15</td>
</tr>
<tr>
<td>40 (unannealed)</td>
<td>40.00 ± 0.16</td>
</tr>
<tr>
<td>40 (unannealed)</td>
<td>39.91 ± 0.17</td>
</tr>
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<td>19.44 ± 0.02</td>
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<td>19.43 ± 0.02</td>
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<td>29.12 ± 0.12</td>
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<td>39.26 ± 0.14</td>
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<td>40 (annealed)</td>
<td>39.98 ± 0.18</td>
</tr>
<tr>
<td>40 (annealed)</td>
<td>39.24 ± 0.13</td>
</tr>
</tbody>
</table>

Table 3-2: HfO$_2$ thicknesses from XRR measurements

<table>
<thead>
<tr>
<th>HfO$_2$ nominal thickness (Å)</th>
<th>SiO$_2$ nominal thickness (Å)</th>
<th>HfO$_2$ thickness (Å)</th>
<th>SiO$_2$ thickness (Å)</th>
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<td>4</td>
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<td>4</td>
</tr>
<tr>
<td>20 (annealed)</td>
<td>30</td>
<td>21</td>
<td>29</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 3-3: ARXPS-derived thickness measurements of 20Å HfO$_2$ stacks
3.3.4 Comparison between SE and Scanning transmission electron microscopy (STEM) characterization of HfO₂ stack

STEM was also performed to check the thickness of HfO₂ measured by SE. Figure 3-6 shows the cross section STEM image of a 60 Å unannealed HfO₂/SiO₂/Si stack. In figure 3-6, the top light gray layer is a carbon layer deposited to protect the sample, and the dark layer below the carbon layer is the HfO₂ layer. The light gray layer under the HfO₂ layer is the lower interfacial SiO₂ layer, and the bottom dark gray region is the Si substrate.

![STEM image of HfO₂ stack](image)

Figure 3-6: TEM characterization of 60 Å unannealed HfO₂ stacks

The thickness of the lower interfacial SiO₂ layer is approximately 1nm, which is shown in figure 3-7. Figure 3-7 is a gray scale image of the green box in figure 3-6. The definition of a film thickness is the distance between 50% of the intensity on both sides of the film. Figure 3-8 shows that the thickness of the HfO₂ is approximately 6.7nm.
The STEM measurement has consistent film thickness with the Aleris™ SE and Woollam VUV VASE™ measurements. The Aleris measures 69.5 Å HfO₂ and 13.1 Å SiO₂, and the Woollam VUV VASE™ SE measures 65.3 Å HfO₂ and 13.5 Å SiO₂ for the same sample. The disagreement on the lower interfacial silicon dioxide layer is about 3 Å and it is attributed to the AMC layer.
3.4 Discussion

3.4.1 VUV is the key to measure HfO$_2$ stacks

The band gap of HfO$_2$ is approximately 6 eV (206nm), and thick films of HfO$_2$ are opaque in the VUV (150-240nm) wavelength region due to band edge adsorption. The band edge absorption of HfO$_2$ changes the profile of its refractive index (real part) through Kramers-Kronig relationship. In the VUV region, the refractive index of SiO$_2$ increases with photon energy while the refractive index of HfO$_2$ decreases with increasing photon energy as shown in figure 3-9. This strong optical contrast is why film metrology for the gate dielectric film stack requires the VUV wavelength region. In conclusion, VUV is the key to measure HfO$_2$ and SiO$_2$ simultaneously.

![Figure 3-9: Complex refractive index of HfO$_2$ and SiO$_2$ from 150nm to 1000nm](image)

3.4.2 Optical modeling of amorphous HfO$_2$ films

66
The accuracy of HfO₂ thickness measurement depends on the accuracy of the optical model used to describe the optical properties of amorphous HfO₂ films. The optical modeling of HfO₂ needs to be discussed in this chapter. The first theoretical model for the optical dispersions of amorphous materials was developed by Forouhi and Bloomer. 76 They developed an expression for the refractive index n and extinction coefficient k as:

\[
k(E) = \frac{A(E - E_g)^2}{E^2 - BE + C},
\]

\[
n(E) = n(\infty) + \frac{B_0 E + C_0}{E^2 - BE + C},
\]

where A, B, C, E₉ and n (\infty) are fitting parameters.

Also, in the equation above, B₀ and C₀ are derived parameters from A, B, C & E₉. The Forouhi and Bloomer model was found to fit some amorphous semiconductor materials successfully, but it was also found to sometimes yield a negative optical band gap which is unphysical. 77 78

Jellison and Modine found deficiencies of the Forouhi and Bloomer model and developed the Tauc Lorentz model. 79,80 They combine the Tauc expression:

\[
G(E) \propto \frac{(E - E_g)^2}{E^2},
\]

with the Lorentz expression:

\[
L(E) = \frac{AE_0 \Gamma E}{(E^2 - E_0^2)^2 + \Gamma^2 E^2},
\]

and

\[
\varepsilon_2(E) = G(E)L(E) = \frac{1}{E} \cdot \frac{A \cdot E_0 \cdot C \cdot (E - E_g)^2}{(E^2 - E_g^2)^2 + C^2 \cdot E^2},
\]

where \(\varepsilon_2\) is the imaginary part of the dielectric function, A is the transition amplitude, E is the photon energy, and \(E_g\) is the band gap energy, which is taken to be the photon
energy where $\varepsilon_2$ goes to zero. $C$ is the broadening coefficient of the oscillator. $E_0$ is the peak position for the imaginary part of the dielectric function $\varepsilon_2$. When $E$ is below $E_g$, $\varepsilon_2$ is zero. The real part of the dielectric function $\varepsilon_1(E)$ can be obtained from $\varepsilon_2(E)$ through the Kramers-Kronig relationship. A typical optical dispersion file of a HfO$_2$ Tauc Lorentz model is shown in figure 3-10, where the x-axis is photon energy and y axis is the imaginary part of the dielectric function.

Figure 3-10: Typical optical dispersion of a Tauc Lorentz model for HfO$_2$

A Cody Lorentz model has also been used to model HfO$_2$ stacks. The Cody-Lorentz oscillator model was developed by Ferlauto, et al. It is designed for amorphous semiconductor and dielectric materials. The concept of the Cody Lorentz model is similar to the Tauc Lorentz model, except that the band edge absorption profile is different. The band edge absorption of the Cody-Lorentz model follows as:

$$\varepsilon_2(E) \propto (E - E_g)^2$$
In the expression above, Cody proposed using a constant dipole matrix element as opposed to the constant momentum matrix element, which is used in a Tauc model. An Urbach tail expression was also developed in the Cody Lorentz model to describe the subband gap absorption.\(^7\)

Similar to the Tauc Lorentz model, the expression for the Cody Lorentz model is described as:

\[
\epsilon_2 = \left\{ \begin{array}{l}
\frac{E_1 \exp \left( \frac{E - E_g - E_t}{E_u} \right)}{E} & 0 \leq E \leq (E_g + E_t) \\
G(E)L(E) = \frac{(E - E_g)^2}{(E - E_g)^2 + E^2} \cdot \frac{AE_0 \Gamma E}{(E - E_g)^2 + \Gamma^2 E^2} & E \geq (E_g + E_t)
\end{array} \right.
\]

\[E_t = (E_i + E_g)G(E)L(E)\]

In the equation above, \(E\) is the photon energy, and \(E_g\) is the band gap parameter from CL model. \(E_g\) is the value of band gap without the Urbach tail. The summation of \(E_t\) and \(E_g\) is where the Urbach tail starts. It should be noted that when \(E_t\) is equal to zero, there is no Urbach tail in the Cody Lorentz model. \(E_u\) is the term that determines how fast the Urbach tail decreases with decreasing photon energy. \(E_0\) is the peak energy for the Lorentz oscillator. It should also be noted that the \(E_0\) may not be the photon energy where the maximum \(\epsilon_2\) value is for the Cody Lorentz model. \(\Gamma\) is the width of the Lorentz oscillator. \(A\) is the oscillator strength. \(E_\rho\) is called transition energy; it is a weighting factor between the Cody model and the Lorentz model. The influence of each parameter from a HfO\(_2\) Cody Lorentz model is shown in figure 3-11.
Compared to the Tauc Lorentz model, the Cody Lorentz model has three more parameters-\(E_u\), \(E_t\) and \(E_p\). These three parameters can make the Cody Lorentz model a better representation of the high-\(\kappa\) optical properties than the Tauc Lorentz model. The effect of these three extra parameters will be discussed in the following paragraphs. Also, both the Tauc Lorentz model and the Cody Lorentz model have \(E_g\) parameter. The \(E_g\) parameter of the two models has slightly different meanings and the details will be discussed in Chapter 5.

The effect of \(E_t\) on the extinction coefficient \(k\) of HfO\(_2\) is shown in figure 3-12. In figure 3-12, the \(E_g\) value from the Cody Lorentz model is 5.97eV, and all the CL model parameter values are fixed, except for the \(E_t\). It can be observed that the Urbach tail increases with increasing \(E_t\) value.
The parameter $E_u$ determines how fast the Urbach tail decreases exponentially as a function of photon energy. The effect of the $E_u$ on the extinction coefficient of HfO$_2$ is shown in figure 3-13. In figure 3-13, $E_t$ is fixed at 0.5eV and all other parameters of the Cody Lorentz model are fixed, except for $E_u$. It can be observed that the Urbach tail decreases with increasing $E_u$ value.
Figure 3-13: Effect of $Eu$ on extinction coefficient $k$

The effect of $Ep$ on the optical profile of the Cody Lorentz model is shown in figure 3-14, where $Ep$ is a weighting factor between Cody model and Lorentz model. It affects the slope of band edge absorption. The y-axis of figure 3-14 is the square root of the imaginary part of the dielectric function ($\varepsilon_2$) in order to demonstrate the effect of $Ep$ to the optical dispersion of HfO$_2$. This treatment of $\varepsilon_2$ is called the Cody method. Details of this method will be discussed in Chapter 5.
3.5 Summary

In this Chapter, it has been shown that SE with VUV capability can decouple the correlation between HfO$_2$ and SiO$_2$ for HfO$_2$/SiO$_2$/Si stacks. SE with VUV is able to measure the thicknesses of both HfO$_2$ and SiO$_2$ films simultaneously. A set of HfO$_2$/SiO$_2$/Si stacks with combination of different HfO$_2$ thicknesses and SiO$_2$ thicknesses was designed. SE with VUV was able to track the film thickness changes of both HfO$_2$ and SiO$_2$. The SE high-$\kappa$ thickness values were confirmed by XRR. The SE SiO$_2$ thickness values were confirmed by ARXPS. Also, for the thickness measurement of a 60 Å HfO$_2$/ 8 Å SiO$_2$/Si stack, the SE and TEM results are consistent. Optical modeling of HfO$_2$ films was also discussed.

3.6 References


"Woollam VUV VASE™ user's manual", J. A. Woollam Co. Inc.


"Private communication with KLA-Tencor."


Chapter 4: Spectroscopic ellipsometry thickness characterization of high-κ gate stacks with La$_2$O$_3$ $V_t$ shift layers

4.1 Introduction

One issue with Hf-based high-κ films is that the threshold voltage ($V_t$) in high-κ/metal gate stacks needs to be reduced in order to improve device performance. In a gate first structure, $V_t$ shift layers, particularly La$_2$O$_3$ and Al$_2$O$_3$, have been shown to be effective in lowering the $V_t$ of n-FET and p-FET devices, respectively. In Chapter 3, it was shown that spectroscopic ellipsometry (SE) is capable of measuring the thicknesses of both a HfO$_2$ and a SiO$_2$ layer simultaneously. However, the addition of the $V_t$ shift layer to the stack presents a further challenge to the measurement of the thicknesses of the layers in the high-κ stack stack. In this chapter, the ability of SE to measure the thicknesses of each individual layer of the HfO$_2$/La$_2$O$_3$/SiO$_2$/p-Si and La$_2$O$_3$/HfO$_2$/SiO$_2$/p-Si stacks is investigated.

4.2 Experimental details

In this chapter, three different SE modeling methods are used to determine the individual layer thicknesses in the multilayered stacks. In the first method, SE data was collected after the deposition of each layer. The thickness of the top layer is measured and modeled by SE while keeping the underlying layers thickness constant. This method will be referred to as the layer-by-layer method. In the second method, SE data was collected after the full stacks (HfO$_2$/La$_2$O$_3$/SiO$_2$/p-Si and La$_2$O$_3$/HfO$_2$/SiO$_2$/p-Si stacks) were deposited. In this case, the thicknesses of the top two layers (HfO$_2$ and La$_2$O$_3$) were
fitted while all of the other parameters for the stack were fixed. This method will be referred to as the simultaneous fitting method. In the third method, SE data from the entire stack (HfO$_2$/La$_2$O$_3$/SiO$_2$/p-Si and La$_2$O$_3$/HfO$_2$/SiO$_2$/p-Si stacks) was modeled as a single layer using a Bruggemen Effective Medium Approximation (BEMA) layer. The BEMA layer consists of HfO$_2$ and La$_2$O$_3$ optical dispersions, and the thicknesses of HfO$_2$ and La$_2$O$_3$ were determined by their concentration in the BEMA layer. This will be referred to as the BEMA method.

It should be noted that in comparison of the three methods mentioned above, the layer-by-layer method can measure the thicknesses for the HfO$_2$ and La$_2$O$_3$ layers, while the simultaneous fitting method and the BEMA method yield significantly less accurate thicknesses. The accuracy of the thicknesses from the three SE methods was evaluated by ARXPS, XRR and RBS. Details will be discussed in this chapter. Also, the optical model development of TiN metal gate will also be discussed in this chapter.

The film stacks measured for this work were grown by Tokyo Electron Limited (TEL) as follows. After HF cleaning of 300 mm p-Si wafers (doping density = 10$^{16}$ cm$^{-3}$), nominally 12 Å thick SiO$_2$ layers were thermally grown by dry oxidation at 1050° C. Alternatively, nominally 8 Å thick SiO$_2$ layers were chemically grown by a wet treatment process. After the SiO$_2$ deposition, atomic layer deposition (ALD) was used to deposit HfO$_2$ and/or La$_2$O$_3$ films. TiN films were grown using chemical vapor deposition (CVD) technique.

All the film stacks discussed in this chapter are shown in Table 4-1. The inline KLA-Tencor Aleris™ SE ($\lambda = 150 – 890$ nm) with a fixed incident angle of 70° was used to
measure the samples after each layer was deposited. A Woollam VUV-VASE™
spectroscopic ellipsometer ($\lambda = 140 – 1000$ nm) with a variable incident angle was also
used to measure samples 1 - 6 once all of the layers were deposited.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Layer 1</th>
<th>Layer 2 (cycles)</th>
<th>Layer 3 (cycles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SiO$_2$*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>SiO$_2$*</td>
<td>HfO$_2$ (40)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>SiO$_2$*</td>
<td>La$_2$O$_3$ (15)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>SiO$_2$*</td>
<td>La$_2$O$_3$ (40)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>SiO$_2$*</td>
<td>La$_2$O$_3$ (15)</td>
<td>HfO$_2$ (40)</td>
</tr>
<tr>
<td>6</td>
<td>SiO$_2$*</td>
<td>HfO$_2$ (40)</td>
<td>La$_2$O$_3$ (15)</td>
</tr>
<tr>
<td>7</td>
<td>SiO$_2$+</td>
<td>La$_2$O$_3$ (5)</td>
<td>HfO$_2$ (40)</td>
</tr>
<tr>
<td>8</td>
<td>SiO$_2$+</td>
<td>La$_2$O$_3$ (10)</td>
<td>HfO$_2$ (40)</td>
</tr>
<tr>
<td>9</td>
<td>SiO$_2$+</td>
<td>La$_2$O$_3$ (15)</td>
<td>HfO$_2$ (40)</td>
</tr>
</tbody>
</table>

Table 4-1: Film stacks measured in this study. (*: 12 Å thick thermally grown, +: 8 Å thick chemically grown)
4.3 Results and discussion

4.3.1 SiO\textsubscript{2} thickness

The three methods of modeling the SE data all involved determining the thickness of the SiO\textsubscript{2} layer using the SE measurement of a SiO\textsubscript{2}/Si sample. It was assumed that the SiO\textsubscript{2} layer thickness did not change after subsequent high-κ deposition and this thickness was set as a fixed parameter in modeling the two and three layer stacks. XPS can also be used to justify the assumption that the SiO\textsubscript{2} layer is the same in the SiO\textsubscript{2}/Si stack as it is in the two and three layer stacks. Figure 4-1 shows XPS data taken at beamline X24A at the National Synchrotron Light Source (NSLS) from samples 1 – 6. The peaks at 150 eV binding energy are the Si 2s from Si substrate, and the peaks at 155 eV binding energy are the Si 2s from SiO\textsubscript{2}. All the XPS spectra are normalized with respect to the Si 2s peak from Si substrate. The normalized spectra of the Si 2s core level show that the SiO\textsubscript{2} layer is not significantly altered when additional high-κ layers are deposited on it. It should be noted that the SiO\textsubscript{2} peak from sample 4 is slightly smaller than other samples. This indicates that the SiO\textsubscript{2} thickness from sample 4 is slightly thinner than other samples. It is estimated to be 2 Å thinner.
Figure 4-1: The Si 2s spectra from various samples show that the SiO₂ layer is not strongly altered by the deposition of the HfO₂ and La₂O₃ layers.

The SE data from sample 1 in table 4-1 was modeled using Si and SiO₂ optical models from J.A. Woollam, Inc. The thickness of the SiO₂ layer measured by the Aleris™ was 13.7 Å and that measured by the VUV-VASE™ was 16.1 Å. The difference in these thicknesses is the airborne molecular contamination (AMC) layer. The Aleris™ is equipped with a laser desorber which desorbs a portion of the AMC, while the VUV-VASE™ is not. Also, the samples were measured in the VUV-VASE™ several weeks after measuring them in the Aleris, this allows more AMC to accumulate.

The thickness of the SiO₂ layer in SiO₂/Si is confirmed with angle resolved XPS (ARXPS) at CNSE. Figure 4-2 shows the normalized Si 2p spectra of all the emission angles. In figure 4-2, the peaks at approximately 99 eV are Si 2p from Si substrate; the peaks at approximately 103.5 eV are Si 2p from SiO₂ layer. The XPS spectra intensity is normalized with respect to Si 2p from Si substrate. All the XPS curves from the bottom

80
red curve to the top gray curve are from the emission angle 24.785° to 81.125°, respectively. It can be observed that the ratio of SiO₂ peaks over Si peaks increases with increasing emission angle.

The ARXPS data can be analyzed according to the following equation to determine the thickness of the SiO₂ film:

\[
\ln(1 + \frac{R}{R_o}) = \frac{d}{\lambda \cos \theta}.
\]

The equation above is derived from the Beer-Lambert equations for photoemission intensity from a substrate covered by an oxide of the substrate material. In this equation, R is the ratio of the photoemission intensities from the SiO₂ film (Si 2pO in figure 4-3) and from the Si substrate (Si 2p in figure 4-3), \( R_o \) is the theoretical ratio of photoemission intensities from ‘infinitely’ thick SiO₂ and Si, \( \lambda \) is the electron attenuation length for the photoelectrons in SiO₂, d is the thickness of SiO₂ and \( \theta \) is the angle of emission with respect to the surface normal. By plotting \( \ln(1 + R/R_o) \) vs. \( 1/\cos \theta \) and performing a linear fit to the data points, as shown in Figure 4-3, and using a value of 36.4 Å for \( \lambda \), the SiO₂ film thickness was determined to be 13.3 Å. This value agrees well with that measured by the Aleris™ (13.7 Å), but not as well with that measured by the VUV-VASE™ (16.1 Å), due to the AMC on the surface.
4.3.2 Optical properties of HfO$_2$ and La$_2$O$_3$ films

In order to measure the thickness of HfO$_2$ and La$_2$O$_3$ in the HfO$_2$/La$_2$O$_3$/SiO$_2$/p-Si and La$_2$O$_3$/HfO$_2$/SiO$_2$/p-Si stacks, the optical properties (index of refraction (n) and extinction coefficient (k)) of the HfO$_2$ and La$_2$O$_3$ films has to be developed by SE. The Cody Lorentz model $^{77}$ was used to represent the HfO$_2$ and La$_2$O$_3$ layers.
The Cody-Lorentz model index of refraction (n) and extinction coefficient (k) dispersions for both the HfO$_2$ film and La$_2$O$_3$ film are shown in Figure 4-4. These n and k dispersions were used for the HfO$_2$ and La$_2$O$_3$ layers in the modeling of the data from the HfO$_2$/La$_2$O$_3$/SiO$_2$/Si and La$_2$O$_3$/HfO$_2$/SiO$_2$/Si stacks. It can be seen from Fig 4-4 that the n of HfO$_2$ is larger than that for La$_2$O$_3$ by ~0.3 for the majority of the measured energy range. The k dispersion of HfO$_2$ shows that there is no optical absorption below 6 eV, while for La$_2$O$_3$ there is no optical absorption below ~6.5 eV as shown in figure 4-4. Despite these small differences, there is strong similarity between the n and k dispersions of HfO$_2$ and La$_2$O$_3$. This can present difficulty when trying to differentiate between these two films in SE modeling as will be shown later in this chapter. Figure 4-5 shows the extinction coefficient (k) of HfO$_2$ and La$_2$O$_3$ from the point-by-point fit. The band gap can be linearly extrapolated from the band edge absorption curves. The details of linear extrapolation will be discussed in chapter 5.

Figure 4-4: Index of refraction (n) and extinction coefficient (k) as a function of photon energy for HfO$_2$ and La$_2$O$_3$
In order to develop the optical dispersion of HfO$_2$, sample 2 in table 4-1 was used. The VUV-VASE™ results will be discussed in this chapter for simplicity. In the modeling of the SE data from HfO$_2$/SiO$_2$/Si, a Cody-Lorentz model was used for the HfO$_2$ layer, and a thickness of 30.3 Å was determined. The HfO$_2$ thickness was also measured by XRR, using a BEDE Metrix-L™ system in order to confirm the results from SE. Figure 4-6 shows the XRR spectrum along with the model spectrum. The HfO$_2$ thickness value for the model spectrum was 26.3 Å with roughness 4.7 Å. This agrees reasonably well with the SE measurements of the thickness of the HfO$_2$, though it is smaller by ~4 Å. It should be noted that the difference between XRR and SE results may be due to the different ways SE and XRR incorporate roughness.
The same approach was used to develop the optical dispersions for La\textsubscript{2}O\textsubscript{3}. The thickness of the La\textsubscript{2}O\textsubscript{3} film from the 40 cycle La\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2}/Si sample (sample 4 in table 4-1) was measured to be 22.7 Å. The optical properties determined from the 40 cycle La\textsubscript{2}O\textsubscript{3} film were used to determine the La\textsubscript{2}O\textsubscript{3} thickness from the 15 cycle La\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2}/Si stack (sample 3 in table 4-2), which was 7.7 Å.

The 15 and 40 cycle La\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2}/Si stacks were also measured by XRR, and the resulting spectra are shown in Figure 4-7 along with XRR spectra from SiO\textsubscript{2}/Si (sample 1 in table 4-1). Figure 4-7 shows that the XRR spectrum from SiO\textsubscript{2}/Si is altered when 15 cycles of La\textsubscript{2}O\textsubscript{3} is deposited on SiO\textsubscript{2}/Si. However, a well-defined fringe was not formed because the 15 cycle La\textsubscript{2}O\textsubscript{3} film is too thin. For the 40 cycle La\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2}/Si stack, a clear fringe is observed, making this data much easier to model. According to the XRR data analysis, the 15 cycle La\textsubscript{2}O\textsubscript{3} film has a thickness of 11.0 Å, and the 40 cycle La\textsubscript{2}O\textsubscript{3} film has a thickness of 24.2 Å. The thickness for the 40 cycle film agrees well with the value
from the SE analysis (22.7 Å), while that of the 15 cycle film deviates further from the respective SE thickness (7.7 Å). Due to the absence of a well-defined fringe in the XRR spectrum from the stack with the thinner La₂O₃ film, however, it is reasonable to conclude that the accuracy of the thickness for this film is reduced.

The 15 and 40 cycles La₂O₃ films (sample 3 & 4 in table 4-1) were also characterized by Rutherford Backscattering Spectroscopy (RBS). These measurements were performed at the Ion Beam Laboratory at the University at Albany using 2 MeV He⁺ ions. The normalized RBS spectra for 15 and 40 cycles La₂O₃/SiO₂/Si are shown in figure 4-8, where the peak at 905 channel number is the La element from La₂O₃. By simulating these RBS peaks with the program RUMP, a thickness ratio between the two La₂O₃ films of 3.7 was determined. By dividing the SE measured thickness of the 40 cycle La₂O₃ (22.7 Å) by the RBS measured thickness ratio, the thickness of the 15 cycle La₂O₃ film is
estimated to be 6.1 Å, assuming the density of La$_2$O$_3$ is constant. This is significantly thinner than the value measured by XRR (11.0 Å), and thinner than, but in reasonably good agreement with, the value measured by SE (7.7 Å).

![RBS spectra of 15 and 40 cycle La$_2$O$_3$/SiO$_2$/Si](image)

**Figure 4-8: RBS spectra of 15 and 40 cycle La$_2$O$_3$/SiO$_2$/Si**

### 4.3.3 Thickness characterization of the HfO$_2$/La$_2$O$_3$/SiO$_2$/p-Si stack

Previously, the SE characterization of La$_2$O$_3$/SiO$_2$/Si and HfO$_2$/SiO$_2$/Si stacks has been discussed. The next step is to characterize the HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stack. Figures 4-9 and 4-10 show the psi ($\psi$) and del ($\Delta$) evolution of SiO$_2$/Si, La$_2$O$_3$/SiO$_2$/Si, and HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stacks, respectively. It can be observed that the 15 cycle La$_2$O$_3$ makes no significant change in psi ($\psi$) throughout the whole wavelength region. However, the 15 cycle La$_2$O$_3$ makes a significant shift on the del ($\Delta$), this indicates that
SE is sensitive to ultra thin film. 40 cycle HfO$_2$ induces a large change in $\psi$ above ~6.5 eV. There is also a clear change in $\Delta$ throughout the spectrum after adding the HfO$_2$.

By modeling the data from HfO$_2$/La$_2$O$_3$/SiO$_2$/Si with the layer-by-layer method, the thickness of the HfO$_2$ layer was measured to be 23.1 Å, as shown in Table 4-2, along with the results of simultaneous fitting and BEMA modeling approaches. When SE data for HfO$_2$/La$_2$O$_3$/SiO$_2$/Si were modeled such that thicknesses of the HfO$_2$ and La$_2$O$_3$ and layers were fitted for simultaneously, the thickness of the HfO$_2$ layer was 28.8 Å and that of the La$_2$O$_3$ layer was 1.2 Å. When a BEMA model was used to determine the thicknesses of the HfO$_2$ and La$_2$O$_3$ layers, thicknesses of 29.1 Å and 0.8 Å were obtained, respectively. In order to evaluate the values from these three modeling methods, RBS will be used to characterize the HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stack.

![Experimental Data](image)

**Figure 4-9:** SE data ($\psi$) for SiO$_2$/Si, La$_2$O$_3$/SiO$_2$/Si, and HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stacks
Figure 4-10: SE data (Δ) for SiO$_2$/Si, La$_2$O$_3$/SiO$_2$/Si, and HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stacks

<table>
<thead>
<tr>
<th>SE method</th>
<th>La$_2$O$_3$ thickness</th>
<th>HfO$_2$ thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer by layer</td>
<td>7.7 Å</td>
<td>23.1 Å</td>
</tr>
<tr>
<td>Simultaneous fitting</td>
<td>1.2 Å</td>
<td>28.8 Å</td>
</tr>
<tr>
<td>BEMA</td>
<td>0.8 Å</td>
<td>29.1 Å</td>
</tr>
</tbody>
</table>

Table 4-2: SE determined La$_2$O$_3$ and HfO$_2$ thicknesses from La$_2$O$_3$/HfO$_2$/SiO$_2$/Si

Figure 4-11 shows the normalized RBS spectra for HfO$_2$/SiO$_2$/Si (sample 2), 15 cycle La$_2$O$_3$/SiO$_2$/Si (sample 3), HfO$_2$/La$_2$O$_3$/SiO$_2$/Si (sample 5) and La$_2$O$_3$/HfO$_2$/SiO$_2$/Si (sample 6) stacks. Two observations can be made from these spectra that are relevant to the SE results shown in table 4-2. The first is that the Hf peak from HfO$_2$/SiO$_2$/Si (sample 2) is larger than that of HfO$_2$/La$_2$O$_3$/SiO$_2$/Si. The second is that the La peak from La$_2$O$_3$/SiO$_2$/Si is approximately the same as that from HfO$_2$/La$_2$O$_3$/SiO$_2$/Si. These observations support the SE results from the layer-by-layer method, in which the HfO$_2$ film in HfO$_2$/SiO$_2$/Si is thicker than that in HfO$_2$/La$_2$O$_3$/SiO$_2$/Si, and the La$_2$O$_3$ film in La$_2$O$_3$/SiO$_2$/Si is the same thickness as that in HfO$_2$/La$_2$O$_3$/SiO$_2$/Si. They also lead to the
conclusion that the results from simultaneous fitting and BEMA methods overestimate the HfO$_2$ thickness and underestimate the La$_2$O$_3$ thickness from HfO$_2$/La$_2$O$_3$/SiO$_2$/Si.

A more quantitative analysis can be performed on the RBS spectra to evaluate the SE results from the layer-by-layer method. The RBS spectra for the HfO$_2$ film on SiO$_2$ and that on La$_2$O$_3$ can be simulated using RUMP, and thicknesses for these films can be extracted. The ratio of these simulated thicknesses was 1.2. By dividing the SE measured thickness of HfO$_2$ from HfO$_2$/SiO$_2$/Si by this thickness ratio, a thickness of 25.3 Å was determined for the thickness of HfO$_2$ on La$_2$O$_3$. This is slightly larger than the SE measured HfO$_2$ thickness from HfO$_2$/La$_2$O$_3$/SiO$_2$/Si of 23.1 Å. It should also be taken into account, however, that there was an HfO$_2$ thickness variation of ~±1 Å across the wafers, and that wafer pieces for RBS were taken from various locations throughout the wafers. Thus, the difference between the SE measured HfO$_2$ thickness for HfO$_2$/La$_2$O$_3$/SiO$_2$/Si and that determined from RBS and SE agree within of the range of experimental uncertainty. We conclude that the RBS measurements support the accuracy of the SE layer-by-layer results, which shows that HfO$_2$ grows at a higher rate on SiO$_2$ than on La$_2$O$_3$. 

90
4.3.4 Thickness characterization of the $\text{La}_2\text{O}_3$/HfO$_2$/SiO$_2$/p-Si stack

Figures 4-12 and 4-13 show the SE data ($\psi$ and $\Delta$) evolution of SiO$_2$/Si, HfO$_2$/SiO$_2$/Si, and $\text{La}_2\text{O}_3$/HfO$_2$/SiO$_2$/Si stacks. It can be observed that addition of 40 cycles of HfO$_2$ noticeably changes the SE data, both $\psi$ and $\Delta$. The addition of 15 cycles of $\text{La}_2\text{O}_3$ on HfO$_2$ changes $\psi$ in the region above 7 eV and $\Delta$ throughout the spectrum, demonstrating the sensitivity that SE has to the presence of a 15 cycle $\text{La}_2\text{O}_3$ film on HfO$_2$/SiO$_2$/Si. Using the layer by layer method, the $\text{La}_2\text{O}_3$ layer thickness was determined to be 4.4 Å, while the HfO$_2$ thickness was fixed at 30.3 Å, as shown in table 4-3. The
simultaneous fitting method gave thicknesses of 34.1 Å and 0 Å for the HfO₂ and La₂O₃ layers, while the BEMA method gave respective thicknesses of 34.0 Å and 0.1 Å.

**Figure 4-12:** SE data (ψ) for SiO₂/Si, HfO₂/SiO₂/Si, La₂O₃/HfO₂/SiO₂/Si

**Figure 4-13:** SE data (Δ) for SiO₂/Si, HfO₂/SiO₂/Si, La₂O₃/HfO₂/SiO₂/Si
<table>
<thead>
<tr>
<th>SE method</th>
<th>HfO₂ thickness</th>
<th>La₂O₃ thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer by layer</td>
<td>30.3 Å</td>
<td>4.4 Å</td>
</tr>
<tr>
<td>Simultaneous fitting</td>
<td>34.1 Å</td>
<td>0 Å</td>
</tr>
<tr>
<td>BEMA</td>
<td>34.0 Å</td>
<td>0.1 Å</td>
</tr>
</tbody>
</table>

Table 4-3: HfO₂ and La₂O₃ thicknesses from La₂O₃/HfO₂/SiO₂/Si

The RBS spectra, shown in figure 4-11, can be used to evaluate the SE results in table 4-3. First, the Hf peak from La₂O₃/HfO₂/SiO₂/Si is slightly smaller than that for HfO₂/SiO₂/Si. This disagrees slightly with the layer-by-layer approach, according to which the Hf peaks should be the same. It also suggests that simultaneous fitting and BEMA methods overestimate the HfO₂ thickness. Secondly, the La peaks for La₂O₃/HfO₂/SiO₂/Si and La₂O₃/SiO₂/Si are nearly the same. Again this disagrees slightly with the layer-by-layer results, which indicate that the La₂O₃ thickness is less on HfO₂ than on SiO₂. It is also a clear indication that the simultaneous fitting and BEMA methods underestimate the La₂O₃ thickness.

The same quantitative analysis used on the RBS spectra above can help to further evaluate the SE layer-by-layer results. By simulating the RBS spectra with RUMP, the ratio of the HfO₂ thicknesses from HfO₂/SiO₂/Si and La₂O₃/HfO₂/SiO₂/Si was determined to be 1.04. Dividing the SE measured thickness of the HfO₂ from HfO₂/SiO₂/Si (30.3 Å) by this ratio gives a thickness of 29.1 Å for HfO₂ in La₂O₃/HfO₂/SiO₂/Si. This RBS and SE derived thickness agrees with the HfO₂ thickness used the layer-by-layer method of 30.3 Å, when thickness variation across the wafer is taken into account.
The disagreement between the RBS results and the SE layer-by-layer results for La$_2$O$_3$/HfO$_2$/SiO$_2$/Si, however, is a discrepancy that cannot be easily explained. The SE layer-by-layer method yielded a La$_2$O$_3$ thickness of 4.4 Å, while the RBS spectra show the La peak for La$_2$O$_3$/HfO$_2$/SiO$_2$/Si was the same as that for La$_2$O$_3$/SiO$_2$/Si, where SE measured the La$_2$O$_3$ thickness to be 7.7 Å. This difference in SE measured La$_2$O$_3$ thicknesses is greater than can be accounted for by film non-uniformity, as the La$_2$O$_3$ film thicknesses were only observed to vary by ~± 0.5 Å across the wafers. The difference between RBS and SE is most likely due to increased roughness in the HfO$_2$ surface as compared with the thermal SiO$_2$ surface.

4.3.5 Evaluation of SE characterization of ultra thin La$_2$O$_3$ films

As a final evaluation of the ability of SE to measure the thicknesses of very thin high-$\kappa$ films in multi-layer stacks, we measured the La$_2$O$_3$ thickness from three La$_2$O$_3$/SiO$_2$/Si stacks (samples 7 – 9 in table 4-1) prior to the deposition of HfO$_2$ using the inline SE Aleris$^{\text{TM}}$. In these three samples, the SiO$_2$ film was a chemically grown oxide with nominal 8 Å thicknesses, and the numbers of La$_2$O$_3$ ALD cycles were 5, 10 and 15. The SE data ($\cos(\Delta)$) from the Aleris$^{\text{TM}}$ for these stacks after the deposition of the La$_2$O$_3$ layers is shown in figure 4-14. This data shows that SE is sensitive to each addition of each additional increment of 5 cycles of La$_2$O$_3$ in the region below 400 nm. This sensitivity can be seen more clearly in figure 4-15 where the difference between the $\cos(\Delta)$ after the La$_2$O$_3$ deposition and the $\cos(\Delta)$ from SiO$_2$/Si is plotted. We measured La$_2$O$_3$ thicknesses for the 5, 10 and 15 cycle La$_2$O$_3$ films of 4.9 Å, 6.7 Å and 8.4 Å, respectively.
Figure 4-14: SE data (Cos(Del)) for SiO$_2$/Si and 5, 10 and 15 cycle La$_2$O$_3$/SiO$_2$/Si

Figure 4-15: SE data (Cos (Del) difference) for 5, 10 and 15 cycle La$_2$O$_3$/SiO$_2$/Si compared to SiO$_2$/Si

The RBS spectra for the completed metal high-κ stacks (TiN/HfO$_2$/La$_2$O$_3$/SiO$_2$/Si) are shown in figure 4-16. These spectra confirm that there is an increase in the amount of La$_2$O$_3$ for each addition of 5 La$_2$O$_3$ cycles, as shown by the SE measurements, which
demonstrates that SE is sensitive to the addition of very thin high-κ oxide layers. It can be concluded from this comparison that SE measured thicknesses of very thin high-κ oxide layers can be reliably compared when the films are grown on the same starting surfaces (chemical SiO₂).

4.4 Optical modeling of TiN

The optical properties of TiN were developed in the same fashion as HfO₂ and La₂O₃. A CVD deposited TiN film was deposited on a 12 Å SiO₂/Si stack. The XRR spectra of this sample are shown in figure 4-17, in where the black curve is the experimental data and the red curve is the modeled spectrum. It can be observed that the modeled spectrum agrees well with the measured spectrum. The thickness of this TiN film from the XRR measurement is approximately 33.9 Å, with surface roughness 7 Å. The Woollam VUV
VASE™ spectra are shown in figures 4-18 and 4-19. The wavelength of the SE measurement is from 140 nm to 1000 nm with a step size 1 nm, the angles of incidence are 40 ° and 70 °. It can be observed that the theoretical curves agree well with the experimental curve. The TiN thickness is determined to be 37.6 Å from the Woollam VUV VASE™ measurement. The complex refractive index of TiN from the modeling is shown in figure 4-20. A combination of Drude model and Lorentz oscillator model was used to model the optical properties of TiN. It should be noted that the absorption feature below 2 eV is due to the free electrons in the TiN conduction band, while the absorption features above 2 eV is due to the inter-band transition.

![Figure 4-17: XRR spectra of a 30 Å TiN/12 Å SiO₂/Si stack](image)

Figure 4-17: XRR spectra of a 30 Å TiN/12 Å SiO₂/Si stack
Figure 4-18: SE spectra $\Psi$ of a 30 Å TiN/12 Å SiO$_2$/Si stack

Figure 4-19: SE spectra $\Delta$ of a 30 Å TiN/12 Å SiO$_2$/Si stack
Figure 4-20: Complex refractive index of TiN

4.5 Summary

It has been shown that the SE layer-by-layer method is capable of measuring the thickness of very thin high-κ films in multilayer stacks to a high degree of accuracy. The SE measurement of SiO$_2$ was confirmed by ARXPS. The SE layer-by-layer measurements of HfO$_2$ in HfO$_2$/SiO$_2$/Si and La$_2$O$_3$ in La$_2$O$_3$/SiO$_2$/Si stacks were confirmed by XRR measurements. The SE layer-by-layer measurement of HfO$_2$ from HfO$_2$/La$_2$O$_3$/SiO$_2$/Si was confirmed with RBS measurements. The SE layer-by-layer measurement of La$_2$O$_3$ from La$_2$O$_3$/HfO$_2$/SiO$_2$/Si, however, was shown to disagree with the thickness the RBS measurements support. This may be due to the La$_2$O$_3$ surface growth difference between HfO$_2$ surface and SiO$_2$ surface. In the case where the La$_2$O$_3$ films were grown on the same starting surface (chemically grown SiO$_2$), the SE layer-by-layer method was able to give La$_2$O$_3$ thicknesses that could be reliably compared. For
both the HfO$_2$/La$_2$O$_3$/SiO$_2$/Si and HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stacks, the simultaneous fitting and BEMA methods do not give reliable HfO$_2$ and La$_2$O$_3$ thicknesses. This can be attributed to the similarities in the n and k of HfO$_2$ and La$_2$O$_3$. Thus, only the layer-by-layer method is useful to accurately measure the thicknesses of all the layers in the stack. This accuracy comes at a trade off of the inconvenience of performing the SE measurement after the deposition of each layer.

4.6 References


Chapter 5 : Band gap measurement of HfO$_2$ stack by spectroscopic ellipsometry

5.1 Introduction

It has been discussed in Chapter 1 that the band alignment of a high-$\kappa$ stack may be described by two parameters, CBO and VBO. CBO is the conduction band offset between HfO$_2$ and Si, and VBO is the valence band offset between HfO$_2$ and Si as shown in figure 5-1. The CBO is an even more important parameter for a HfO$_2$ stack because it affects the leakage currents through the gate by electrons. The VBO of a HfO$_2$ stack may be measured by XPS, and CBO may be calculated once the band gap of HfO$_2$ is determined, as the band gap for Si is 1.12eV. SE can be used to measure the band gap of HfO$_2$ films; however, there are different methods to extract band gap values from SE measurements. This may lead to ambiguity and will be discussed in detail in this chapter. Also, a complete band alignment of a HfO$_2$/SiO$_2$/Si stack will be discussed in this chapter.

![Figure 5-1: Band diagram of a HfO$_2$/SiO$_2$/Si stack](image)
Band gap measurement has been an important characterization of high-κ film stacks. The band gaps of a transition metal/rare earth oxide are determined by the band structures. Generally, the highest occupied valence bands are the non-bonding oxygen atom 2p states. The lowest conduction bands are from the transition metal atomic d states as shown as the $E_g$ value in figure 5-2. The next higher conduction band is the transition metal atomic p and s states as shown as the “$E_g$ ionic” in figure 5-2.

![Figure 5-2: Transition metal band gap](image)

Currently, besides the optical band gap measurement using VUV-SE, other metrology techniques have also been applied to measure the band gap of HfO$_2$ films. These techniques include photo conductivity, XPS core level energy loss, electron energy loss spectroscopy (EELS), and UV photoemission spectroscopy combined with inverse photoemission spectroscopy (IPS). A disadvantage of PC, EELS, and IPS is that they are not widely available. A disadvantage of the XPS core level energy loss method for HfO$_2$ and hafnium silicates is that the presence of Hf 4s core level at a
binding energy close to the O 1s energy loss peak obscures the extraction of the band gap when using O 1s core level.

In general, different metrology techniques generate consistent values of band gap of HfO₂ films, although a small offset may exist. For SE, the reported band gap values may range from 5.2eV to around 6.1 eV. ⁹,29,92,94,101-109 One possible reason for this is the presence of different HfO₂ crystal phases in the measured films.⁹⁴ It should also be noted that the SE measurement may generate different Eg values depending on the methods of band gap extrapolation. In this chapter, the band gap measurement using SE will be evaluated, the band gap values from different extrapolation methods from an SE measurement will be compared, and the reason why they generate different band gap values will be addressed.

5.2 SE band gap measurement of HfO₂ films

SE is traditionally used to measure the thicknesses of thin films. Besides the thickness measurement of high-κ stacks, we also investigated the band gap of HfO₂ using SE. During a SE measurement, once the thickness of the high-κ layer is determined by an optical model, we can back-calculate the complex refractive index of HfO₂ with higher sensitivity to each individual wavelength by using a “point-by-point fit”. This point-by-point fit requires a high-κ layer thickness input, which can be predetermined from optical modeling. ³⁶ This point-by-point fitting calculates the n and k values of a film directly from the raw experimental data (ψ and Δ) at each individual wavelength without considering other ψ and Δ values at other wavelength values. The point-by-point fit has more sensitivity to the refractive index for each wavelength compared to optical modeling, because optical modeling takes into consideration of all the experimental
values ($\psi$ and $\Delta$) from all the different wavelength values to determine refractive index of each wavelength by using a mathematical model.

The SE measurements were performed using Woollam VUV VASE™. The Cody Lorentz model and Tauc Lorentz model were used to model these HfO$_2$ films. Figure 5-3 shows the extinction coefficient $k$ of 40Å and 20Å unannealed HfO$_2$ films. Figure 5-4 shows the extinction coefficient $k$ of 40Å and 20Å annealed HfO$_2$ films. In figure 5-3 and 5-4, “experimental” means the data calculated from the point-by-point fit, and “model” means the extinction coefficients $k$ described by the Cody Lorentz model. From figure 5-3 and figure 5-4, it can be observed that the Cody Lorentz model matches the experimental data quite well. For the unannealed HfO$_2$ films, the band gap of 20Å HfO$_2$ is higher than the 40Å HfO$_2$. For the 40Å HfO$_2$, thermal annealing generates significant sub-band gap absorption. We attribute this sub-band absorption to the crystallization of HfO$_2$ film.

Although the extinction coefficients $k$ from optical models agree well with point-by-point fit from the experimental data, the band gap measurement of HfO$_2$ remains a challenge. We can either report the $E_g$ parameter value from the Cody Lorentz model and Tauc Lorentz model, or we can extrapolate the band gap value from the point-by-point fit. However, there are several issues that need to be addressed: 1) how to extrapolate the band gap value from a point-by-point fit, 2) how the band gap value $E_g$ parameter from Tauc Lorentz model compares to the $E_g$ parameter from Cody Lorentz model, 3) how the $E_g$ parameter from models compares to the $E_g$ extrapolated from the point-by-point fit.
5.2.1 Band gap extrapolation from experimental data
In order to extract the band gap value of HfO$_2$ films from the experimental point-by-point data, there are several linear extrapolation methods. The first method is to linearly extrapolate the band gap using extinction coefficient $k(E)$ as a function of photon energy. The second method is the band gap linear extrapolation from the imaginary part of a dielectric function $\varepsilon_2(E)$. The third method is the linear extrapolation from the absorption coefficient $\alpha(E)$. The fourth method to determine the band gap is the use of what will be referred as the Tauc method. The fifth method is to use what will be referred as the Cody method. In order to compare the different methods, we demonstrate each of them on SE data from a 40Å unannealed HfO$_2$.

The imaginary part of dielectric function $\varepsilon_2$ is the product of refractive index $n$ and extinction coefficient $k$ as:

$$\varepsilon_2(E) = 2n(E)k(E).$$

The absorption coefficient $\alpha$ is directly related to the extinction coefficient $k$ by:

$$\alpha(E) = \frac{4\pi k(E)}{\lambda},$$

where $\lambda$ is the wavelength of a light, $E$ is photon energy, $h$ is the Plank constant, and $c$ is the speed of light in vacuum. The first three methods use the values of $k$, $\varepsilon_2$, and $\alpha$ as a function of photon energy according to these expressions to linearly extrapolate the band gap value from the point-by-point fit.

Tauc method uses a different approach to calculate the band gap. Tauc et al. derived an equation for the band edge absorption of amorphous semiconductor or dielectric materials.
\[ \varepsilon_2(E) \propto \frac{(E - E_g)^2}{E^2}. \]

When \( E \) is close to \( E_g \),

\[ E - E_g \propto \left[ \varepsilon_2(E) E^2 \right]^{1/2} = \varepsilon_2(E) E^{1/2} = \left[ 2n(E)k(E)^{1/2} \right]E \]

\[ = \left( 2n(E) \frac{\alpha(E)hc}{4\pi E} \right)^{1/2} E \propto \left[ \alpha(E)n(E)E \right]^{1/2}. \]

The band gap can be extrapolated from this empirical expression \( [\alpha(E)n(E)E]^{1/2} \) as a function of photon energy. This empirical expression makes the band edge absorption more linear, and thus easier to extrapolate the band gap value from. This method has been widely used in literature to extrapolate the band gap of HfO\(_2\) films.\(^{93,94}\)

Similarly, Cody method is based on a Cody model for amorphous materials.\(^{110}\) The band edge absorption of Cody model is described as:

\[ \varepsilon_2(E) \propto (E - E_g)^2. \]

When \( E \) is close to \( E_g \),

\[ E - E_g \propto \left[ \varepsilon_2(E) \right]^{1/2} = \left[ \alpha(E)n(E) / E \right]^{1/2}. \]

The Cody method can also make the band edge absorption more linear, and thus makes it easier to extrapolate the band gap.

Figures 5-5 to 5-9 show the band gap values extrapolated using the five different methods mentioned above. On these figures, a linear fit on the lower portion of the curves were performed (between 20% and 50% of the maximum dependent variable value). The highly non-linear tail of the curve, typically referred to as the Urbach tail, was excluded.\(^{112,113}\) The band gap value was taken to be the energy where the fitted line crossed the
photon energy axis. The errors associated with this line fitting are determined to be 0.02eV from the linear fitting.

**Figure 5-5:** Band gap extrapolation from extinction coefficient $k(E)$ ($E_g=5.94eV$)

**Figure 5-6:** Band gap extrapolation from imaginary part of dielectric function ($E_g=5.91eV$)
Figure 5-7: Band gap extrapolation from absorption coefficient ($E_g=6.04\text{eV}$)

Figure 5-8: Band gap extrapolation from Tauc method using the whole band edge absorption for the extrapolation ($E_g=5.48\text{eV}$)
From figures 5.5-5.9, it can be observed that band gap values from the largest to smallest are from the $\alpha$ method (method 3, $E_g=6.04$ eV), the $\varepsilon_2$ method (method 2, $E_g=5.91$ eV), the k method (method 1, $E_g=5.94$ eV), the Tauc method (method 4, $E_g=5.48$ eV), and the Cody method (method 5, $E_g=5.36$ eV).

In general, the band gap values extrapolated from method 3 are the largest. The reason that method 3 has larger band gap values compared to method 1 is that the absorption coefficient $\alpha$ is a product of extinction coefficient $k$ and photon energy $E$. This photon energy term adds an additional concave-up nature to the absorption coefficient compared to the extinction coefficient. This additional concave-up nature from method 3 makes the linear extrapolation band gap value larger. It can also be observed that method 1 and method 2 have similar band gap values.

Method 4 and method 5 have the smallest value of band gap, with method 5 having a slightly smaller value than method 4. The reason that method 4 has a larger band gap than method 5 is exactly the same reason that the method 3 has a larger band gap than method 5.
1. The photon energy term in method 4 adds additional concave-up nature to the Tauc method.

The reason that methods 4 and 5 generate smaller band gap values is due to the fact that the Tauc and Cody methods use the square root of the imaginary part of a dielectric function. This adds a more convex up nature to the Tauc & Cody method, thus generating a smaller band gap value when linearly extrapolating band gap values.

The comparison of the five methods mentioned above is illustrated in figure 5-10. In figure 5-10, all five different methods were used on a Tauc Lorentz model for the 40 Å unannealed ALD HfO₂ film. The five methods were normalized in figure 5-10 for easier comparison.

![Figure 5-10: Normalized values from each method](image)

**5.2.2 Band gap measurement from Tauc Lorentz model and Cody Lorentz model**
Besides the linear extrapolation from the experimental curves generated by the “point-by-point fit” method, we may also report the band gap parameter values from the Tauc Lorentz and Cody Lorentz models. For the 40Å unannealed HfO$_2$ film, the band gap parameter values from the Tauc Lorentz model and Cody Lorentz (CL) model are 5.53eV and 5.97eV, respectively. The Cody Lorentz model always generated a larger band gap value than the Tauc Lorentz model for the HfO$_2$ samples we measured. This can be explained by comparing the theoretical functional forms of the Tauc Lorentz model and the Cody Lorentz model.

The Tauc Lorentz (TL) model is a combination of the Tauc model and the Lorentz model$^7$ as:

$$\varepsilon_2(E) = T(E)L(E) = \frac{A_T(E-E_g)^2}{E^2} \cdot \frac{A_L E_0 CE}{(E^2-E_0^2)^2 + C^2 E^2} = \frac{1}{E} \cdot \frac{A \cdot E_0 \cdot C \cdot (E-E_g)^2}{(E^2-E_0^2)^2 + C^2 \cdot E^2},$$

where $A$ is the TL oscillator strength, $C$ is the width of the Lorentz oscillator, $E$ is photon energy, and $E_g$ is the band gap value. In the TL model, $E_g$ is the value in which the $\varepsilon_2$ equals zero. The $E_g$ value from the model is always slightly smaller than the band gap extrapolated from methods 1, 2, and 3 because the Lorentz oscillator makes the $\varepsilon_2$ profile of TL above the band gap concave-up, as shown in figure 5-10. Figure 5-11 is a comparison of the extinction coefficients from the Tauc Lorentz model (TL), Cody Lorentz model (CL), and experimental data from point-by-point fit (ppf) for 40Å unannealed HfO$_2$ film. Thus, there is a small tail below the band gap, which may be determined by a linear extrapolation using methods 1, 2, and 3, due to the combination of the Tauc model and the Lorentz model. The band gap values linearly extrapolated from
methods 4 and 5 are very close to the Eg parameter value from a Tauc Lorentz model as shown in figure 5-10.

![Extinction coefficient k vs Photon energy (eV)](image)

**Figure 5-11: Comparison between Cody Lorentz model, Tauc Lorentz model and point-by-point fitting**

The Cody Lorentz model with Urbach tail has slight complication when extrapolating the band gap due to the Urbach tail. The Cody Lorentz model was developed by A. S. Ferlauto, et al. \(^{36}\) The function form of Cody Lorentz model is:

\[
\begin{align*}
E_2 &= \frac{E_i \exp \left( \frac{E - E_g - E_i}{E_g} \right)}{1 - \exp \left( \frac{E - E_g - E_i}{E_g} \right)} \quad 0 \leq E \leq (E_g + E_i) \\
G(E)L(E) &= \frac{(E - E_g)^2}{(E - E_g)^2 + E_p^2} \quad E \geq (E_g + E_i) \\
E_i &= (E_f + E_g)G(E)L(E)
\end{align*}
\]

where \(E\) is the photon energy, and \(E_g\) is the band gap parameter from CL model. The summation of \(E_i\) and \(E_g\) is where the Urbach tail starts. It should be noted that when \(E_f\) is
equal to zero, there is no Urbach tail in the Cody Lorentz model. $E_u$ is the term that determines how fast the Urbach tail decreases with decreasing photon energy. $E_0$ is the peak energy for the Lorentz oscillator. It should also be noted that the $E_0$ may not be the photon energy where the maximum $\varepsilon_2$ value is for the Cody Lorentz model. $\Gamma$ is the width of the Lorentz oscillator. $E_p$ is called transition energy; it is a weighting factor between the Cody model and the Lorentz model. Compared to the Tauc Lorentz model, Cody Lorentz model has three more parameters - $Eu$, $Et$ and $E_p$.

The Urbach tail from a Cody Lorentz model describes the sub-band gap absorption. Because of existence of the Urbach tail from a Cody Lorentz model, the $Eg$ parameter value from a Cody Lorentz model does not have to decrease itself to compensate for sub-band gap absorption during a fitting procedure. The Tauc Lorentz model, on the other hand, has to decrease the $Eg$ parameter value to compensate for the sub-band gap absorption. Thus, the $Eg$ value from a Cody Lorentz was always larger than the $Eg$ value in the Tauc Lorentz model for the HfO$_2$ samples we measured. In figure 5-11, although the location of $\varepsilon_2(E)$ equals zero for the Cody Lorentz model and is smaller than the Tauc Lorentz model, the $Eg$ parameter from the Cody Lorentz model value is higher.

Unannealed HfO$_2$ band gap values are compared in figure 5-12 and table 5-1. Figure 5-12 shows the extinction coefficient k curves from point-by-point fit. Table 5-1 shows the band gap values from the profiles in figure 5-12 using five different linear extrapolation methods. Table 5.1 also shows the parameter band gap values $Eg$ from the Tauc Lorentz and Cody Lorentz models for these three films in figure 5-12.
It can be observed from figure 5-12 that the band gaps of thinner films are larger. This trend agrees with a result in the literature which shows that the band gap for 30 Å HfO$_2$ is greater than that of 100 Å HfO$_2$ film, as measured by SE.\textsuperscript{10} This difference was attributed to smaller grain size in the thinner film. However, no other study of the comparison of the band gaps between 20, 30, and 40 Å HfO$_2$ films has been reported.

In table 5-1, it can be observed that the range of band gap values for the five different methods is from 5.9 to 6.17 eV for the 20 Å film. For the 40 Å film, a wider range of band gap values, from 5.63 to 6.04 eV is observed. This wider range of values can be attributed to the greater intensity of the extinction coefficient near the lower energy edge of the curves, as different methods take this intensity into account differently.

![Figure 5-12: Extinction coefficient of unannealed HfO2 films](image-url)
Table 5-1: Band gap values (eV) from different methods for unannealed HfO$_2$ films

<table>
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<th>k method</th>
<th>$\varepsilon_2$ method</th>
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<th>Tauc method</th>
<th>Cody method</th>
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<td>5.98</td>
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</table>

5.2.3 Conclusion of SE band gap measurement of HfO$_2$ films

In general, the order of the five different extrapolation methods for a point-by-point fit from small to large is: Cody method, Tauc method, k method, $\varepsilon_2$ method, and $\alpha$ method. The parameter $E_g$ value from the Tauc Lorentz model is close to method 4 and method 5, because $E_g$ value from Tauc Lorentz has to compensate for the sub-band gap absorption, and method 4 and method 5 tend to extrapolate this value. The $E_g$ values from the Cody Lorentz model tend to be very close to $\varepsilon_2$ method (method 3) because the Cody Lorentz model has an Urbach tail and $E_g$ does not have to lower itself to compensate for the sub-band gap absorption during a fitting procedure. $E_g$ parameter value from the Cody Lorentz model is the band gap value without an Urbach tail, by definition. However, due to the correlation between $E_g$ parameter with other parameters in the CL model, $E_g$ parameter value may be slightly different from the linear Extrapolation method 3 from a CL model. Also, when $E_t$ is large, the linear Extrapolation from a CL model is difficult.

In conclusion, the band gap values from the experimental data extrapolation using methods 1, 2, and 3 tend to show the band gap without sub-band gap absorption. Method 4 and method 5 tend to show the band gap value with sub-band gap absorption (Urbach tail). As for the modeling, the $E_g$ value from a Tauc Lorentz model tends to generate a
band gap value including sub-band gap absorption, while the Cody Lorentz model tends to generate a band gap value excluding sub-band absorption.

5.3 Dependence of band gap on the silicate percentage and nitrogen content

It has been observed from our experimental data that the silicate percentage affects the band edge absorption of Hf$_x$Si$_{1-x}$O$_2$ films. Figure 5-13 shows the extinction coefficient $k$ of HfO$_2$, Hf$_{0.7}$Si$_{0.3}$O$_2$, Hf$_{0.55}$Si$_{0.45}$O$_2$, and Hf$_{0.4}$Si$_{0.6}$O$_2$ films. The slope of the band edge absorption decreases with increasing silicate percentage. The band gaps of the Hf$_x$Si$_{1-x}$O$_2$ films are not affected significantly by the silicate percentage.

![Figure 5-13: Extinction coefficient of high-κ films with different silicate concentration](image)

The effect of nitridation on Hf$_x$Si$_{1-x}$O$_2$ films can be seen in the dispersion in Figure 5-14, which shows measurements of films with 30% silicate concentration and no, low, and high nitrogen doses. The band gap can be observed to decrease with increasing nitrogen dosage.
Figure 5-15 shows the dispersions of high nitrogen-dosed films with various silicate concentrations. The result is similar to what is shown in Figure 5-13, where the band edge absorption is observed to decrease with increasing silicate concentration, but the band gap is not affected significantly by the silicate percentage.

Figure 5-14: Extinction coefficient of $\text{Hf}_{0.7}\text{Si}_{0.3}\text{O}_2$ with no, low, and high N dose

Figure 5-15: Extinction coefficient of $\text{Hf}_x\text{Si}_{1-x}\text{O}_2$ with high N dose
5.4 VBO and CBO measurement of HfO\textsubscript{2} stack

It was discussed in Chapter 1 that the CBO between high-\(\kappa\) and Si substrate is an important parameter because it affects the gate leakage current due to electrons. One of the requirements of high-\(\kappa\) films is that the CBO is at least 1 eV. In this chapter, the CBO measurement of HfO\textsubscript{2}/SiO\textsubscript{2}/Si stacks will be discussed.

CBO can be determined once the VBO and high-\(\kappa\) band gap are determined. The VBO between HfO\textsubscript{2} and Si substrate is the energy difference between valence band maximum of HfO\textsubscript{2} and that of Si as shown in figure 5-16. The valence band maximum measurement from XPS was discussed in Chapter 2. For a HfO\textsubscript{2}/SiO\textsubscript{2}/Si sample, only the valence band of HfO\textsubscript{2} is visible, the VBO between HfO\textsubscript{2} and Si may be calculated by measuring one core level from Hf and one core level from Si.\textsuperscript{114} In figure 5-16, the VBO may be calculated using:

\[
VBO_{mn} = \left( E_{L_n} - \Delta E_{L_n} \right) - \left( E_{L_m} - \Delta E_{L_m} \right),
\]

where \( E_{L_n} \) is the nth layer’s binding energy of a core level, and \( \Delta E_{L_n} \) is the energy difference between the core level and the valence band maximum of this layer.
The $\Delta E_{L3}$ for the Si layer can be determined by using hydrogen terminated Si because both the Si 2p core level and Si valence band are visible as shown in figure 5-17. The XPS measurement in figure 5-17 was performed on the Fisher Thermo Theta Probe XPS system at CNSE. The Si 2p core level energy is determined to be $99.67\pm0.03$ eV and the valence band edge is determined to be $0.73\pm0.03$ eV from the linear fit in figure 5-17. The $\Delta E_{L3}$ is determined to be $98.94\pm0.04$ eV. This is in agreement with previous measurements.\textsuperscript{115,116}
Similarly, the $\Delta E_{1,2}$ for the SiO$_2$ layer was determined using a 12 Å SiO$_2$/Si sample. The SiO$_2$ was grown thermally at 1050 °C in oxygen atmosphere. The valence band edge of SiO$_2$ is shown in figure 5-18 (b). The valence band maximum is determined to be 5.38 eV from the fitting in figure 5-18 (b). The peak center of Si 2p from SiO$_2$ is shown in figure 5-18 (a). The peak center is determined to be 103.75 eV. It should be noted that the value for SiO$_2$ is the long scan of the sample. A short scan was also performed on this sample, and the binding energy was found to be 0.27 eV less. The shift of the SiO$_2$ binding energy is due to the charging effect of an XPS measurement, where the electronic states are shifted to higher binding energy by the positively charged holes left behind by the photoelectrons, if the holes are not drained quickly enough. The valence band spectrum of SiO$_2$ is also from the long scan, so the $\Delta E_{1,2}$ is the energy difference measured in the long scan, and it is determined to be 98.37 eV. The detail of the charge correction is discussed elsewhere.  

The valence band maximum may be directly
measured as shown in figure 5-19. The valence band maximum of HfO$_2$ from a 20Å HfO$_2$/SiO$_2$/Si stack is determined to be 3.85 eV.

Figure 5-18: Si 2p from SiO$_2$ and the VBM of SiO$_2$ from a 12 Å SiO$_2$/Si sample 29 (Image is from: E. Bersch, M. Di, S. Consiglio, R. D. Clark, G. J. Leusink, and A. C. Diebold, "Complete band offset characterization of the HfO$_2$/SiO$_2$/Si stack using charge corrected x-ray photoelectron spectroscopy," Jour. Appl. Phys. 107, 043702 (2010.).)

Figure 5-19: Valence band maximum of HfO$_2$ from a 20Å HfO$_2$/SiO$_2$/Si stack 29 (Image is from: E. Bersch, M. Di, S. Consiglio, R. D. Clark, G. J. Leusink, and A. C. Diebold, "Complete band offset characterization of the HfO$_2$/SiO$_2$/Si stack using charge corrected x-ray photoelectron spectroscopy," Jour. Appl. Phys. 107, 043702 (2010.).)
From figure 5-19, the VBO between SiO\(_2\) and Si may be calculated as:

\[
(99.73-98.94)-(103.81-98.37) = -4.65 \text{ eV}.
\]

The VBO between HfO\(_2\) and Si is determined to be:

\[
(99.73-98.94)-3.85 = -3.06 \text{ eV}.
\]

The next step is the band gap measurement of HfO\(_2\) film. The band gap of a 20 Å unannealed HfO\(_2\) is determined to be 5.95 eV, as shown in figure 5-20, where the Cody method was used to extrapolate the band gap value.

Using all the information mentioned above, a complete band alignment picture of a 20Å HfO\(_2\)/SiO\(_2\)/Si can be determined. The complete band structure of the stack is shown in figure 5-21. It can be observed that the VBO between HfO\(_2\) and Si is 3.06 eV, and the CBO between HfO\(_2\) and Si is 1.77 eV. It should be noted that the band alignment discussed in this dissertation is not corrected for charging. The detail of charging correction is discussed elsewhere. It should also be noted that the high-\(\kappa\) stacks with...
TiN metal gate on top have no charging effect. Details of band alignments from TiN/HfO$_2$/SiO$_2$/Si stacks will be discussed in Chapter 6.

![Figure 5-21: Complete band alignment of a 20Å HfO$_2$/SiO$_2$/Si stack using combination of SE and XPS](image)

**5.5 Summary**

Band gap values of HfO$_2$ can be measured using SE. There are two categories for SE to measure band gap values. The first category is to use the $E_g$ parameter values from the Tauc Lorentz or the Cody Lorentz model. The $E_g$ parameter value from the Tauc Lorentz model includes the sub-band gap absorption (Urbach tail) while the $E_g$ parameter value from the Cody Lorentz model does not. The second category is to use the point-by-point fit optical dispersion to linearly extrapolate the band gap values. At least five methods exist for the linear extrapolation, $k$ method, $\varepsilon_2$ method, $\alpha$ method, Tauc method, and Cody method. Systematic differences exist between these methods, although in the literature, all the five different methods are used for the band gap measurement of HfO$_2$. When comparing the band gap values extrapolated from different methods, the systematic difference needs to be taken into account. It should be noted that the Tauc method and
Cody method generate band gap values similar to the $E_g$ parameter from the Tauc Lorentz model. The k method and $\varepsilon_2$ method generate band gap values similar to the $E_g$ parameter from the Cody Lorentz model. The $\alpha$ method has larger band gap values than any other methods due to the additional concave up nature.

The band gap values measured from SE can be combined with XPS to measure the CBO values for a HfO$_2$/SiO$_2$/Si stack. XPS can measure the VBO values between layers by measuring the VBMs of each layer. The details of VBM measurement is discussed in Chapter 2. By determine all the VBO and CBO values, a complete band alignment picture can be achieved for a HfO$_2$/SiO$_2$/Si stack.

The HfO$_2$ /SiO$_2$/Si thickness measurement from Chapter 3, the HfO$_2$/La$_2$O$_3$/SiO$_2$/Si thickness measurement from Chapter 4, the SE band gap measurement of HfO$_2$ from Chapter 5, and the XPS VBO measurement from Chapter 5 sets the foundation to investigate how the La$_2$O$_3$ changes the flat band voltage of TiN/HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stacks. Details of this study will be discussed in Chapter 6.

5.6 References


"Woollam VUV VASE™ user's manual", J. A. Woollam Co. Inc.


G. M. Ferreira A. S. Ferlauto, J. M. Pearce, C. R. Wronski, and R. W. Collins, "Analytical model for the optical functions of amorphous semiconductors from


Chapter 6: The effect of La$_2$O$_3$ on the flat band voltage of TiN/HfO$_2$/SiO$_2$/Si stacks and band alignment of TiN/HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stacks

6.1 Introduction: $V_T$ shift layers

One issue with HfO$_2$ based high-$\kappa$ stacks is that the threshold voltage ($V_T$) needs to be reduced for both NMOS and PMOS. From capacitance-voltage (C-V) tests, it has been experimentally found that aluminum oxide (Al$_2$O$_3$) can reduce the $V_T$ for PMOS, and that magnesium oxide (MgO) and lanthanum oxide (La$_2$O$_3$) can reduce the $V_T$ for NMOS. The process of depositing the capping layers is still being optimized, and questions such as where is the optimum location for the layer, what is the optimum amount of material within the high-$\kappa$ stack are still being investigated. One of the reasons that the deposition process of this capping layer is still being optimized is that the mechanism of how the capping layers work is not fully understood yet. Several groups have proposed that a dipole at the high-$\kappa$/SiO$_2$ interface is the mechanism for the $V_T$ reduction by the capping layer. Several explanations for the cause of this dipole have been proposed such as oxygen areal density theory, oxygen vacancy, group electro-negativity. In addition, ab initio calculations on atomic models have been performed to gain insight into the $V_T$ shift mechanism. Along with the theoretical explorations, experimental research has been carried out to better understand the origin for the threshold voltage shift.
A brief survey of experimental work on the \( V_T \) shift layer will be presented to give a background on the work that has been done to date. H. Jagannathan et. al, have designed and fabricated a series of TiN/HfO\(_2\)/SiO\(_2\)/Si stacks with MgO and Al\(_2\)O\(_3\) capping layers. MgO is a possible capping layer for NMOS devices, and Al\(_2\)O\(_3\) is a leading capping layer for PMOS devices. As shown in figure 6-1, two locations are used to deposit the capping layers: above the HfO\(_2\) (high-\( \kappa \)) and below the HfO\(_2\). Various annealing conditions were also performed on these samples with different capping layer thicknesses.

![Fabrication process for MgO and Al\(_2\)O\(_3\) capping layers](image)

Figure 6-1: Fabrication process for MgO and Al\(_2\)O\(_3\) capping layers \(^{18}\) (Image is from: H. Jagannathan, V. Narayanan, and S. Brown, "Engineering High Dielectric Constant Materials for Band-Edge CMOS Applications," ECS Trans. 16 (5), 19-26 (2008).)

Figure 6-2 shows the capacitance-voltage (C-V) curves from the samples in figure 6-1. It can be observed that the MgO shifts the C-V curves to the negative voltage direction, and Al\(_2\)O\(_3\) shifts the C-V curves to the positive voltage direction relative to the reference sample. The reference sample is just an HfO\(_2\) film without any capping layer. These shifts correspond to a lowering of \( V_T \) for both NMOS and PMOS devices.
Figure 6-2: C-V curve shift due to MgO & Al$_2$O$_3$.\(^{18}\) (Image is from: H. Jagannathan, V. Narayanan, and S. Brown, "Engineering High Dielectric Constant Materials for Band-Edge CMOS Applications," ECS Trans. 16 (5), 19-26 (2008).)

Figure 6-3 shows a study of the position of the Al$_2$O$_3$ film within the stack. It can be observed that the bottom Al$_2$O$_3$ shifts the C-V curve by ~0.3 eV, while the top Al$_2$O$_3$ stacks have no shift at all when annealed to 800 °C or less. This indicates that the high-$\kappa$/SiO$_2$ interface is critical to the $V_T$ shift, and the top high-$\kappa$ interface is not. A similar trend can be observed for MgO capping layers as shown in figure 6-4, emphasizing the importance of the high-$\kappa$/SiO$_2$ interface. The shift in the C-V curves for the top MgO films may be due to diffusion of the Mg to the HfO$_2$/SiO$_2$ interface.\(^{18}\)
Figure 6-3: Comparison between C-V curves from stacks with Al₂O₃ capping layers. (Image is from: H. Jagannathan, V. Narayanan, and S. Brown, "Engineering High Dielectric Constant Materials for Band-Edge CMOS Applications," ECS Trans. 16 (5), 19-26 (2008).)

Figure 6-4: Comparison between C-V curves from stacks with MgO capping. (Image is from: H. Jagannathan, V. Narayanan, and S. Brown, "Engineering High Dielectric Constant Materials for Band-Edge CMOS Applications," ECS Trans. 16 (5), 19-26 (2008).)
Another study that shows the importance of the high-κ/SiO₂, in the adjustment of \( V_T \) was performed by Iwamoto, et al. \(^{20}\) In this study, the high-κ/SiO₂ interface was modified as shown in figure 6-5. In one set of samples, the bottom Al₂O₃ thickness was 2 nm and the top HfO₂ layer thickness was varied from 0 to 2 nm. For these samples, the flat band voltage is stayed constant at ~0.55eV. Then, the bottom HfO₂ was kept at 2nm, and the top Al₂O₃ layer was varied in thickness from 0 to 2 nm. For these samples, the flat band voltage was constant at ~0.3eV, as shown in figure 6-5a. This data shows that the flat band voltage is independent of the top high-κ layer thickness.

In the next comparison, the top HfO₂ was kept constant at 2nm, and the bottom Al₂O₃ thickness was varied from 0 to 2 nm. For these samples, the flat band voltage increased from 0.3 eV to 0.55 eV with increasing bottom Al₂O₃. Finally, the top Al₂O₃ was kept at 2nm, and the bottom HfO₂ layer was increased from 0 to 2 nm. The flat band voltage for these samples decreased from 0.55 eV to 0.3 eV, with increasing bottom HfO₂ layer. The data for the two comparisons are shown in figure 6-5b. This data also highlights the importance of the high-κ/SiO₂ interface in shifting the flat band voltage.
Figure 6-5: Flat band voltage ($V_{FB}$) vs. (a) top and (b) bottom high-κ thickness.\(^{20}\) (Image is from: K. Iwamoto, Y. Kamimuta, A. Ogawa, Y. Watanabe, S. Migita, W. Mizubayashi, Y. Morita, M. Takahashi, H. Ota, T. Nabatame, and A. Toriumi, "Experimental evidence for the flatband voltage shift of high-κ metal-oxide-semiconductor devices due to the dipole formation at the high-κ/SiO$_2$ interface," Applied Physics Letters 92, 132907 (2008).)

Besides TaN, Iwamoto et al. also used p+ type poly silicon as the gate material. Figure 6-6 is the flat band voltages from four comparisons-a, b, c, and d. The same trends for stacks with TaN gates can also be observed from stacks the p+ poly silicon gates. For the samples with p+ poly silicon gates, the flat band voltages vary from 0.1 V to 0.35 V as the thickness of the Al$_2$O$_3$ is increased, unlike 0.3 V and 0.55 V for stacks with TaN gates, as shown in figure 6-5. This shift in the $V_{fb}$ vs. bottom Al$_2$O$_3$ thickness curve is due to the work function difference between gate materials, poly silicon and TaN.
For the NMOS devices, La$_2$O$_3$ is commonly used as the capping layers to adjust the flat band voltage of high-$\kappa$/metal gate stacks. K. Kakushima et al. have performed a study where the amount of La$_2$O$_3$ between HfO$_2$ and SiO$_2$ films in W/HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stacks was varied. Figure 6-7 shows C-V curves of the samples with different amount of La$_2$O$_3$ layers which range from 0 nm to 1nm. It can be observed that the C-V curves shift towards the negative voltage direction with increasing La$_2$O$_3$ material.
Kakushima et al. have also performed synchrotron XPS on these samples. The photon energy of the XPS system is 7940 eV. Figure 6-8 is the Si 1s peaks of these samples. It can be observed that the binding energy of Si 1s decreases with increasing La$_2$O$_3$. It is shifting more towards the Si binding energy of a N$^+$ type silicon. Overall, the C-V curves from figure 6-7 and the XPS spectra from figure 6-8 are shifting systematically as the amount of La$_2$O$_3$ is increased. Both of these shifts indicate increasing downward band bending in Si as the amount of La$_2$O$_3$ increases.
6.2 Outline of the research

In the study performed by Kakushima et al, it was demonstrated that the Si binding energy and the C-V curve shifted towards the same direction, however, the exact relationship between the two parameters was not demonstrated. Also, SiO₂ approximately 3.5 nm to 4.5 nm thick was used, which is too thick to be technologically relevant for modern CMOS devices. In addition, the La₂O₃ is only deposited in between SiO₂ and HfO₂; so the location of La₂O₃ was not systematically studied. The work presented in this chapter builds on the work of Kakushima et al.

The goal of this research is to experimentally investigate how the La₂O₃ changes the flat band voltage and threshold voltage of high-κ/metal gate stacks. We used technologically relevant gate stacks. For example, atomic layer deposition (ALD)
processes developed by our industrial collaborator Tokyo Electron Limited (TEL) were used to deposit the HfO$_2$ and La$_2$O$_3$ layers, rather than physical vapor deposition (PVD). Also, chemical vapor deposition (CVD) technique was used to deposit TiN metal gates. Finally, the SiO$_2$ films were chemically grown 8 Å films. Thus, the results we obtained films can be related directly to a working CMOS transistor.

It has been shown in the literature that the high-κ/SiO$_2$ interface is the key to adjusting the flat band voltage; thus the high-κ/SiO$_2$ interface is the focus of this study. First, the high-κ side of the interface was manipulated at high-κ/SiO$_2$ interface, as the relative amount and position of La$_2$O$_3$ was systematically varied. The results of this study are discussed in Chapter 6. Secondly, the SiO$_2$ side of the interface was manipulated by changing the thickness and the chemical state of SiO$_2$. The SiO$_2$ films are 12, 20, and 30 Å thermal SiO$_2$ and 8 Å chemical oxides. The results of the SiO$_2$ study will be discussed in Chapter 7.

The capacitance-voltage (C-V) tests were used to measure the flat band voltage of the samples, but C-V cannot measure any other information about the stacks. A complementary technique, XPS, was also used to study the high-κ/metal gates stacks; assisting C-V to fully investigate how the La$_2$O$_3$ changes the flat band voltage of high-κ/metal gate stacks. Also, the band alignment of high-κ/metal gate stacks was characterized by measuring the valence band offset (VBO) between HfO$_2$ and Si substrate. Additionally, the thicknesses of the high-κ/metal gates stacks were investigated using SE, XRR, and ARXPS, in conjunction with RBS.
6.3 Experimental details

6.3.1 Experimental design

In this chapter, the high-κ films on SiO$_2$ are varied while keeping all the SiO$_2$ layers between samples consistent. In Chapter 7, the high-κ films are kept consistent while varying the properties of SiO$_2$. For Chapter 6, two sets of sister samples were designed. One set of samples was designed for the XPS measurements; the other set was fabricated for the C-V measurements. The two sets of samples were identical, except for the thickness of TiN metal gate films. The TiN thickness for the XPS measurement was approximately 30 Å, while the TiN thickness for the C-V measurement was 500 Å. We compared the raw spectra from SE Aleris™ tool between the sister wafers before TiN deposition, and the raw spectra were found to be identical, which indicates that the high-κ stacks before TiN deposition between sister wafers were identical.

Two comparisons were designed in order to explore the mechanism of how the La$_2$O$_3$ affects the flat band voltage. The first comparison was to study how the amount of La$_2$O$_3$ affects the flat band voltage; the second comparison was to investigate how the position of La$_2$O$_3$ affects the flat band voltage. Seven samples were fabricated for the two different comparisons. The list of samples is shown in table 6-1. For samples 1-4 in table 6-1, the amounts of La$_2$O$_3$ were varied while the amount of HfO$_2$ was kept constant. We deposited 0, 5, 10, and 15 ALD cycles of La$_2$O$_3$, and kept 40 cycles of HfO$_2$ on the top. For the second comparison, which involved of samples 4-7 in table 6-1, we varied the relative position of 15 cycles of La$_2$O$_3$ within the stack. We deposited 0, 5, 10, and 40 cycles of bottom HfO$_2$ below La$_2$O$_3$ films. The total cycle numbers for the HfO$_2$ was 40. These two types of stacks are shown in figure 6-9.
6.3.2 Fabrication of samples

For the samples in table 6-1, which were grown by Tokyo Electron Limited (TEL), the first step was to deposit the chemical SiO$_2$ layer. First, 300 mm P type Si wafers with 100 crystal orientation were etched in hydrogen fluoride solution to remove the native oxide to create a hydrogen terminated Si surface. Then a 8 Å chemical oxide was deposited on top of the SiO$_2$. The chemical SiO$_2$ was grown using a wet chemistry method. The thickness of this SiO$_2$ was measured using SE and ARXPS.

The next step was the high-$\kappa$ layer deposition, which consists of HfO$_2$ and La$_2$O$_3$. The HfO$_2$ and La$_2$O$_3$ were deposited on top of SiO$_2$ using atomic layer deposition (ALD).
The last step was the metal gate TiN deposition using chemical vapor deposition (CVD) process. It should be noted that all of these samples are not annealed in order to limit the thermal diffusion of La$_2$O$_3$ within a high-\(\kappa\)/metal gate stack.

6.3.3 Characterization of samples

C-V measurements were performed on sister wafers of these samples. The only difference between sister wafers was the thickness of TiN metal gate. The TiN thickness for the C-V measurement was 500 Å, and the TiN thickness for the XPS measurement was 30 Å. In order to confirm the consistency of high-\(\kappa\) layers between sister wafers, the raw SE spectra are collected by the Aleris$^{\text{TM}}$ before TiN deposition, and the results show that all the dielectric layers between sister wafers are consistent.

The TiN layer on the C-V wafers were patterned in a 40\(\mu\)m by 40 \(\mu\)m square to form a MOS capacitor (MOSCAP) structure. The actual C-V measurements were performed using an Agilent Technologies 4284A LCR meter. The C-V curves of the samples are shown in appendix IV together with the flat band voltage values extracted from the C-V curves. It should be noted that the C-V curves are normalized with respect to the highest value of capacitance. The only information that we extracted from the C-V curves was the flat band voltage.

C-V measurements provide flat band voltages, but they do not provide additional information about why the flat band voltage is shifting. In order to investigate how the La$_2$O$_3$ shifts the flat band voltage, XPS measurements were performed. We used two different XPS systems to characterize the high-\(\kappa\)/metal gate samples. One XPS system was the Thermo Fisher Theta Probe$^{\text{TM}}$ at the College of Nanoscale Science and
Engineering (CNSE); the other XPS system was at beam line X24A of the National Synchrotron Light Source (NSLS) at Brookhaven National Lab (BNL).

The beam energy at CNSE was 1486.7 eV from a Al Kα X-ray beam. The X-ray beam energy that we used in the X-24A is 2140.0 eV. The pass energy that we used at BNL (the CNSE) was 27 eV (125 eV) with XPS spectrum energy uncertainty of 0.07eV (0.03 eV), which is the step size of the analyzer. In this dissertation, we used the Au 4f core level and Au Fermi level to calibrate the energy levels of our measurements on the two different XPS systems. The geometry of the XPS setup of this system is shown in figure 6-10. The angle between the incoming X-ray and the sample surface is 5 °. The analyzer is normal to the incoming X-ray, thus the angle between the sample surfaces to the analyzer is 85 °, which correspond to an emission angle of 5 ° with respect to the surface normal. It should be noted that we measured the Au 4f level in between every sample as the energy calibration of XPS spectra.

![Geometry of XPS measurement at X-24A, NSLS, BNL](image)

Figure 6-10: Geometry of XPS measurement at X-24A, NSLS, BNL

6.4 Experimental results

6.4.1 Spectroscopic ellipsometry (SE) characterization
All the samples in table 6-1 were characterized by SE using the Aleris™ tool. The optical models of silicon and silicon dioxide used for the measurement are provided by J. A. Woollam Co. Inc. The optical properties of HfO$_2$ and La$_2$O$_3$ used here are shown in figure 4-4. The optical model for TiN is shown in figure 4-20. During the Aleris measurement, a laser i-Desorber with 25mW power was used to reduce the airborne molecular contamination layer (AMC). An industry standard 49 points polar map was performed on these wafers. The edge exclusion of all the Aleris™ measurements is 3mm, where edge exclusion is defined as the distance between the edges of a wafer to the most outside points of the 49 point polar maps. Table 6-2 is the average thickness of the 49 point measurements for the samples from table 6-2. The thickness uniformity maps are shown in appendix III. It should also be noted that for the SE modeling of these samples, each film is assumed to have no roughness.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>SiO$_2$ thk (Å)</th>
<th>First high-k thk (Å)</th>
<th>Total high-k thk (Å)</th>
<th>TiN thk (Å)</th>
</tr>
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<tr>
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<td>28</td>
<td>34.2</td>
</tr>
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<td>11</td>
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<td>29.8</td>
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</tr>
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<td>28.2</td>
<td>30.7</td>
</tr>
<tr>
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<td>11.8</td>
<td>28</td>
<td>30.9</td>
</tr>
<tr>
<td>7</td>
<td>11.1</td>
<td>31.8</td>
<td>31.8</td>
<td>33.1</td>
</tr>
</tbody>
</table>

Table 6-2: SE thickness characterization of table 6-1 by the Aleris™

6.4.2 Increasing the amount of bottom La$_2$O$_3$

Samples 1-4 in table 6-1 are 0, 5, 10, and 15 ALD cycles of bottom La$_2$O$_3$. These samples are used in the first comparison to investigate how this increasing amount of La$_2$O$_3$ affects the flat band voltage. SE confirms that the amount of La$_2$O$_3$ increases with increasing ALD cycle numbers, as shown in table 6-2. Besides SE, RBS was also
performed on these four samples. Details of the RBS characterization were discussed in Chapter 4.

6.4.2.1 Flat band measurement of using C-V characterization

Figure 6-11 shows the C-V curve of the center point of each wafer from samples 1-4 in table 6-1. It can be observed that the C-V curves shift to the more negative gate voltage values with increasing bottom La$_2$O$_3$. The biggest change occurs between 0 to 5 cycles of La$_2$O$_3$. In order to extract the flat band voltage from these curves, the method of Hauser was used. The AC frequency of the C-V measurements was 100 kHz. In total, nine capacitors were measured on each wafer, and the average of flat band voltages is reported in this dissertation.

![Figure 6-11: C-V curves at the center of each wafer for samples 1-4 in table 6.1, where the amount of bottom La$_2$O$_3$ is being varied](image)

Figure 6-12 shows the flat band voltages extracted from C-V measurements as a function of bottom La$_2$O$_3$ ALD cycle number. It can be observed that the flat band
voltage changes to more negative values with increasing La$_2$O$_3$. The flat band voltage decreases from -0.3 V to -1.1 V. Another interesting observation is that the change in flat band voltage from 0 to 5 cycles was the largest, and the changes from 5 to 10 cycles and from 10 to 15 cycles were much smaller. This suggests that the formation of the La$_2$O$_3$/SiO$_2$ interface is the key event in the shifting of the flat band voltage, and that adding more La$_2$O$_3$ on top of this is less important. It should be noted that the range of flat band voltage values for each wafer is within 0.04 V. As discussed in Chapter 1, the more negative value in flat band voltage means a reduced threshold voltage for NMOS devices.

![Graph](image)

**Figure 6-12: Flat band voltage vs. bottom La$_2$O$_3$ cycle number**

### 6.4.2.2 Si band bending using XPS characterization

Previous XPS measurements of HfO$_2$/SiO$_2$/Si stacks have shown evidence of charging. We performed a charging study using the CNSE XPS system by observing a given core level over time. We observed that for a high-$\kappa$ stack with 30 Å TiN films, no
charging occurred. This can be attributed to the fact that the metal gate TiN dissipates the positive charges created by the loss of photoelectrons generated by the X-ray beam. The metallic property of 30 Å TiN can be observed in the XPS spectra. Figure 6-13 shows the valence band XPS spectra of a 30 Å and 10 Å thick TiN on gate dielectrics where thicknesses of these films are measured by SE. The spectra are normalized with respect to the highest value in counts. From figure 6-13, it can be observed that the 30 Å film has more electron counts around the Fermi level (0 eV binding energy), while the 10 Å has no significant counts in this region. This indicates that the 30 Å TiN is a purely metallic component, while the 10 Å TiN film is predominantly oxidized.

![Figure 6-13: XPS spectra of the valence band of TiN films](image)

Figure 6-14 shows the XPS spectra taken from the X-24A beam line. The counts are normalized with respect to the maximum peak height. The two peaks around 100 eV binding energy are the Si 2p 3/2 and Si 2p 1/2 core levels from Si substrate, with the taller peak being the Si 2p 3/2 level. The peaks around 107 eV binding energy are the La
4d 3/2 peaks from the La$_2$O$_3$ within the stacks. The peaks around 104 eV binding energy are the combination of both Si 2p from SiO$_2$ interface layer and the La 4d 5/2 from the La$_2$O$_3$. Because the La$_2$O$_3$ layer from each sample is at the same location within a stack, the peak height of La 4d 3/2 can be used to compare the amount of La$_2$O$_3$. It can be observed from figure 6-14 that the peaks at 107 eV are increasing in intensity along with La$_2$O$_3$ ALD cycle number, which confirms that the amount of La$_2$O$_3$ is increasing with increasing ALD cycle number. It can also be observed that the Si substrate 2p binding energy is shifting to higher values with increasing La$_2$O$_3$. This suggests that the Si surface band is bending more downward with increasing amount of La$_2$O$_3$.\textsuperscript{127}

Figure 6-15 shows the Si 2p and La 4d spectra from the four samples measured by the CNSE XPS system. These spectra show the same trends as those discussed in figure 6-14, an increasing La 4d 3/2 peak with La$_2$O$_3$ cycle number, and a shifting Si 2p peak. It can be observed that the data in figure 6-15 is noisier than the data in figure 6-14. This is due to the fact that the kinetic energy of photoelectrons from Si, SiO$_2$, and La$_2$O$_3$ peaks measured by the BNL XPS system has higher energy value than the kinetic energy of the same peaks measured at the CNSE XPS system. The photoelectrons from the BNL XPS system are attenuated less by the TiN over-layers.
From a device point of view, the Si 2p binding energy is not valuable— the amount of Si surface band bending is more useful. The value of Si surface band bending can be calculated from the Si binding energy. The calculation method is shown in figure 6-16. In figure 6-16, $E_c$ is the conduction band edge, $E_v$ is the valence band edge, and $E_f$ is the Fermi level. For a TiN/high-$\kappa$ stack/Si (MOS) system, the Fermi level of TiN ($E_f$)
equals the Fermi level of bulk Si substrate. The binding energy of Si 2p 3/2 (BE_{Si 2p}) is the energy difference between the Fermi level of Si and the core level Si 2p 3/2. Si band bending (\(\Phi_s\)) is the energy difference between the valence band edge (\(E_v\)) at Si surface and the valence band edge of bulk. It can be observed from figure 6-16 that Si band bending (\(\Phi_s\)) equals the binding energy of Si (BE_{Si 2p}) minus \(\Delta_1\) and \(\Delta_2\). \(\Delta_2\) equals 0.2 eV because the doping level of these p type Si is \(10^{16}/\text{cm}^3\). \(\Delta_1\) was measured on a hydrogen terminated Si sample, and the value of \(\Delta_1\) equals 98.84 eV when the Si 2p 3/2 and Si 2p 1/2 peaks are resolved, and 98.94 eV when they are not. The details of how \(\Delta_1\) was determined are discussed in Chapter 5.

\[ \Phi_s = \text{BE}_{\text{Si 2p}} - \Delta_1 - \Delta_2 \]

Figure 6-16: Si band bending calculation from XPS binding energy Si 2p 3/2

The Si band bending determined from the BNL XPS measurements for samples 1-4 from table 6-1 as function of the bottom La_{2}O_{3} ALD cycle numbers in Figure 6-17. In figure 6-17, the red data points represent the Si band bending, and the blue data points
represent the flat band voltage values extracted from the C-V measurements. It can be observed that both the Si band bending and flat band voltage move to more negative values with increasing La$_2$O$_3$ ALD cycle number. Another observation that can be made is that, as the La$_2$O$_3$ cycle number increased, the flat band voltages moved to more negative values than the Si band bending, especially for the 10 and 15 cycles. This separation between the flat band voltage and Si band bending for more negative band bending values will be discussed further.

![Figure 6-17: Si surface band bending and flat band voltage vs. bottom La$_2$O$_3$ ALD cycle numbers](image)

6.4.3 Varying the amount of bottom HfO$_2$

For the bottom HfO$_2$ comparisons, samples 4-7 in table 6.1 are used. The purpose of this comparison was to see how the flat band voltage and Si band bending is modified by the amount of HfO$_2$ between the La$_2$O$_3$ and SiO$_2$. 

150
6.4.3.1 C-V characterization of bottom HfO$_2$ samples

Figure 6-18 shows the comparison of C-V curves from the center point of 0, 5, 10, and 40 ALD cycles bottom HfO$_2$ samples. The normalized C-V curves from the all the data points on the three samples with 5, 10, and 40 cycle bottom HfO$_2$ layer are shown in appendix IV. It can be observed that the C-V curves are shifting to the positive voltage direction with increasing bottom HfO$_2$ thickness. The extracted flat band voltages from the C-V curves as a function of bottom HfO$_2$ cycles are shown in figure 6-21. This figure also shows the flat band voltages becoming less negative as the amount of bottom HfO$_2$ increases.

![C-V curves comparison between 0, 5, 10, and 40 cycles bottom HfO$_2$](image)

Figure 6-18: C-V curves comparison between 0, 5, 10, and 40 cycles bottom HfO$_2$

6.4.3.2 XPS characterization of bottom HfO$_2$ samples

Figure 6-19 shows the XPS spectra of high-κ/metal gate samples with 0, 5, 10, and 40 cycles of bottom HfO$_2$ film and 15 cycles La$_2$O$_3$ on top of it. The XPS spectra are
normalized with respect to the Si 2p 3/2 peak. The peaks at 100 eV binding energy are
the Si 2p 3/2 and Si 2p 1/2 peaks from Si substrate. The peaks at 103 eV binding energy
are the Si 2p 3/2, Si 2p 1/2 from SiO₂, and also the La 4d 5/2 from La₂O₃ layer. The
peaks at 107 eV are the La 4d 3/2 from the La₂O₃ layer. It can be observed that the Si 2p
3/2 and 1/2 peaks from Si substrate are shifting towards lower binding energy with
increasing bottom HfO₂ ALD cycle number, indicating a less downward Si surface band
bending. It can be also observed that the La 4d peaks from the 40 cycle bottom HfO₂
sample are significantly higher than other samples; this is not due to the larger amount of
La₂O₃ than in other samples, but the fact that since the La₂O₃ is on top of HfO₂, and the
photoelectrons from La₂O₃ are not attenuated by HfO₂, unlike other samples in the graph.
Figure 6-20 is the XPS spectra taken at the CNSE; which show the same trends as the
XPS data taken at BNL, as shown in figure 6-19.

![XPS Spectra](image)

**Figure 6-19:** XPS spectra of stacks with bottom HfO₂ from BNL
Besides the flat band voltages, Figure 6-21 also shows the Si band bending as a function of bottom HfO$_2$ cycles. It can be observed that the Si band bending becomes less negative as the amount of bottom HfO$_2$ increases, which is consistent with the flat band voltage results. As with the bottom La$_2$O$_3$ study, the addition of the first 5 cycles of bottom HfO$_2$ gives the largest change in flat band voltage and Si band bending. This highlights once more the importance of the high-κ/SiO$_2$ interface. Another interesting point is that the Si band bending value (-0.3) in the 40 cycle bottom HfO$_2$ stack (shown in figure 6-21) is the same as the 0 cycle bottom La$_2$O$_3$ stack (-0.3 V) (shown in figure 6-17). This indicates that the top La$_2$O$_3$ is not a factor in adjusting the flat band voltage and threshold voltage.
6.4.4 Valence band offset (VBO) characterization

One of the advantages of XPS measurements is that we can also measure how the energy levels of other material in the stack besides Si are affected by the La$_2$O$_3$. In order to investigate the reason for the different Si band bending values, it is necessary to investigate the band alignment of the stacks with and without La$_2$O$_3$. Figure 6-22 is an illustration of the band alignment of a TiN/HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stack. In figure 6-22, $E_c$ is the conduction band edge of each layer, $E_v$ is the valence band edge of each layer, and $E_f$ is the Fermi level. The energy difference between $E_c$ and $E_v$ is defined as band gap ($E_g$). The band gap for silicon is 1.12 eV. The band gap of La$_2$O$_3$ was measured using SE, and it is approximately 6.5 eV. The band gap of HfO$_2$ was also measured using SE, and the value is approximately 6 eV. The band gaps of La$_2$O$_3$ and HfO$_2$ determined by SE are shown in figure 4-5. The metal gate (TiN) has no band gap due to its metallic properties. In figure 6-22, the Fermi level of TiN is lined up with the Fermi level of Si substrate. One
aspect of the band alignment is the valence band offset (VBO). The VBO between HfO\(_2\) and Si substrate is defined as the energy difference of the HfO\(_2\) valence band edge and the Si valence band edge, as shown in figure 6-23. XPS measurements can be used to measure the VBO of a high-\(\kappa\)/metal gate stack. In particular, we will to focus the band alignment between HfO\(_2\) and Si because high-\(\kappa\)/SiO\(_2\) interface is the key to adjusting the flat band voltage and these two materials are on opposite sides of this interface.

![Figure 6-22: Illustration of band alignment of a high-\(\kappa\)/metal gate stack](image)

The VBO between HfO\(_2\) and Si cannot be measured directly from a TiN/HfO\(_2\)/La\(_2\)O\(_3\)/SiO\(_2\)/Si sample, due to the fact that the valence band edges from both HfO\(_2\) and Si are invisible because the photoelectrons from the HfO\(_2\) and Si are attenuated. Only the valence band from the metal gate TiN is visible. The valence band edge of the HfO\(_2\) and Si can be measured by measuring the core levels of Hf and Si, as shown in figure 6-23. It has been shown earlier in figures 6-16 how to measure the Si valence band edge from Si 2p 3/2 core level. Similarly, if we can measure the \(\Delta_{\text{Hf}}\) between Hf 4f level and valence band edge of HfO\(_2\) from one sample, then VBO can be calculated.
The $\Delta_{\text{Hf}}$ was measured on a 40 cycles ALD HfO$_2$/12 Å SiO$_2$/Si sample. Figure 6-24 shows the X-24A XPS spectrum of Hf 4f from this sample. In figure 6-24, the black curve is the measured spectrum, the peak at 18 eV is the Hf 4f 7/2 peak, and the peak at 20 eV is the Hf 4f 5/2 peak from HfO$_2$ film. It should be noted that this black curve is modified by subtracting a Shirley background. The two green curves are the Gaussian peaks used to fit the experimental spectrum, and the red curve is the sum of the two green Gaussian peaks. From the fitting, the peak center of Hf 4f 7/2 is determined to be 18.02 eV, and the Hf 4f 5/2 is determined to be 19.68 eV. The Hf 4f 7/2 peak is chosen for the $\Delta_{\text{Hf}}$ calculation.

The HfO$_2$ valence band XPS spectrum was shown in figure 5-19. The spectrum was measured from a 40 cycles ALD HfO$_2$/12 Å SiO$_2$/Si sample. The valence band edge is...
determined to be 3.85 eV. The $\Delta_{\text{Hf}}$ is determined to be 14.10 eV, and the VBO between HfO$_2$ and Si can be calculated using equation as:

$$VBO = (BE_{\text{Si} 2p \text{3/2}} - 98.94) - (BE_{\text{Hf} 4f \text{7/2}} - 14.10) \text{ eV.}$$

![Figure 6-24: Hf 4f XPS spectrum from the 40 cycle HfO$_2$/12 Å SiO$_2$/Si stack](image)

We calculated all the VBO values for all the samples listed in table 6-1 using the method illustrated in figure 6-25. The VBO between HfO$_2$ and Si substrate changed systematically. Figure 6-25 shows that the VBO decreased from 3.2 eV to 2.5 eV with increasing bottom La$_2$O$_3$ ALD cycle numbers. Figure 6-26 shows that the VBO changed back from 2.5 eV to 3.2 eV with increasing bottom HfO$_2$ ALD cycle numbers.
6.5 Results and discussion

A systematic shift in flat band voltage was observed by adjusting the structure of high-κ stacks. We also observed the shift in Si surface band bending and valence band
offset between (HfO₂ and Si) from XPS measurements. The Si band bending shift had the same trend with flat band voltage. The VBO was also observed to shift systematically. A model that accounts for these observations will be described below. Figure 6-27 shows the plot of flat band voltage vs. Si band bending from the samples discussed above. How they are related will be discussed in this section.

![Figure 6-27: Flat band voltage vs. Si band bending for the samples in table 6.1 (Sample number is labeled)](image)

**6.5.1 Band alignment of high-κ stacks and cause of different band bending**

The VBO between HfO₂ and Si is a measure of band alignment within a high-κ stack. Figure 6-28 is the HfO₂/SiO₂/Si band alignment without La₂O₃ deposition. The band alignment in figure 6-28 is before TiN deposition, so the work function of TiN has no effect on the band alignment yet. The VBO is 3.2 eV. Figure 6-29 is the band alignment after 15 cycles of ALD La₂O₃ deposition between HfO₂ and SiO₂. The VBO between HfO₂ and Si is 2.5 eV from the XPS measurements. The band diagram in figure 6-29 is
also before TiN deposition and the work function of TiN has no effect on the band alignment. By comparing figures 6-28 and 6-29, it can be concluded that the energy level of Si surface and the energy level of SiO₂ layer are shifted downward by La₂O₃ deposition. If it is assumed that the vacuum level (E_{VAC}) in figure 6-28 is continuous across HfO₂, SiO₂, and Si, then a dipole at the La₂O₃/SiO₂ interface, which is represented by a discontinuity in the vacuum level as shown in figure 6-29, can account for the reduced VBO. According to this model, the change in the VBO equals the magnitude of the dipole, which in this case is 0.7 eV.

To be more specific, the magnitude of the change in the dipole between the HfO₂/SiO₂ interface and the La₂O₃/SiO₂ interface is 0.7 eV. Since we do not know the interface dipole moment between HfO₂ and SiO₂, we represent the vacuum level as continuous at this interface, and note the change in the dipole as the change in the VBO when the La₂O₃ layer is added.
Figure 6-28: VBO for a HfO$_2$/SiO$_2$/Si stack with assumed continuous vacuum level at high-$\kappa$/SiO$_2$ interface

After TiN deposition on top of the high-$\kappa$ stacks, the Fermi level of TiN is lined up with the Fermi level of Si substrate at equilibrium. Because of the work function
difference between TiN and Si, band bending occurs at the Si surface. The amount of downward Si band bending is 0.28 eV shown in figure 6-30. Figure 6-30 shows the band alignment of a TiN/HfO$_2$/SiO$_2$/Si stack. From our experiments, the band alignment between TiN and HfO$_2$ was the same for all the samples. We assume that the vacuum level of TiN/HfO$_2$ interface is continuous, which does not affect our results because the TiN/HfO$_2$ interface is the same for all of our samples.

![Figure 6-30: Band alignment before applying any gate voltage of a TiN/HfO$_2$/SiO$_2$/Si stack](image)

The difference in Si band bending between the TiN/HfO$_2$/SiO$_2$/Si stacks with and without La$_2$O$_3$, as shown in figures 6-28 and 6-29, respectively, can also be explained using the dipole model. The dipole lowers the energy of the SiO$_2$ and Si. This means that there is a greater difference between the TiN and Si Fermi levels for the stacks with the La$_2$O$_3$ film, which will result in greater Si band bending after the TiN film is deposited. Figures 6-30 and 6-31 show the band diagrams of the TiN/HfO$_2$/SiO$_2$/Si stacks without
and with La$_2$O$_3$, respectively. After the TiN layer was deposited, the Si band bending was changed by 0.6 eV by adding the La$_2$O$_3$ layer, as shown in figure 6-31. Thus, the dipole model accounts for both the change in the VBO and the change in the Si band bending.

We account for the cases of intermediate band bending (5 cycles bottom La$_2$O$_3$ or 5 or 10 cycles of bottom HfO$_2$) in the following way. In these cases, the bottom layer is possibly not continuous, so the interface is a combination of HfO$_2$/SiO$_2$ and La$_2$O$_3$/SiO$_2$. Thus, there is a contribution from both polarity dipoles (HfO$_2$/SiO$_2$ and La$_2$O$_3$/SiO$_2$) at the interface and the dipole is a net dipole of these contributions.

### 6.5.2 Relationship between flat band voltage and Si band bending

Figure 6-27 has shown the experimental correlation between the flat band voltage and Si band bending. This section will discuss how the flat band voltage and Si downward
band bending are theoretically correlated. Figures 6-17 and 6-21 show that the flat band voltage and Si downward band bending are shifting in the same direction. The flat band voltage is shifting to a more negative value compared to the Si band bending, especially for a larger Si band bending value. Figure 6-32 is a diagram of a MOS structure at equilibrium, in which the Fermi level of the gate equalizes with the Fermi level of the Si substrate. When fixed charge in the oxide is neglected, the definition of flat band voltage is the work function difference between the metal and Si substrate, where the work function of Si is the energy difference between the vacuum level and Si Fermi level, which equals the electron affinity of Si (χ_s) plus the energy difference of conduction band edge (E_c) and its Fermi level (E_F). Another way to express the flat band voltage is that it equals the Si band bending (Φ_s) plus the voltage drop across the dielectrics (V_{dielectrics}).

![Diagram of a MOS structure at equilibrium](image)

**Figure 6-32: Flat band voltage definition**

\[
V_{FB} = [\Phi_m - (\chi_s + E_c - E_F)]/q = \Phi_s/q + V_{dielectrics}
\]
The Si band bending at the surface corresponds to an electric field at the Si surface that is normal to the surface. The relationship between the electric field and Si band bending at Si surface is described as:

\[ E_{Si} = \frac{\sqrt{2kT}}{qL_D} \left[ \left( e^{-\frac{q\Phi_s}{kT}} + \frac{q\Phi_s}{kT} - 1 \right) + \frac{n_0}{p_0} \left( e^{-\frac{q\Phi_s}{kT}} - \frac{q\Phi_s}{kT} - 1 \right) \right]^{1/2} \]

\[ L_D = \frac{\varepsilon_{Si}kT}{q^2p_0} \]

where \( E_{Si} \) is the electric field at Si surface, \( k \) is the Boltzmann constant, \( T \) is temperature, \( q \) is the charge of one electron, \( \Phi_s \) is the Si band bending, \( n_0 \) is the electron density in the Si bulk, \( p_0 \) is the hole density in the Si bulk, \( \varepsilon_{Si} \) is the Si dielectric constant, and \( L_D \) is called Debye length.

Figure 6-33 shows the electric field as a function of Si band bending for the samples that we used in this study, where \( p_0=10^{16}\text{cm}^{-3}, n_0=10^4\text{cm}^{-3}, \varepsilon_{Si}=11, \) and \( T=300k \). In figure 6-33, Si has upward band bending between 0 and 0.2 eV, and downward band bending between 0 and -1 eV. For the samples in this dissertation, the energy difference between the Fermi level and valence band edge is approximately 0.2 eV. It can be observed that the electric field is close to zero, except for the regions where the Fermi level is close to the conduction band edge or the valence band edge.
The electric field at Si surface is related to the electric field in the gate dielectrics. We used the boundary condition that the electric displacement (D) is continuous through all the interfaces. The electric displacement is the product of electric field and the dielectric constant of a medium. It should be noted that the effects from the fixed charge in high-κ and interface trap charges at any interfaces are ignored. Using to the boundary condition for electric displacement, the following electric field relationship can be derived:

\[ D = E \varepsilon \]

\[ D_{\text{high-k}} = D_{\text{SiO}_2} = D_{\text{Si}} \]

\[ E_{\text{high-k}} \cdot \varepsilon_{\text{high-k}} = E_{\text{SiO}_2} \cdot \varepsilon_{\text{SiO}_2} = E_{\text{Si}} \cdot \varepsilon_{\text{Si}} \]

where \( \varepsilon_{\text{high-κ}} \) equals to 20, and \( \varepsilon_{\text{SiO}_2} \) equals to 3.9.

The voltage across the SiO\(_2\) layer and high-κ layer can be written as:

\[ V_{\text{high-k}} = -E_{\text{high-k}} \cdot d_{\text{high-k}} \]

\[ V_{\text{SiO}_2} = -E_{\text{SiO}_2} \cdot d_{\text{SiO}_2} \]

Figure 6-33: Electric field as a function of Si band bending
where the thickness of high-κ is 3 nm and the thickness of SiO₂ is 1 nm. The thickness values are taken from the Aleris™ ellipsometry measurement. It should be noted that we treat the dielectric constant of La₂O₃ the same as that of HfO₂, and the total high-κ thickness is 3 nm. The voltage drop across 1 nm SiO₂ layer and 3 nm high-κ layer as a function of Si surface band bending is shown in figure 6-34.

![Figure 6-34: Voltage drop across 1nm SiO₂ and 3 nm high-κ as a function of Si surface band bending](image)

From the calculations mentioned above, the flat band voltage can be plotted as a function of Si band bending using the following equation:

\[ V_{FB}(\Phi_s) = V_{SiO_2}(\Phi_s) + V_{high-κ}(\Phi_s) + \Phi_s / q \]

Figure 6-35 shows the plot of flat band voltage as a function of Si band bending together with the measured data using XPS and C-V. It can be observed from the theoretical curve that the flat band voltage decreases monotonically with Si band bending; the ratio of flat
band voltage over the Si band bending is unity when the Si band bending is not at the extreme. The extreme Si band bending means that the Si Fermi level is close to either the conduction band edge or the valence band edge. At the extreme region, the flat band voltage changes faster than the non-extreme Si band bending region, due to the fact that the electric field in these extreme regions is strong as shown in figure 6-34. From figure 6-35, it can be observed that the agreement between the theoretical curve and experimental data is good. This agreement supports not only the ability of C-V to measure $V_{fb}$, which is well established, but the ability of XPS to measure the Si band bending, which is much less well established. Thus, XPS can be used to screen $V_T$ shift layer candidates for other materials without fabricating MOSCAP structures, which can be very costly.

![Figure 6-35: Experimental data compared to the theoretical model curve](image)

We also investigated the theoretical plat of $V_{FB}$ vs. Si band bending as a function of SiO$_2$ thickness and HfO$_2$ thickness. Figure 6-36 shows several curves, each calculated
with a different SiO$_2$ thickness. The overlay of these curves shows that there is no significant change of the curves between -0.7 eV and 0.05 eV in Si band bending. However, for the extreme band bending, a change of 2 Å in SiO$_2$ thickness alters $V_{FB}$ slightly. Figure 6-37 shows the dependence of $V_{FB}$ on HfO$_2$ thickness. It can be observed that there is no significant change of the curves between -0.7 eV and 0.05 eV in Si band bending. However, for the extreme band bending, a change of 10 Å in HfO$_2$ thickness alters $V_{FB}$ slightly.

![Figure 6-36: Dependence of flat band voltage on SiO$_2$ thickness](image_url)
6.5.3 Optimum La$_2$O$_3$ $V_T$ shift layer

It has been shown in figure 6-27 that the 15 cycle bottom La$_2$O$_3$ sample has the most negative flat band voltage value and Si band bending value, followed by the 10 and 5 cycle bottom La$_2$O$_3$ samples. However, these three samples are not ideal for a NMOS device. For a transistor with p type doping level $10^{16}$ cm$^{-3}$. The energy difference between $E_i$ and $E_f$ is 0.35 eV, so the inversion point of the Si will occur when the Si band bending is -0.7 eV. (Details of this calculation are discussed in Chapter 1. A transistor with bottom 5, 10, and 15 cycles La$_2$O$_3$ will always be on, since he Si downward band bending of these samples is more than -0.8 eV.

For the samples in this dissertation, the sample with top La$_2$O$_3$ has no effect on the flat band voltage shift compared to a pure HfO$_2$ stack. The best samples we measured for a working transistor are the samples 5 or 10 cycles of bottom HfO$_2$, as these would be
able to be turned on with a small amount of gate voltage (0.1-0.2 V) and then turned off again by removing it.

6.6 Charge density change for corresponding interface dipole moment change

According to our interpretation of the XPS measurements from TiN/HfO$_2$/SiO$_2$/Si and TiN/HfO$_2$/SiO$_2$/La$_2$O$_3$/Si stacks, as discussed in section 6.5, 15 cycles of bottom La$_2$O$_3$ can cause a 0.7eV change in the VBO which is equal to the change in the Si band bending as well as the change in the interface dipole between the high-κ and SiO$_2$ layers. Figure 6-38 shows the band alignment comparison between the stacks with and without La$_2$O$_3$. According to our model, the 15 cycles of bottom La$_2$O$_3$ results in the interface dipole change, which shifts the energy level of Si downward, thus causing a smaller HfO$_2$-Si VBO and more Si downward band bending. A change in the dipole moment indicates that the amount of charge density at the high-κ/SiO$_2$ interface is changing. It is informative to estimate the amount of change in charge density at the high-κ/SiO$_2$ that causes the 0.7 eV change in the interface dipole.
Figure 6-38: Direct comparison of band alignment between TiN/HfO₂/SiO₂/Si and TiN/HfO₂/La₂O₃/SiO₂/Si stacks

An equation that relates the change in flat band voltage to the amount of charge in the interface dipole was derived by Yamamoto et al.:

\[
\Delta V_{FB} = -\left( \frac{Q \cdot d_1}{\varepsilon_{SiO_2}} + \frac{Q \cdot x}{\varepsilon_{HfLaO_x}} \right) - \frac{Q \cdot (x - d_2)}{\varepsilon_{HfLaO_x}} = -Q \left( \frac{d_1}{\varepsilon_{SiO_2}} + \frac{d_2}{\varepsilon_{HfLaO_x}} \right),
\]

where \( \varepsilon \) is the dielectric constant of a material and \( Q \) is the charge density on each side of the dipole. This dipole is between SiO₂ and high-κ layer with the SiO₂ layer being the positive side of the dipole as shown in figure 6-39. In the equation above and shown in figure 6-39, the distance of the positive charges to the SiO₂/high-κ interface is \( d_1 \) and the distance of the negative charges to the SiO₂/high-κ interface is \( d_2 \).
This model can be used to calculate the amount of interface dipole moment change from our experiments by using:

\[
\Delta V_{\text{dipole}} = \rho e \left( \frac{d_{\text{SiO}_2}}{\varepsilon_{\text{SiO}_2}} + \frac{d_{\text{HfO}_2}}{\varepsilon_{\text{HfO}_2}} \right),
\]

where \( \Delta V_{\text{dipole}} \) is the interface dipole change between TiN/HfO\(_2\)/SiO\(_2\)/Si and TiN/HfO\(_2\)/SiO\(_2\)/La\(_2\)O\(_3\)/Si stacks. This term \( \Delta V_{\text{dipole}} \) can substrate for \( \Delta V_{\text{FB}} \) because the change in the dipole is equal to the change in the Si band bending, which to a good approximation, equals \( \Delta V_{\text{FB}} \). Also in this equation, \( \rho \) is the change in the electron areal density, \( e \) is the electron charge, and \( d \) is the distance between the charges and high-\( \kappa \)/SiO\(_2\) interface as shown in figure 6-40. The interface dipole total thickness is assumed to be 3 Å, and 1.5 Å is on each side of the high-\( \kappa \)/SiO\(_2\) interface. The dielectric constants of HfO\(_2\) and SiO\(_2\) are 20 and 3.9, respectively. The change in the electron areal density \( (\rho) \) at the high-\( \kappa \)/SiO\(_2\) interface is calculated to be \( 8.43 \times 10^{13} \text{ cm}^{-2} \) between the TiN/HfO\(_2\)/SiO\(_2\)/Si and TiN/HfO\(_2\)/SiO\(_2\)/La\(_2\)O\(_3\)/Si stacks. This value for the change in electron areal density at the high-\( \kappa \)/SiO\(_2\) interface will be referred to again later in this
section. In terms of physical interpretation, the change in charge density at the high-κ/SiO₂ interface may possibly result from a change in ion density or a change in electron density.

![Figure 6-40: Interface dipole model between SiO₂ and HfO₂](image)

A model for the ion density change was proposed by Kita et al. Figure 6-41 shows the oxygen areal density theory. In figure 6-41 (a), the high-κ layer has a lower oxygen areal density (σ) compared to the SiO₂ layer. Thus, the oxygen is transferred into the high-κ layer from the SiO₂ layer resulting in O⁻ in the high-κ layer and positively charged oxygen vacancies in the SiO₂ layer as shown in figure 6-41 (b). This shift in the oxygen atoms causes the interface dipole between high-κ and SiO₂ as shown in figure 6-41 (c).

![Figure 6-41: Oxygen areal density by Kita et al.](image)

Figure 6-41: Oxygen areal density by Kita et al. (Image is from K. Kita and A. Toriumi, "Origin of electric dipoles formed at high-k/SiO₂ interface," Applied Physics Letters 94, 132902 (2009))
Oxygen areal densities for several oxides are shown in figure 6-42 (b). It can be observed that HfO₂ has a greater oxygen areal density than SiO₂. Therefore, there will be oxygen transferred from the HfO₂ to SiO₂, resulting in a dipole with negative charges in the SiO₂ side. It can also be observed that La₂O₃ has a lower oxygen areal density than SiO₂. In this case, the oxygen atoms will be transferred into the La₂O₃ from the SiO₂ layer, resulting in a dipole with positive charges in the SiO₂ side. The polarities of these dipoles are consistent with the model that we used to accounts for our results.

![Figure 6-42: correlation between V_{FB} shift and normalized oxygen areal density](Image is from K. Kita and A. Toriumi, "Origin of electric dipoles formed at high-k/SiO₂ interface," Applied Physics Letters 94, 132902 (2009))

A quantitative comparison between the calculation of the change in electron density at the high-κ/SiO₂ interface and the oxygen areal density model of Kita et al can be made in the following way. First, the density of HfO₂ molecules in solid HfO₂ is estimated by multiplying mass density of HfO₂ (9.68 g/cm³), the molecular mass (210 g/mol) of HfO₂ and Avogadro’s number. Raising this density to the 2/3 power converts it to an areal density, and multiplying it by 2 (for the number of O atoms in a molecule) gives the areal density of O atoms in HfO₂, which is 1.9x10^{15} cm⁻². By assuming that each O atom that is transferred across the high-κ/SiO₂ interface carries a single net negative charge (O⁻), the change in the O areal density required to change the interface dipole by 0.7 eV is equal to the change in electron areal density (calculated above, 8.43x10^{13} cm⁻²). Dividing this
change in O areal density by the O areal density in solid HfO$_2$ gives a percent change of 4.4%.

The percentage change in O areal density between the HfO$_2$/SiO$_2$ and La$_2$O$_3$/SiO$_2$ interfaces can also be estimated from the normalized O areal densities for HfO$_2$ and La$_2$O$_3$ determined by Kita et al., as shown in figure 6-42b. For the HfO$_2$/SiO$_2$ (La$_2$O$_3$/SiO$_2$) interface, the normalized O areal density concentration will be 1.1 (0.95), which is the midpoint between the normalized O areal density for HfO$_2$ (La$_2$O$_3$) and that for SiO$_2$. Thus, the difference between the normalized O areal densities for these interfaces divided by that for HfO$_2$/SiO$_2$ corresponds to a 12.5% change in O areal density. A comparison of the percentage O areal density changes calculated based on the models of Yamamoto et al. Kita et al. shows that these two values differ by a factor of ~3. Thus, they can be considered to agree on the basis of an order of magnitude comparison.

Another theory, which explains the formation of the dipole by a transfer of electrons, is group electronegativity theory as proposed by Jagannathan et al. Electronegativity is defined as the ability of an atom or molecule to attract electrons. Higher electronegativity values indicate stronger attractions for electrons. Table 6-3 shows the Pauling electronegativities of several elements and group electronegativities of several compounds for selected V$_T$ shift layers. According to group electronegativity theory, HfO$_2$ will give up negative charges to SiO$_2$ due to its lower group electronegativity, resulting in a dipole with the negative charges on the SiO$_2$ side. The group electronegativity of La$_2$O$_3$ is even less than that of HfO$_2$, which would result in a stronger dipole with the negative charges on the SiO$_2$ side. According to our model, the La$_2$O$_3$
interface results in a dipole with the positive charge on the SiO₂ side. Thus, our results can not be explained by the group electronegativity theory.

A second issue with the group electronegative theory is that the HfO₂ and Al₂O₃ have very similar electronegativities (2.49 and 2.54, respectively) while those of HfO₂ and MgO are significantly different (2.49 and 2.12, respectively). According to the results shown in figure 6-2, the shifts in flat band voltage by adding MgO capping layer and adding Al₂O₃ capping layer are roughly equal in magnitude and opposite in direction. Thus, there is poor quantitative agreement between the shifts in flat band voltage and the differences in group electronegativity.

Table 6-3: Group electro-negativities of various materials (Table is from H. Jagannathan, V. Narayanan, and S. Brown, "Engineering High Dielectric Constant Materials for Band-Edge CMOS Applications," ECS Trans. 16 (5), 19-26 (2008))

<table>
<thead>
<tr>
<th>Element</th>
<th>Pauling Electronegativity</th>
<th>Dielectric Cap AₓBᵧ</th>
<th>Geometric Mean Electronegativity (Sanderson Criterion) (A'B')¹/ₓ⁺ᵧ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>0.89</td>
<td>BaO</td>
<td>1.75</td>
</tr>
<tr>
<td>La</td>
<td>1.1</td>
<td>LaN</td>
<td>1.83</td>
</tr>
<tr>
<td>Mg</td>
<td>1.31</td>
<td>MgO</td>
<td>2.12</td>
</tr>
<tr>
<td>Sr</td>
<td>0.95</td>
<td>La₂O₃</td>
<td>2.18</td>
</tr>
<tr>
<td>Hf</td>
<td>1.3</td>
<td>SrTiO₃</td>
<td>2.26</td>
</tr>
<tr>
<td>Al</td>
<td>1.61</td>
<td>HfO₂</td>
<td>2.49</td>
</tr>
<tr>
<td>Ti</td>
<td>1.54</td>
<td>Al₂O₃</td>
<td>2.54</td>
</tr>
<tr>
<td>Si</td>
<td>1.9</td>
<td>Al₂N</td>
<td>2.56</td>
</tr>
<tr>
<td>O</td>
<td>3.44</td>
<td>TiO₂</td>
<td>2.63</td>
</tr>
<tr>
<td>N</td>
<td>3.04</td>
<td>SiO₂</td>
<td>2.82</td>
</tr>
</tbody>
</table>

6.7 Summary

Through the C-V and XPS measurements of TiN/HfO₂/La₂O₃/SiO₂/p-Si stacks, where the amount and position of the La₂O₃ layer was varied, we have observed a trend that as the amount of bottom La₂O₃ is increased, both the flat band voltage and the Si band
bending become more negative, and as the amount of bottom HfO$_2$ is increased, both the flatband voltage and the Si band bending become less negative. The flat band voltage shifts and the Si band bending are correlated.

We also observed a trend in which the HfO$_2$-Si VBO decreases with an increase in the amount of bottom La$_2$O$_3$ and increase with the amount of bottom HfO$_2$. These trends can both be accounted for by a band alignment model, where there is a dipole at the La$_2$O$_3$/SiO$_2$ interface. This model is consistent with several reports in the literature, which propose the formation of a dipole at the La$_2$O$_3$/SiO$_2$ interface.\textsuperscript{20,22}

The La$_2$O$_3$ changes the dipole moment, and the interface dipole changes the band alignment between Si and HfO$_2$. In this way, La$_2$O$_3$ shifts the Si energy level downwards relative to HfO$_2$. This downward shift in Si energy level is the reason for the increased Si downward band bending with the addition of La$_2$O$_3$. By developing a theoretical model for flat band voltage vs. Si band bending, we showed that the relationship between the flat band voltages and Si band bending that we measured agrees with the theoretical curve.

6.8 References


Chapter 7: The effect of the SiO$_2$ layer on the threshold voltage of TiN/HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stacks

7.1 Introduction

As discussed in Chapter 6, there is strong evidence that the cause of the La$_2$O$_3$ induced $V_T$ shift is a change of the dipole moment at the high-$\kappa$/SiO$_2$ interface. The mechanism for the formation of this change in the dipole moment is still not well understood. Various mechanisms for the dipole have been proposed\textsuperscript{118,119} such as oxygen areal density theory,\textsuperscript{122} oxygen vacancies,\textsuperscript{123} group electronegativity,\textsuperscript{124} and chemical bonding.\textsuperscript{120,121} In addition to the proposed mechanisms, ab initio calculations on atomic models have been performed to support experimental results.\textsuperscript{125} However, the proposed explanations for the formation of the dipole do not give a satisfactory explanation of the experimental results. Thus, the mechanism for the formation of the dipole is still under investigation.

In Chapter 6, it was shown that varying the amount and position of La$_2$O$_3$ affects the flat band voltage of high-$\kappa$/metal gate stacks; and this change was attributed to a changing dipole at the high-$\kappa$/SiO$_2$ interface. Another way to possibly alter this interface is by varying the SiO$_2$ layer. In the majority of the published studies, the SiO$_2$ layer is kept constant for a given study.\textsuperscript{21,22,118,130} However, Iwamoto et al., fabricated stacks with both 1 nm and 4 nm thick SiO$_2$ layers, and observed the same threshold voltage shift for both SiO$_2$ thicknesses.\textsuperscript{20} Also, Yamamoto et al, measured stacks with 1 and 10 nm thick SiO$_2$ layers and also observed the same threshold voltage shift.\textsuperscript{117} An issue with
these studies, though, is that they probed a range of SiO$_2$ thicknesses that are not used in CMOS devices employing HfO$_2$. Abe and Miyata probed SiO$_2$ thicknesses from 10 nm all the way to no SiO$_2$ layer by slowly withdrawing a wafer from the HF solution from one side of the wafer to the other side. An HfO$_2$ film was grown on top of this graded SiO$_2$ layer, and metal gates were deposited so that C-V measurements could be made at various locations on the wafer. While this study examined the SiO$_2$ layers of relevant device thicknesses (<1 nm), the growth method (thermal oxidation and etching) of the SiO$_2$ layer was not what is used in devices. We have performed a study comparing stacks with three different thermal SiO$_2$ (12, 20, 30 Å) with stacks with 8 Å chemically grown silicon oxides in order to compare the effect of the thickness and the growth method of the SiO$_2$ layer. All the samples that will be discussed in this chapter are shown in table 7-1.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>SiO$_2$ thickness (Å)</th>
<th>La$_2$O$_3$ cycle #</th>
<th>HfO$_2$ cycle #</th>
<th>TiN thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8</td>
<td>0</td>
<td>40</td>
<td>50</td>
</tr>
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<td>12</td>
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</tr>
<tr>
<td>3</td>
<td>8</td>
<td>15</td>
<td>40</td>
<td>50</td>
</tr>
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<td>4</td>
<td>8</td>
<td>10</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
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</tr>
<tr>
<td>8</td>
<td>30</td>
<td>15</td>
<td>40</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 7-1: Sample sets to investigate how SiO$_2$ affects flat band voltage of high-$\kappa$ metal gate stacks

7.2 Effect of SiO$_2$ on HfO$_2$/SiO$_2$/Si stacks

Both XPS and C-V measurements were performed on the samples in table 7-1. For the XPS measurements, the thickness of the TiN layers was 3 nm. The XPS measurements were taken from at beam line X-24A of the NSLS at BNL and the Thermo
Fisher Theta Probe™ XPS system at the CNSE. The C-V measurements were performed on the samples with 500nm TiN layers using the Agilent Technologies 4284A LCR meter. Figure 7-1 shows the comparison of BNL XPS spectra from TiN/HfO$_2$/SiO$_2$/Si stacks with a nominal 8 Å chemically grown SiO$_2$ layer and a nominal 12 Å thermally grown SiO$_2$ layer. (samples 1 and 2 in table 7-1, respectively). The peak energy of Si 2p 3/2 for sample 1 is 99.24 eV (Si band bending of -0.20 eV), and the peak energy of Si 2p 3/2 for sample 2 is 99.21 eV (Si band bending of -0.17 eV). Thus, the sample with the chemical oxide shows slightly greater negative band banding. Figure 7-2 shows the comparison of CNSE XPS spectra between samples 1 and 2 in table 7-1, The peak energy of Si 2p for sample 1 is 99.51 eV (Si band bending of -0.37 eV), and the peak energy of Si 2p for sample 2 is 99.37 eV (Si band bending of -0.23 eV). These measurements show that sample with the chemical oxide has more downward Si band bending by 0.14 eV. It was shown in Chapter 6 that the flat band voltage and Si band bending measurements agree relative well with each other, though for greater Si band bending, they differ more. A detailed model describing the relationship between the two parameters was given in Chapter 6. In this Chapter, however, they will both be considered as measures of the Si band bending which is a reasonable approximation.

The difference between the Si band bending measured between identical samples at BNL and the CNSE can be attributed to the greater depth sensitivity of the measurement at BNL. One factor in this greater depth sensitivity is that X-ray energy we used at BNL (2140.0 eV) was ~650 eV greater than that used the CNSE (1486.7 eV), which means the electron attenuation length ($\lambda$) of the photoelectrons was longer at BNL. Another factor was that emission angle ($\theta$) was smaller at BNL ($5^\circ$) than at the CNSE ($42^\circ$). The factors
increase the intensity \( (I) \) of photoelectrons emitted from a given depth according to the equation:

\[
I = I_0 e^{-d/\lambda \cos \theta},
\]

where \( I_0 \) is the intensity of photoelectrons from the surface.

Figure 7-1: X24A XPS spectra for 30 Å TiN/40 cycle HfO₂/12 Å SiO₂/Si and 30 Å TiN/40 cycle HfO₂/8 Å SiO₂/Si
The C-V curves from the samples with the 8 Å chemical oxide and with the 12 Å thermal oxide (9 points per sample) are shown in figure 7-3. It can be observed that the C-V curves from the sample with the chemical oxide are shifted negatively from those with the thermal oxide. A flat band voltage was extracted from each curve, and the flat band voltages from the 9 points were averaged. The flat band voltage values of each sample in table 7-1 are shown in table 7-2. The flat band voltage for sample with the chemical oxide is -0.28 eV, and that for the sample with the thermal oxide is -0.15 eV. These results show that the sample with the chemically oxide has greater downward Si band bending by 0.13 V.
Table 7-2: Flat band voltage values measured from C-V tests

<table>
<thead>
<tr>
<th>Sample #</th>
<th>SiO2 thickness (Å)</th>
<th>La2O3 cycle #</th>
<th>HfO2 cycle #</th>
<th>TiN thickness (nm)</th>
<th>Mean Vfb</th>
<th>Max Vfb</th>
<th>Min Vfb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8</td>
<td>0</td>
<td>40</td>
<td>50</td>
<td>-0.28</td>
<td>-0.26</td>
<td>-0.30</td>
</tr>
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<td>2</td>
<td>12</td>
<td>0</td>
<td>40</td>
<td>50</td>
<td>-0.15</td>
<td>-0.16</td>
<td>-0.14</td>
</tr>
<tr>
<td>3</td>
<td>8</td>
<td>15</td>
<td>40</td>
<td>50</td>
<td>-1.11</td>
<td>-1.08</td>
<td>-1.12</td>
</tr>
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<td>4</td>
<td>8</td>
<td>10</td>
<td>40</td>
<td>50</td>
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<td>-1.03</td>
<td>-1.07</td>
</tr>
<tr>
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<td>-0.63</td>
</tr>
<tr>
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</tr>
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<td>50</td>
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<td>15</td>
<td>40</td>
<td>50</td>
<td>-0.73</td>
<td>-0.74</td>
<td>-0.73</td>
</tr>
</tbody>
</table>

Figure 7-3: C-V curve for 30 Å TiN/40 cycle HfO2/12 Å thermal SiO2/Si and 30 Å TiN/40 cycle HfO2/8 Å chemical SiO2/Si stacks

To summarize, the BNL XPS indicates the Si band bending is essentially the same for the chemical SiO2 and thermal SiO2 samples. According to CNSE XPS, the chemical oxide sample has -0.14 eV more downward band bending than the thermal oxide sample. The C-V results show that there is more downward Si band bending, which agrees well with the CNSE XPS data.
The XPS and C-V results can be compared with results from Abe and Miyata, who performed C-V measurements on Ir/HfO$_2$/SiO$_2$/Si stacks, where the SiO$_2$ thickness was graded from 0-10 nm with a top constant thick HfO$_2$ layer. Results from Abe and Miyata are shown in figure 7-4. It can be observed that the C-V curves shift toward the positive direction with increasing SiO$_2$ thickness for curves with inflection points between 0.5 to 0.7 V. For the curves with inflection points at approximately 0.9 V, increasing the thickness of SiO$_2$ did not shift the curve.

![Graph showing C-V curves from Ir/HfO$_2$/SiO$_2$/Si stack with various SiO$_2$ thicknesses.](image)

**Figure 7-4**: C-V curves from Ir/HfO$_2$/SiO$_2$/Si stack with various SiO$_2$ thicknesses (Image is from Y. Abe and N. Miyata, "Dipole formation at direct-contact HfO$_2$/Si interface," Appl. Phys. Lett. 90, 172906 (2007))

The flat band voltage values extracted from the C-V curves in figure 7-4 are shown in figure 7-5. It can be observed that the flat band voltage is a constant when the SiO$_2$ thickness is above 7 Å, and the flat band voltage decreases with decreasing SiO$_2$ thickness when SiO$_2$ thickness is below 7 Å. This flat band voltage shift is attributed to an interface dipole at HfO$_2$/Si interface. The result in figure 7-5 agrees with our observation that there is a reduction in the flat band voltage by -0.15 V for the chemical
oxide (8 Å) stack compared with the thermal oxide (12 Å) stack, but in our case, the SiO$_2$ thickness where the flat band voltage drop off occurs is slightly larger than 7 Å.

![Figure 7-5: flat band voltage as a function of SiO$_2$ thickness](Image is from N. Miyata, Y. Abe, and T. Yasuda, "Conductance spectroscopy study on interface electronic states of HfO$_2$/Si structures: comparison with interface dipole," Applied Physics Express 2, 035502 (2009))

### 7.3 Effect of 8 Å and 12 Å SiO$_2$ on the flat band voltage shift of HfO$_2$/La$_2$O$_3$/SiO$_2$ stacks

In order to investigate the effect of the SiO$_2$ layer on the stacks containing bottom La$_2$O$_3$, a TiN/HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stack with an 8 Å chemical oxide layer was compared with one with a 12 Å thermal oxide layer (samples 3 and 6, respectively). The SiO$_2$ thicknesses of the two stacks were measured using SE. Details of the SE measurements are shown in Appendix V. Figure 7-6 shows the comparison of XPS spectra from BNL between samples with the chemical and thermal oxides. The peak energy of Si 2p 3/2 for the chemical oxide sample is 99.81 eV (Si band bending is -0.77 eV), and the peak energy of Si 2p 3/2 for the 12 Å thermal oxide sample is 99.44 eV (Si band bending is -0.40 eV). Thus, that the chemical oxide sample has 0.37 eV more Si downward Si band bending, which is notable as the difference in Si band bending due to the difference in SiO$_2$ layers for TiN/HfO$_2$/SiO$_2$/Si samples was only 0.03 eV according to the BNL data.
Before continuing the comparison between the TiN/HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stacks with the chemical oxide and 12 Å thermal oxide samples further, an observation concerning figure 7-6 should be noted. It can be observed from figure 7-6 that the La 4d 3/2 peak at 107 eV binding energy from chemical oxide sample is higher than that of the thermal oxide sample. This indicates that the amount of La$_2$O$_3$ on chemical oxide is greater than that on thermal oxide. In order to make a better comparison between effects of the different SiO$_2$ layers, the amount of La$_2$O$_3$ should be the same on each sample. Figure 7-7 shows spectra from samples with 15, 10, and 5 cycles of La$_2$O$_3$ on 8 Å chemical oxide (samples 3, 4 and 5, respectively) and 15 cycle La$_2$O$_3$ on 12 Å thermal oxide (sample 6). By comparing the La 4d 3/2 in these spectra, it can be observed that the peak intensity for the 10 cycle La$_2$O$_3$ on chemical oxide sample is the same as 15 cycle La$_2$O$_3$ on thermal oxide. This indicates that the La$_2$O$_3$ thicknesses for these samples are the same. SE and RBS measurements also confirm that the amount of La$_2$O$_3$ is the same for the two samples. The Si 2p 3/2 binding energy of the sample 4 is 99.79 eV (Si band bending of -0.75 eV), which differs of sample 6 by 0.35 eV, which is larger than the difference between the Si band bending in the TiN/HfO$_2$/SiO$_2$/Si samples with the chemical oxide and thermal oxide layers (samples 1 and 2, respectively) measured at BNL (0.03 eV). The Si 2p peak from sample 1 measured at the CNSE had 100.03 eV, which indicates a Si band bending of -0.89 eV. The Si 2p peak from sample 2 measured at the CNSE had a binding energy of 99.70 eV, which gives a Si band bending of -0.56 eV. The difference between these two Si band bending values is consistent with the difference between the values measured at BNL. Again, we attribute the greater band bending measured at the CNSE to the greater bulk sensitivity of the measurement at BNL.
The C-V curves of from the TiN/HfO$_2$/La$_2$O$_3$/SiO$_2$/Si samples with the chemical and thermal oxide layers (samples 4 and 6, respectively) are shown in figure 7-8. It can be seen that the C-V curves from the sample with the chemical oxide layer (sample 4) are shifted negatively with respect to those from the sample with the thermal oxide (sample 6). The flat band voltage of sample 4 is -1.05V, and the flat band voltage of sample 5 is -0.73V. The difference between the two values is -0.32 V. Thus, both the XPS and C-V results show that there is greater downward band bending for TiN/HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stacks with chemical oxide layers. Furthermore, the difference in Si band bending for stack with a chemical and a stack with a thermal oxide is greater for stacks with bottom La$_2$O$_3$ (samples 4 and 6) than without bottom La$_2$O$_3$ (samples 1 and 2).

![Figure 7-6: XPS spectra for TiN/HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stacks.](image)

**Figure 7-6:** X-24A XPS spectra for 30 Å TiN/40 cycle HfO$_2$/15 cycle La$_2$O$_3$/12 Å SiO$_2$/Si and 30 Å TiN/40 cycle HfO$_2$/15 cycle La$_2$O$_3$/8 Å SiO$_2$/Si.
Figure 7-7: X-24A XPS spectra for 30 Å TiN/40 cycle HfO₂/15 cycle La₂O₃/12 Å SiO₂/Si, 30 Å TiN/40 cycle HfO₂/5 cycle La₂O₃/8 Å SiO₂/Si, 30 Å TiN/40 cycle HfO₂/10 cycle La₂O₃/8 Å SiO₂/Si, and 30 Å TiN/40 cycle HfO₂/15 cycle La₂O₃/8 Å SiO₂/Si

Figure 7-8: C-V curves for samples 4 and 6 in table 7-1
The difference between the downward Si band bending in TiN/HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stacks with thermal and chemical oxide layers raises the question of whether this difference is due to a difference in thickness of the SiO$_2$ or the difference in chemistry. In order to investigate the effect of the thickness of the SiO$_2$ on the flat band voltage of HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stacks, stacks with 12, 20, 30 Å of thermal oxide were measured with C-V. Figure 7-9 shows the C-V curves from these samples taken from the center point of each sample. It appears that these curves are not shifted significantly with respect to each other. Extracted flat band voltages for these samples are -0.73, -0.74, and -0.73 V for the 12, 20, and 30 Å oxide samples (samples 6, 7 and 8), respectively. This comparison shows that increasing the thickness of thermal oxide from 12 to 30 Å does not change the flat band voltage. This result agrees with other results that show no thickness dependence on the SiO$_2$ layer for stacks with capping layers with SiO$_2$ thicknesses greater than 1nm. $^{20,117}$
7.4 Discussion

The question still remains about whether it is the thickness difference between the 8 Å chemical oxide and 12 Å thermal oxide or the chemistry between the two SiO$_2$ films that causes the in the flat band voltage. It has been shown in the literature that SiO$_2$ below 1nm has a high percentage of Si atoms that are not fully bonded with O (referred to as sub-oxide). Muller et al have shown this using scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS). Figures 7-10 shows an STEM image of SiO$_2$/Si and two EELS spectra. One EELS spectrum was taken at a position that the STEM image shows to be at the SiO$_2$/Si interface. Another EELS spectrum was taken from what appears to be the SiO$_2$ film. These spectra clearly differ. Figure 7-11 shows another STEM image and corresponding EELS spectra. Two EELS spectra, taken from the SiO$_2$ film show a bulk-like SiO$_2$ spectrum, but the EELS spectra
taken above and below the positions from which the bulk-like spectra were taken show very different spectra. This analysis shows that for very thin SiO$_2$ (~10 Å or less), there is a high percentage of sub-oxide.

The difference in the chemistry between a chemical and a thermal SiO$_2$ layer can be studied with XPS. Figure 7-12 shows normalized XPS spectra from three samples; they are hydrogen terminated silicon, silicon with 8 Å chemical oxides, and silicon with 12 Å thermal oxide. It can be observed that the Si 2p peak corresponding to the SiO$_2$ layer (binding energy ~103 eV) is greater for thermal SiO$_2$ than chemical SiO$_2$, indicating that the thermal oxide is thicker. It can also be observed that the SiO$_2$ peak binding energy of chemical SiO$_2$ is lower than that of thermal SiO$_2$. This suggests that the thermal SiO$_2$ has more Si that is fully bonded with O. 58 Thus, the question of whether the thickness or the chemistry is responsible for the difference in stacks with chemically and thermally grown oxide layers is difficult to answer because the chemistry of the SiO$_2$ layer is unavoidably altered as it becomes thinner than 10 Å. In addition, sub 10 Å SiO$_2$ layers grown by chemical and thermal methods can not be compared because the minimum thickness for thermally grown oxide is approximately 12 Å. 134

It has been proposed that the amount of O at the interface between the HfO$_2$ and SiO$_2$ layers can be an important factor in the strength of the interface dipole. Demkov et al performed calculations which showed that the band offset at the HfO$_2$/SiO$_2$ interface can change by as much as 2.8 eV based on the amount of O at the interface. 135 Similarly, it could be that a lower amount of O at the La$_2$O$_3$/SiO$_2$ interface for the stacks with the chemical SiO$_2$ layers would result in a stronger dipole at that interface, which would result in greater Si band bending.
Figure 7-10: EELS O K edge difference between interface SiO$_2$ and bulk SiO$_2$ at an atomic smooth interface 5 (Image is from D. A. Muller, T. Sorsch, S. Moccio, F. H. Baumann, K. Evans-Lutterodt, and G. Timp, "The electronic structure at the atomic scale of ultrathin gate oxides," Nature 399 (24), 758-761 (1999))

Figure 7-11: EELS spectra of ultra thin SiO$_2$ 5 (Image is from D. A. Muller, T. Sorsch, S. Moccio, F. H. Baumann, K. Evans-Lutterodt, and G. Timp, "The electronic structure at the atomic scale of ultrathin gate oxides," Nature 399 (24), 758-761 (1999))


7.5 Summary

In this chapter it was shown that thermal and chemical SiO$_2$ films have different impact on the flat band voltage shift of TiN/HfO$_2$/SiO$_2$/Si and TiN/HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stacks. The chemical SiO$_2$ has a more Si downward Si band bending than the thermal SiO$_2$ by 0.15 eV for the stacks without La$_2$O$_3$. This is consistent with the results from Abe and Miyata. For the TiN/HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stacks, the flat band voltage of stacks with 12, 20, and 30 Å thermal SiO$_2$ have the same flat band voltage values. The TiN/HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stack with chemical SiO$_2$ has a more Si downward band bending than the thermal SiO$_2$ for more than 0.3 eV. This is possibly due to the fact that chemical oxide, which is less than 10 Å thick, has more suboxide than the thermal oxide.

7.6 References


Chapter 8: Summary and future research directions

In this dissertation, a combination of capacitance-voltage (C-V) and X-ray photoelectron spectroscopy (XPS) measurements was used to study how La$_2$O$_3$ shifts the flat band voltage of TiN/HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stacks. C-V was used to measure the flat band voltage of TiN/HfO$_2$/La$_2$O$_3$/SiO$_2$/Si and TiN/HfO$_2$/SiO$_2$/Si stacks, and XPS was used to measure the Si band bending and HfO$_2$-Si valence band offset (VBO). The measurements yielded results that could be explained by a band alignment model with a dipole at the high-κ/SiO$_2$ interface. The relationship between the experimental flat band voltage and Si band bending was compared with the theoretical relationship between these two quantities and the two agree well.

In order to achieve the research goals mentioned above, several metrology techniques were employed in this research. These techniques include spectroscopic ellipsometry (SE), X-ray reflectivity (XRR), Rutherford backscattering spectroscopy (RBS), X-ray photoelectron spectroscopy (XPS), angle-resolved XPS (ARXPS), capacitance-voltage (C-V), and transmission electron microscopy (TEM). The high-κ films are grown by Tokyo Electron Limited (TEL) using atomic layer deposition (ALD) and chemical vapor deposition (CVD) techniques, and the metal gate TiN films were grown using CVD technique.

The first part of the research was to measure the thicknesses SiO$_2$ and HfO$_2$ simultaneously for a HfO$_2$/SiO$_2$/Si stack. By having the vacuum ultraviolet (VUV) (150nm-240nm) part of the light, the correlation between SiO$_2$ thickness and HfO$_2$ thickness was reduced. The measurement errors of the SE measurement on SiO$_2$ and
high-κ films were evaluated by performing a precision measurement. The SE measurements of high-κ thickness were confirmed with XRR, and the SE measurements of SiO₂ thickness were confirmed by ARXPS. TEM was also used to measure HfO₂ and SiO₂ thicknesses, and the results were consistent with those from SE.

The second part of the research was to measure the SiO₂, La₂O₃ and HfO₂ thicknesses for HfO₂/La₂O₃/SiO₂/Si and La₂O₃/HfO₂/SiO₂/Si stacks. It was found that the layer-by-layer modeling strategy of SE measurements can accurately measure the film thicknesses in these stacks. The simultaneous modeling and BEMA modeling approaches were not able to separate the thicknesses of the La₂O₃ and HfO₂ due to the similar optical properties of these two materials. The SE results from the layer-by-layer modeling were consistent with the RBS characterization of these stacks. It should be noted that we also performed XRR and TEM on the HfO₂/La₂O₃/SiO₂/Si and La₂O₃/HfO₂/SiO₂/Si stacks, and these two techniques were also not able to measure the La₂O₃ and HfO₂ simultaneously.

The third aspect was the measurement of band gap of the HfO₂ films by SE. There are several methods to extrapolate the band gap of HfO₂ and systematic differences exist between these methods as discussed in Chapter 5. The band gap measurement of HfO₂ is important because it can be combined with the XPS measurement of a HfO₂-Si or HfO₂-SiO₂ VBO to find the corresponding conduction band offsets (CBOs).

The three previous are included in the next goal of this research, which was to understand how La₂O₃ affects the threshold voltage of a TiN/HfO₂/La₂O₃/SiO₂/Si stack. A set of samples was designed that systematically varied the amount of La₂O₃ as well as the position of La₂O₃ within high-κ/metal gate stacks. A combination of C-V and XPS
measurements were performed on the TiN/HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stacks. C-V can measure the flat band voltage of high-$\kappa$/metal gate stacks, but it does not provide additional information about how the flat band voltage is shifted. By performing the XPS measurements, it was observed that the downward Si band bending increased as more La$_2$O$_3$ was deposited between the HfO$_2$ and SiO$_2$. It was also observed that the downward Si band bending decreased when HfO$_2$ was deposited between the La$_2$O$_3$ and SiO$_2$ layers. The Si band bending was found to agree well with the flat band voltage when the band bending was small, but to differ more when the band bending was larger. A theoretical model was developed to account for the experimental relationship between Si band bending and flat band voltage. This dissertation is the first documentation quantitatively correlating the flat band voltage with the Si band bending for high-$\kappa$/metal gate stacks with La$_2$O$_3$ capping layers.

A model was also developed to account for the trends observed in the XPS measurements of the Si band bending and the HfO$_2$-Si VBO. In this model, the La$_2$O$_3$ changes the interface dipole between HfO$_2$ and SiO$_2$, which changes the band alignment. The band alignment change alters the Fermi level of Si substrate relative to the rest of the stack, and thus it changes the Si band bending and the flat band voltage.

This dissertation also provides the first data showing that different SiO$_2$ chemistry affects the flat band voltage and Si band bending for TiN/HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stacks. While the thickness of thermal SiO$_2$ has very limited effect on the flat band voltage of high-$\kappa$/metal gate stacks, a chemically grown SiO$_2$ is causes greater negative flat band voltage and negative Si band bending. This is most likely due to the significant fraction of sub-oxide in chemically grown SiO$_2$ layers that are less than 1 nm thick.
One future research direction of this research will be to investigate the surface coverage measurement of La$_2$O$_3$ and HfO$_2$ films on SiO$_2$. It has been discussed in this dissertation that the high-κ/SiO$_2$ interface is the key for the threshold voltage shift, and that small amounts (5 cycles) of La$_2$O$_3$ and HfO$_2$ at the interface can shift the flat band voltage by several tenths of a volt. What is not clear is how many cycles of La$_2$O$_3$ or HfO$_2$ are needed to give a continuous layer, as it is likely that there is not a continuous layer for depositions of 5 and 10 cycles. Possible metrologies for this task include low energy ion scattering spectroscopy (LEIS), which is very sensitive to surface coverage, and ARXPS. Though ARXPS has been used to determine fractional coverages, it has certain limitations such as assuming cylindrical shapes for the islands on SiO$_2$.

Another future research direction is to study the chemistry of the TiN/HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stacks. Since the chemistry of the SiO$_2$ chemistry affects the band alignment of high-κ/metal gate stacks directly. It is important to study how the deposition of the La$_2$O$_3$, HfO$_2$, and TiN layers affects the oxygen concentration within the SiO$_2$. Another technique we are considering for future research is IR spectroscopic ellipsometry (IRSE). This technique is capable of studying specific chemical bonds in a solid, and may provide information about the bonding at the high-κ/SiO$_2$ interface. These investigations of the chemistry within the TiN/HfO$_2$/La$_2$O$_3$/SiO$_2$/Si stacks may be of use in the study of the physical origin of the flat band voltage shift, which is likely a dipole at the high-κ/SiO$_2$ interface.
Appendices

Appendix I: Determination of the measurement precision of high-κ thickness using KLA-Tencor Aleris™

In order to study the precision of SE thickness measurement on High-κ films, the Aleris™ tool was used. The wavelength of the Aleris™ 8500 ranges from 150 nm to 800 nm. Wavelength from 150 nm - 235 nm is the VUV (Vacuum Ultraviolet) region. The Aleris™ also has a laser desorber option to remove surface airborne molecular contamination (AMC) layer. The measurements reported in this discussion are from the following samples: annealed 40Å HfO₂/10Å SiO₂/Si, unannealed 40Å HfO₂/10Å SiO₂/Si, and 13Å SiO₂/Si. The multilayer structures with the HfO₂ films on top will be referred to as HfO₂ stacks.

For the precision test, a set of 36 matrix points (6 by 6 points array) are set up in the center of a wafer. The distance between two adjacent points is 150 μm. Each point was measured three times before moving to the next point, and these three measurements were averaged to give the measurement for that point. The 36 points are measured without taking a wafer off the wafer stage. Two different sets of measurements are performed on each wafer. For one of these sets, the laser desorber was used before the measurement of each of the 36 points. For the other set, the laser desorber was not used. It should also be noted that the sites measured with and without laser desorber were separated from each other by several mm.
The measurement results from 36 points are compared to each other. The percentage standard deviation of the 36 measurements is calculated to evaluate the tool’s precision. It is assumed that the sample is uniform in the small area where the 36 points are measured. The measurement results of the three samples are shown in table I-1. It can be observed that the precision of the Aleris™ is high. In most cases, a percentage standard deviation is 0.7% or below.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean SiO₂ Thickness (Å)</th>
<th>Mean HfO₂ Thickness (Å)</th>
<th>% Standard deviation of SiO₂</th>
<th>% Standard deviation of HfO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unannealed HfO₂/SiO₂/Si*</td>
<td>14.1</td>
<td>45.5</td>
<td>0.2</td>
<td>0.04</td>
</tr>
<tr>
<td>Unannealed HfO₂/SiO₂/Si**</td>
<td>13.3</td>
<td>45.8</td>
<td>0.3</td>
<td>0.06</td>
</tr>
<tr>
<td>Annealed HfO₂/SiO₂/Si*</td>
<td>13.8</td>
<td>41.8</td>
<td>0.7</td>
<td>0.1</td>
</tr>
<tr>
<td>Annealed HfO₂/SiO₂/Si**</td>
<td>13.7</td>
<td>41.9</td>
<td>0.3</td>
<td>0.08</td>
</tr>
<tr>
<td>13Å SiO₂**</td>
<td>13.4</td>
<td>0</td>
<td>0.3</td>
<td>0</td>
</tr>
<tr>
<td>13Å SiO₂*</td>
<td>14.0</td>
<td>0</td>
<td>0.1</td>
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</tr>
</tbody>
</table>

Table I-1: Static repeatability gauge study result summary. (*no laser desorber, **with laser desorber)
Appendix II: XRR and ARXPS figures from Chapter 3

XRR Spectra of HfO₂/SiO₂ stacks in chapter 3:

Figure II-1: 20Å unannealed HfO₂/10Å SiO₂/Si

Figure II-2: 20Å unannealed HfO₂/20Å SiO₂/Si
Figure II-3: 20 Å unannealed HfO$_2$/30 Å SiO$_2$/Si

Figure II-4: 20 Å annealed HfO$_2$/10 Å SiO$_2$/Si
Figure II-5: 20 Å annealed HfO$_2$/20 Å SiO$_2$/Si

Figure II-6: 20 Å annealed HfO$_2$/30 Å SiO$_2$/Si
Figure II-7: 30 Å unannealed HfO$_2$/10 Å SiO$_2$/Si

Figure II-8: 30 Å annealed HfO$_2$/10 Å SiO$_2$/Si
Figure II-9: 40 Å unannealed HfO$_2$/10 Å SiO$_2$/Si

Figure II-10: 40 Å unannealed HfO$_2$/20 Å SiO$_2$/Si
Figure II-11: 40 Å unannealed HfO$_2$/30 Å SiO$_2$/Si

Figure II-12: 40 Å annealed HfO$_2$/10 Å SiO$_2$/Si
Figure II-13: 40 Å annealed HfO$_2$/20 Å SiO$_2$/Si

Figure II-14: 40 Å annealed HfO$_2$/30 Å SiO$_2$/Si
The following graphs are the ARXPS analysis of HfO$_2$/SiO$_2$/Si stacks from chapter 3:

Figure II-15: ARXPS depth profile of 20 Å unannealed HfO$_2$/10 Å SiO$_2$/Si

Figure II-16: ARXPS depth profile of 20 Å unannealed HfO$_2$/20 Å SiO$_2$/Si
Figure II-17: ARXPS depth profile of 20 Å unannealed HfO$_2$/30 Å SiO$_2$/Si

Figure II-18: ARXPS depth profile of 30 Å unannealed HfO$_2$/10 Å SiO$_2$/Si

Figure II-19: ARXPS depth profile of 20 Å annealed HfO$_2$/10 Å SiO$_2$/Si
Figure II-20: ARXPS depth profile of 20 Å annealed HfO$_2$/20 Å SiO$_2$/Si
Appendix III: SE Aleris™ thickness measurements of samples in Table 6-1

Table 6-1: Sample list of varying high-κ films on 8 Å chemical SiO₂

All the following graphs in this dissertation are notch down wafer orientation. The following figures are the SiO₂ thickness uniformity on a 300 mm wafer:

![Figure III-1: SiO₂ thickness for sample 1 in table 6-1]

![Figure III-2: SiO₂ thickness for sample 2 in table 6.1]
Figure III-3: SiO$_2$ thickness for sample 3 in table 6.1

Figure III-4: SiO$_2$ thickness for sample 4 in table 6.1

Figure III-5: SiO$_2$ thickness for sample 5 in table 6.1
Figure III-6: SiO\(_2\) thickness for sample 6 in table 6.1

Figure III-7: SiO\(_2\) thickness for sample 7 in table 6.1

The following graphs are the first layer high-\(\kappa\) thickness uniformity across 300 mm wafers:

Figure III-8: thickness uniformity of 5 cycle ALD La\(_2\)O\(_3\) of sample 2 in Table 6-1
Figure III-9: thickness uniformity of 10 cycle ALD La$_2$O$_3$ of sample 3 in Table 6-1

Figure III-10: thickness uniformity of 15 cycle ALD La$_2$O$_3$ of sample 4 in Table 6-1

Figure III-11: total thickness uniformity of 15 cycle ALD La$_2$O$_3$ and 5 cycle HfO$_2$ of sample 5 in Table 6-1
Figure III-12: total thickness uniformity of 15 cycle ALD $\text{La}_2\text{O}_3$ and 10 cycle HfO$_2$ of sample 6 in Table 6-1

Figure III-12: total thickness uniformity of 15 cycle ALD $\text{La}_2\text{O}_3$ and 40 cycle HfO$_2$ of sample 7 in Table 6-1

The following figures are the total high-κ thickness uniformity on a 300 mm wafer after the 2$^{nd}$ high-κ deposition. The Bruggeman effective medium approximation (BEMA) model $^{33,35}$ was used to measure the total thickness of high-κ stacks, which is the total thickness of $\text{La}_2\text{O}_3$ and HfO$_2$. The BEMA model consists of the optical dispersions of HfO$_2$ and $\text{La}_2\text{O}_3$ described in chapter 4.
Figure III-13: total high-κ thickness of 40 cycle HfO$_2$/ 0 cycle La$_2$O$_3$/ 8 Å SiO$_2$/Si (sample 1)

Figure III-14: total high-κ thickness of 40 cycle HfO$_2$/ 5 cycle La$_2$O$_3$/ 8 Å SiO$_2$/Si (sample 2)

Figure III-15: total high-κ thickness of 40 cycle HfO$_2$/ 10 cycle La$_2$O$_3$/ 8 Å SiO$_2$/Si (sample 3)
Figure III-16: total high-κ thickness of 40 cycle HfO$_2$/ 15 cycle La$_2$O$_3$ 8 Å SiO$_2$/Si (sample 4)

Figure III-17: Total thigh-κ thickness of 35 cycle HfO$_2$/ 15 cycle La$_2$O$_3$/ 5 cycle HfO$_2$/ 10 Å SiO$_2$/Si stack (sample 5)

Figure III-18: Total thigh-κ thickness of 30 cycle HfO$_2$/ 15 cycle La$_2$O$_3$/ 10 cycle HfO$_2$/ 10 Å SiO$_2$/Si stack (sample 6)
The following figures are the metal gate TiN thicknesses for the samples in table 6-1. The optical properties of TiN used in the modeling is described in detail in Chapter 4.

![Figure III-19: TiN thickness of sample 1](image1)

![Figure III-20: TiN thickness of sample 2](image2)
Figure III-21: TiN thickness of sample 3

Figure III-22: TiN thickness of sample 4

Figure III-23: TiN thickness of sample 5

Figure III-24: TiN thickness of sample 6
Figure III-25: TiN thickness of sample 7
Appendix IV: C-V curves of samples in table 6-1

Figure IV-1: C-V curves for 500 Å TiN/ 40 cycle HfO$_2$/ 0 cycle La$_2$O$_3$/ 8 Å SiO$_2$/Si stack (sample 1)

Figure IV-2: C-V curves for 500 Å TiN/ 40 cycle HfO$_2$/ 5 cycle La$_2$O$_3$/ 8 Å SiO$_2$/Si stack (sample 2)
Figure IV-3: C-V curves for 500 Å TiN/ 40 cycle HfO$_2$/ 10 cycle La$_2$O$_3$/ 8 Å SiO$_2$/Si stack (sample 3)

Figure IV-4: C-V curves for 500 Å TiN/ 40 cycle HfO$_2$/ 15 cycle La$_2$O$_3$/ 8 Å SiO$_2$/Si stack (sample 4)
Figure IV-5: C-V curve of 500 Å TiN / 35 cycle HfO$_2$ / 15 cycle La$_2$O$_3$ / 5 cycle HfO$_2$ / 10 Å SiO$_2$/Si stack (sample 5)

Figure IV-6: C-V curve of 500 Å TiN / 30 cycle HfO$_2$ / 15 cycle La$_2$O$_3$ / 10 cycle HfO$_2$ / 10 Å SiO$_2$/Si stack (sample 6)
Figure IV-7: C-V curve of 500 Å TiN / 0 cycle HfO \textsubscript{2} / 15 cycle La\textsubscript{2}O\textsubscript{3} / 40 cycle HfO\textsubscript{2} / 10 Å SiO\textsubscript{2}/Si stack (sample 7)

<table>
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<th>Sample #</th>
<th>SiO\textsubscript{2} thickness (Å)</th>
<th>HfO\textsubscript{2} cycle #</th>
<th>La\textsubscript{2}O\textsubscript{3} cycle #</th>
<th>HfO\textsubscript{2} cycle #</th>
<th>SiO\textsubscript{2} thickness (nm)</th>
<th>Mean V\textsubscript{fb}</th>
<th>Max V\textsubscript{fb}</th>
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Table IV-1: flat band voltage from table 6-1
Appendix V: SE characterization and C-V curves of samples in table 7-1

Table 7-1: Sample sets to investigate how SiO$_2$ affect flat band voltage of high-κ/metal gate stacks

<table>
<thead>
<tr>
<th>Sample #</th>
<th>SiO$_2$ thickness (Å)</th>
<th>La2O3 cycle #</th>
<th>HfO2 cycle #</th>
<th>TiN thickness (nm)</th>
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Figure V-1: A typical nominal thick 12 Å thermally grown SiO$_2$ thickness on a 300 mm wafer (samples 2 & 5)
Figure V-2: HfO$_2$ thickness from the 500 Å TiN/40 cycle HfO$_2$/12 Å SiO$_2$/Si stack (sample 2)

Figure V-3: Total high-κ thickness of the 500 Å TiN/40 cycle HfO$_2$/15 cycle La$_2$O$_3$/12 Å SiO$_2$/Si stack (sample 5)
Figure V-4: 20 Å thermal SiO$_2$ thickness (sample 6)

Figure V-5: 30 Å thermal SiO$_2$ thickness (sample 7)
Figure V-6: Total high-$\kappa$ thickness of 500 Å TiN/40 cycle HfO$_2$/15 cycle La$_2$O$_3$/20 Å SiO$_2$/Si stack (sample 6)

Figure V-7: Total high-$\kappa$ thickness of 500 Å TiN/40 cycle HfO$_2$/15 cycle La$_2$O$_3$/30 Å SiO$_2$/Si stack (sample 7)
Figure V-8: C-V curve of 500 Å TiN/40 cycle HfO$_2$/15 cycle La$_2$O$_3$/12 Å SiO$_2$/Si (sample 5)

Figure V-9: C-V curve of 500 Å TiN/40 cycle HfO$_2$/15 cycle La$_2$O$_3$/20 Å SiO$_2$/Si (sample 6)
Figure V-10: C-V curve of 500 Å TiN/40 cycle HfO₂/15 cycle La₂O₃/30 Å SiO₂/Si (sample 7)
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