ABSTRACT

HYUNGTAK SEO. Characterization of High-k Dielectrics and Interfaces on Device Reliability. (Under the direction of Gerald Lucovsky).

Transition metal and rare earth elemental and complex oxide high-k dielectrics and their interfaces with Si and Ge substrates were investigated in an effort to (i) understand the physical origin of intrinsic pre-existing, and extrinsic process-induced defects and to thereby (ii) achieve enhanced reliability in advanced devices such as metal oxide semiconductor capacitors and field effect transistors, MOSCAPs and MOSFETs, respectively.

Intrinsic pre-existing bonding defects in nanocrystalline high-k dielectrics are associated with discrete energy states near the conduction and valence band edges. These defects are localized at nanocrystalline grain boundaries and have been detected by measurements based on several different spectroscopic techniques including soft X-ray absorption and photoelectron spectroscopies, spectroscopic ellipsometry and internal photoemission spectroscopy. Estimated pre-existing defect densities in nanocrystalline high-k dielectrics by these spectroscopic measurements are typically of order $10^{12}$ cm$^{-2}$ in films that are more than 3 nm thick, but can be reduced by about an order of magnitude in noncrystalline HfSiON dielectrics, and in nanocrystalline films that are $\leq 2$nm thick.

Nanocrystalline LaScO$_3$ films display significant conduction band changes associated with Jahn-Teller (J-T) term splitting of anti-bonding Sc 3d* states as function of increases in grain size for annealing in Ar up to 1000°C. A coherent $\pi$-bonding interaction between Sc 3d and O 2p states in Sc-O octahedrons is responsible for the J-T term splitting, and additionally for the generation of localized defects at grain boundaries when the nanocrystallite size is greater than the 3~4 nm scale of order for this bonding interaction.
Ni-doping into BaSrTiO$_3$ (BST) changes the local bonding distortion by partial replacement of Ti$^{3+}$ atoms with Ni$^{2+}$ in divacancy defect states. This reduces the defect density by a factor of five to seven-fold and shifts the defect states closer to the conduction band edge by $\sim 0.3$ eV compared to undoped BST. A significant enhancement of metal-insulator-meta (MIM) capacitor reliability was achieved by suppression, and recovery of symmetry in the MIM leakage current. This increased resistance to dielectric breakdown by shifting the onset by more than 20 V.

Ge/GeON/HfO$_2$ and HfSiON show significant charge trapping ($\text{mid-}10^{12} \sim 10^{13}$ cm$^2$) at the interfacial GeON layers. This trapping results from native GeO$_x$, GeON and GeN$_x$ layers which have a conduction band offset energy with respect to the Ge substrate that is less than the conduction band offset energy of the HfO$_2$ and HfSiON dielectrics with respect to Ge. The engineering solution for elimination of this potential well charge trapping is by intentional removal of native Ge dielectric interfacial layers. The annealing of nitrided Ge substrates at temperatures between 600°C and 800°C in Ar eliminated the interfacial transition layer Ge-N bonding; however, there is evidence based on medium energy ion scattering (MEIS) that it failed to completely suppress Ge-Hf-O subcutaneous reactions that result in interfacial trapping at levels lower than the GeON, GeO$_x$ and GeN$_x$ that are introduced in conventional processing with intentionally deposited/or grown native Ge dielectric interfacial layers. Together with NH$_4$OH cleaning, interfacial defect densities at n-Ge/HfSiON gate stacks have been reduced to that levels in the mid-$10^{11}$ cm$^2$ that provide a possible engineering solution pathway for Ge n-FETs.
DEDICATION

With love to my family and my wife's devotion
Hyungtak Seo was born in Busan, South Korea on Aug. 17, 1976. He obtained his B.S. degree in Materials Science and Engineering, Hanyang University, Seoul, South Korea in 2000. He continued to study for M.S. degree in Semiconductor Materials Laboratory, Hanyang Univ. and obtained M.S. degree in Materials Science and Engineering in 2002. During the master course, he focused his research on the novel dry semiconductor cleaning processes using remote plasma in conjunction with the memory division of Samsung Electronics. After his graduate study, he worked as researcher in Research Institute of Industrial Science in Hanyang University from 2002 to 2003. He was accepted for the young researcher program of Korean Ministry of Science and Technology in Korea Research Institute of Standards and Science, Daejeon, Korea in 2003. In this position, he actively researched semiconductor plasma diagnosis with newly developed cut-off probe and ion detectable Quadrupole Mass Spectrometer from 2003 to 2004. From August 2004, he proceeded to the United States and enrolled in the Ph.D. program in Dept. of Electrical and Computer Engineering at North Carolina State University, Raleigh. He joined as research assistant in Prof. Lucovsky's lab and conducted the research on characterization of high-k gate dielectrics and its interface to metal/channel on reliability of (i) Si- and Ge-MOSFETs, (ii) MIM memory capacitor cells, and (iii) other novel devices by correlation between electrical (CV/IV/BTI) and spectroscopic measurement focusing on the defect minimization present in high-k gate dielectrics and interfaces. During Ph.D. course, he was accepted for a visiting scholar in IMEC, Leuven, Belgium where he studied on metal/high-k gate stacks on Ge-channel MOSFETs from May to Aug. 2007.
ACKNOWLEDGEMENTS

First of all, I would like to thank the advisory committee members, Dr. Gerald Lucovsky, Dr. Carl Osburn, Dr. David Aspens, and Dr. Veena Misra for their generous guidance and review on this work. Their guidance from the very first time when I started Ph.D. study made not only my work but life in NCSU much better and more complete. I would like to give my special thanks to my advisor, Dr. Gerald Lucovsky. He has always been ahead for giving a very correct direction to my study in a kind way. I have learned a lot of valuable and great knowledge and the way of thinking as a scientist but also as a person. I am absolutely sure that his teaching to me will be “the bible” for my work all my life.

I also would like to expand my thanks to my former and current colleagues, Dr. Kwonbum Chung, JP Long, Dr. Relja Vasic, Dr. Sanghyun Lee, Dr. Sang Jeong Oh, Nick Stoute. It was a great experience that I worked and enjoyed my time in the lab with all of you.

Personally, I owe lots of things to my friends in NCSU, Chulwoo Oh, Jiyoung Chung, Chanyeon Won, Sangtae Bae, Hoonseok Kim, Jeesung Chung, Dr. Taesik Han, Sangoh Han, Byungdon Kong, Byungil Kwak, Jinseok Park, Bongmook Lee and all people who I know even though they are not listed here, for their friendship. I will not forget the precious time with you.

I must also express my appreciation to my family in Korea, parents, brother, sister, parents-in-law, brother-in-law, and their family, for their unwavering support and love during my studying. Lastly, I would like to express my deepest appreciation to my wife, son, and daughter for being there from start to finish with lots of patience and understanding. Without their efforts, this work would have never been possible. Forever will be my love to you.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>LIST OF FIGURE</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>vii</td>
</tr>
</tbody>
</table>

## 1 Introduction

1.1 Need of High-k Dielectrics in Scaled Down CMOS and Memory Circuits...1
1.2 Reliability Issues of High-k Dielectric Gate Stacks....................4
1.3 Intrinsic Chemical and Physical Properties of TM/RE Oxides..........5
1.4 Crystal-Field and Jahn-Teller Term Splitting............................6
1.5 Spectroscopic Techniques: XAS and SE..................................9
1.5.1 X-ray Absorption Spectroscopy (XAS)..................................9
1.5.2 Spectroscopic Ellipsometry (SE)......................................11
1.6 Electrical Techniques: C-V and I-V......................................16
1.7 Overview of Dissertation................................................17
1.8 References............................................................19

## 2 Spectroscopic Detection of Defects present in TM/RE Elemental/Complex High-k Oxides

Abstract..................................................................................28
2.1 Introduction.........................................................................29
2.2 Experimental Procedures..................................................29
2.3 Results and Discussion.....................................................30
2.3.1 Defects in TiO$_2$ and HfO$_2$...........................................30
2.3.2 Defect Suppression in Ti- and Hf-Si oxynitrides...................33
2.4 Summary............................................................................36
2.5 References..........................................................................37

## 3 Correlation of Length Scale of TM/RE Oxides and Interfaces to Intrinsic Defects

Abstract..................................................................................47
3.1 Introduction.........................................................................48
3.2 Experimental Procedures..................................................48
3.3 Results and Discussion.....................................................49
4 Defect Band Engineering of BaSrTiO₃ Dielectrics in Metal Insulator Metal Capacitor by Ni Doping

Abstract

4.1 Introduction

4.2 Experimental Procedures

4.3 Results and Discussion

4.4 Conclusions

4.5 References

5 Preparation of Native Oxide and Carbon Minimized Ge surface by NH₄OH Cleaning for Deposition of High-k Dielectrics

Abstract

5.1 Introduction

5.2 Experimental Procedures

5.3 Results and Discussion

5.4 References

6 Correlation Between Defects identified by Spectroscopic Measurements and charge Trapping at Ge/HfO₂ and HfSiON Interfaces with GeON Layer

Abstract

6.1 Introduction

6.2 Experimental Procedures

6.3 Spectroscopic Identification on Defects: MEIS, SE, and XAS Results

6.4 Electrical Properties of Hf based High-k on Ge

6.5 Summary

6.6 References

7 Concluding Remarks and Future Work
LIST OF FIGURES

Fig 1.1. Electronic band edge diagrams of SiO₂ (left) and TM/RE high-k oxides (ZrO₂, right) constructed by molecular orbital (MO) theory.................................................................22

Fig 1.2. Schematic CB and VB band edge MO states in TiO₂.................................................................23

Fig. 1.3. Schematic d-state evolution in TiO₂ and HfO₂ consisting of CB edge states........24

Fig. 1.4. Schematic scheme of spectroscopic measurements on TM/RE oxides..........25

Fig. 1.5. Schematic diagram of the ellipsometry (top) and the ellipsometric modeling process........................................................................................................................................26

Fig. 1.6. (a) Schematic diagram of the pseudodielectric function. (b) On left, what model assumes (electromagnetically sharp interface). On right hand side, what is encountered in reality (interface layers, contamination, surface roughness).................................................................27

Fig. 2.1. NEXAS spectra for TiO₂: (a) O K₁ and (b) Ti L₃ edges.................................39

Fig. 2.2. Photon energies of Ti d-state features: (a) O K₁ edge vs Ti L₃ edge and (b) ε₂ vs O K₁ edge..................................................................................................................................................40

Fig. 2.3. (a) VUV SE ε₂ spectrum and (b) SXPS VB structure versus photon energy for TiO₂..................................................................................................................................................41
Fig. 2.4. (a) SXPS VB structure versus binding energy and (b) VUV SE $\varepsilon_2$ spectrum versus photon energy for HfO$_2$.

Fig. 2.5. Band edge and pre-existing defects determined by spectroscopic studies for (a) HfO$_2$ and (b) TiO$_2$.

Fig. 2.6. O K$_1$ and $\varepsilon_2$ spectra for low and high Si$_3$N$_4$ content Ti Si oxynitride alloys.

Fig. 2.7. $\varepsilon_2$ spectra for (a) low- and (b) high-Si$_3$N$_4$ content Hf-Si oxynitride alloys before and after annealing.

Fig. 2.8. Schematic representation of local bonding arrangement in optimized Zr(Hf)-Si oxynitride alloy with $\sim$33-40 % Si$_3$N$_4$, and 30-33 % SiO$_2$ and HfO$_2$.

Fig. 3.1. Sc L$_3$ edge XAS spectra for (a) as-deposited and (b) 1000 °C annealed nanocrystalline LaScO$_3$.

Fig. 3.2. O K$_1$ edge XAS spectra for (a) as-deposited and (b) 1000 °C annealed nanocrystalline LaScO$_3$.

Fig. 3.3. La M$_{2,3}$ edge XAS spectra for (a) as-deposited and (b) 1000 °C annealed nanocrystalline LaScO$_3$.

Fig. 3.4. Calculated conduction band edge d-states for TiO$_2$: the crystal field (C-F) splitting for i) a regular or undistorted octahedral distribution of O neighbors, ii) a geometric distortion with the same nearest neighbor bonding as rutile and iii) a grain boundary distortion.

Fig 3.5. Linear scaling between features of the Sc L$_3$ edge, and O K$_1$ edge spectrum for
1000°C annealed LaScO₃ thin film………………………………………………………………..63

Fig. 3.6. Imaginary part of the complex dielectric constant versus photon energy for as-deposited and annealed LaScO₃ thin films between 700 and 1000 °C…………………………64

Fig. 3.7. HRTEM images of (a) as-deposited and (b) 1000°C annealed LaScO₃………………65

Fig. 3.8. Band edge PC for nano-crystalline as-deposited LaScO₃ film…………………………66

Fig. 3.9. (a) XAS O K₁ edge spectrum and (b) VUV SE spectra for 0.38 nm of LaAlO₃ on SrTiO₃ for different oxygen pressure in film deposition………………………………..67

Fig. 4.1 (a) schematic representation of MIM (Pt/Ni-BST/Pt) capacitor. The bottom Pt electrode is placed on Ti/SiO₂/Si stack which emulates the actual layers in DRAM storage cell and (b) Dielectric constants of MIM capacitor extracted from high-frequency (1 MHz) C-V analysis with Ni-doped and undoped BST dielectrics. The undoped BST showed the slightly higher dielectric constant. There was no significant dielectric loss across the applied voltage……………………………………………………………………………………………..78

Fig. 4.2. J-V Characteristic of Ni-doped and undoped BST MIM cells at room temperature. Traces are included for both positive and negative gate bias in a spectral range from –20 V to + 20 V………………………………………………………………………………………….....79

Fig. 4.3. Epsilon 2 (ε₂) extracted from SE measurements of undoped and Ni-doped BST. (a) The solid circle points are as-deposited films (room temperature), and the open circles films annealed in Ar at 800°C. (b) ε₂ for as deposited in undoped and Ni-doped BST in a narrower spectral regime from 2.6 to 4.0 eV. This regime emphasizes changes in the spectral character of the band edge defect states………………………………………………….80
Fig. 4.4. Local bonding of Ti-atoms (gray) and O-atoms (black) in i) undistored octahedral arrangements in which all bond lengths, $a_x$, $a_y$ and $a_z$ are equal, ii) orthorhombic arrangements in which all bond lengths are unequal, and iii) in tetragonal arrangements with two equal bond lengths.

Fig. 4.5. Schematic energy band diagram for conduction band empty anti-bonding states, and band edge defects states for undoped and Ni-doped BST obtained from analysis of $\varepsilon_2$ spectra. Solid lines, and bold face energy level positions, and energy differences reflect strong features in $\varepsilon_2$, whereas, dashed lines, and plain text indicate significantly weaker spectral features.

Fig. 4.6. Band alignment for that includes band edge defects in undoped (heavy solid line) and Ni-doped (dashed line) BST MIM capacitors. The Pt 6s state Fermi level is indicated metal gate Fermi levels are indicated, as well as the Pt 5d state filled band. Transport processes are indicated by arrows beginning in the Pt electrodes of the cathode (negative) and differentiated by the character of these arrows.

Fig. 5.1. The plot for Imaginary parts of pseudo dielectric function for (100) Ge surfaces with and without different surface treatment: NH$_4$OH-based, HF-based, H$_2$O$_2$/HF, and No treatment (Bare wafer).

Fig. 5.2. The plot for GeO$_2$ thickness evolution during the NH$_4$OH-based surface treatment for (a) (111) and (b) (100) Ge surfaces. The GeO$_2$ thickness was extracted from the real-time SE measurements with cleaning process.

Fig. 5.3. The plot for GeO$_2$ regrowth evolution during the air exposure of the cleaned (a) (111) and (b) (100) surface as a function of exposure time. Both of surface orientations show the similar regrowth feature in the ambient.

Fig. 5.4. AES (a) wide and (b) narrow scan spectra for (100) Ge surface with and without
surface treatments: Bare, HF-, and NH₄OH-based cleaning. For wide energy scan, there are energy peak states associated to germanium (45~50 eV), carbon (268 eV) and oxygen (509 eV) species. For narrow energy scan, there are Ge peaks related to two different bonding states, Ge-O (44 eV) and Ge-Ge (48 eV).

Fig. 6.1. Compositional depth profile obtained by simulating MEIS energy spectra for as-deposited and annealed (a) HfO₂ films and (b) HfSiON films on Ge(100) substrates. Dotted line and arrow indicate the Ge substrates and the direction of the films. The spot with the error bar represents the fitting error in the depth direction and the relative concentration.

Fig. 6.2. Imaginary dielectric function (ε²) spectra from SE measurement for as-deposited and annealed HfO₂ and HfSiON films on Ge(100) substrates. D₁ and D₂ indicate the defect states located below the conduction band edge.

Fig. 6.3. XAS spectra below the absorption edge of the O K₁ feature for (a) HfO₂ and (b) HfSiON films on Ge(100) substrates. Two deconvoluted peaks, labeled D₁ and D₂, indicate the defect states determined by Gaussian fitting of the XAS O K₁ edge spectra.

Fig. 6.4. Relative strengths of defect features determined from Gaussian fits to O K₁ edge spectra.

Fig. 6.5. XAS spectra below the absorption edge of the N K₁ feature for (a) HfSiON and (b) HfO₂ films on Ge(100) substrates as a function of PDA temperature.

Fig. 6.6. C-V hysteresis traces for (a) as-deposited, (b) 650 °C, and (c) 700 °C annealed HfSiON. The oxide trapped charge density is extracted at V FB.

Fig. 6.7. C-V hysteresis traces for (a) as-deposited, (b) 600 °C, and (c) 650 °C annealed HfO₂. The oxide trapped charge density is extracted at V FB.
Fig. 6.8. Plot of $N_{\text{EFF}}$ as a function of $N_{\text{inj}}$ for as deposited and annealed HfO$_2$ and HfSiON.

Fig. 6.9. The relation between the oxide trapped charge density, $N_{\text{ot}}$ and $V_{\text{FB}}$ extracted from C-V hysteresis as a function of PDA temperature for (a) HfSiON and (b) HfO$_2$.

Fig. 6.10. J-V plots for test devices with (a) as deposited and (b) 650 °C annealed HfSiON and (c) as deposited and (c) 600 °C annealed HfO$_2$. There is an enhancement of leakage current characteristics for each annealed device compared to the as deposited.

Fig. 6.11. J-V plot for test devices with as deposited and 900 °C annealed HfSiON on SiON/Si. The HfSiON was deposited in the exactly same recipe as high-k/Ge devices.

Fig. 6.12. (a) Band alignments between (i) n-type Ge, GeO$_2$ and HfO$_2$ and (ii) n-type Ge, Ge$_3$N$_4$ and HfO$_2$ and (b) substrate injection for an n-type Ge, GeO$_2$ and HfO$_2$ stack in (a), with and Al gate electrode, for which the conduction band offset energy between Ge and GeO$_2$ which is less than that between Ge and HfO$_2$, and for a gate stack on n-Si and with an SiON interfacial region, which is greater than that between Si and HfO$_2$.

Fig. 6.13. Energy band alignment between an substrate/high-k gate dielectric stack and Al metal gate electrode for substrate injection: (a) HfSiON on an SiON on Si(100) for the J–V plot in Fig. 6.9 and (b) HfSiON in direct bonding contact with Ge for J–V in Fig. 6.8 (b).
1 INTRODUCTION

1.1 Need of High-k Dielectrics in Scaled Down CMOS and Memory Circuits

After enormous growth of the semiconductor industry over several decades, microelectronics technology is facing the one of the most significant challenges in its history. The SiO2 layer in metal oxide semiconductor field effect transistor (MOSFET), which was regarded as "a gift from nature", is rapidly approaching its physical limit due to direct tunneling [1,2]. The aggressive effort to achieve faster and more functional chips continued to scale the SiO2 or SiON dielectric thickness as gate lengths are scaled down. This effort to integrate the thinner gate oxides is derived from the physical scaling benefits in MOSFETs such as higher switching speed or less delay time, less power consumption, and higher density of transistors. It is clear to understand this relationship between improved transistor performance (transient response time of transistor switching, $\tau$, and oxide capacitance, $C_{ox}$, and saturation drain current, $I_{D,sat}$) scaling factors from following simple MOSFET governing equations:

$$\tau = \frac{C_{load} \cdot V_{dd}}{I_{D,sat}}$$  \hspace{1cm} 1.1

$$C_{ox} = \frac{\varepsilon_{ox}}{t_{ox}}$$  \hspace{1cm} 1.2

$$I_{D,sat} = \left( \frac{W}{2L} \right) \mu_{eff} C_{ox} (V_{gs} - V_{T})^2$$  \hspace{1cm} 1.3

where, $C_{load}$ is the load capacitor of transistor, $V_{dd}$ is the supply voltage, $\varepsilon_{ox}$ is the dielectric constant of gate dielectric, $t_{ox}$ is the thickness of gate dielectric, $W$ is the channel width, $L$ is the gate length, $\mu_{eff}$ is the effective mobility of charge carrier, $V_{gs}$ is the gate-
source bias, and $V_T$ is the threshold voltage.

This advanced MOSFET processing technology requires gate oxide thickness less than 1.5 nm and extending below 1 nm [3]. However, SiO$_2$ based gate dielectric has been supposed to reach a physical limit beyond 45 nm gate length MOSFET technology [4]. The level of ultra thin SiO$_2$/SiON suffers from the direct tunneling through gate stacks. At these thicknesses, SiON has a direct tunneling current of greater than $10^3$ A/cm$^2$ for high-performance logic chips and 0.1 A/cm$^2$ for low power chips [3].

Therefore, SiO$_2$ or SiON might not be used toward MOSFETs with gate oxide thickness less than 1 nm. The solution for this limitation has been investigated by a replacement of gate oxide from SiO$_2$ to high-k dielectrics in the material context of transition and rare earth elemental/complex oxides [5-7]. As noted in Eq. 1.1~1.3, benefits from replacement of gate dielectrics in MOSFETs by high-k dielectrics are multiple and significant: (i) suppression of leakage current by using physically thicker films while maintaining same equivalent oxide thickness (EOT) although there might be limited suppression of leakage current level mitigated by the lowered barrier height and (ii) increase of drain current by raising oxide capacitances.

In a circuit point of view, introduction of high-k gate dielectrics are of great advantage. First of all, for logic devices for application such as mobile devices specially requiring the low stand-by voltage, the suppression of power dissipation is a primary concern and therefore, gate leakage current suppression to the lower levels in unit transistor is critical for whole system respect [8,9]. Therefore, high-k dielectrics are essential to enable to keep the scaling of logic devices continued, as in the projection of road map, down to 32 nm gate length and
equivalently to $< 1$ nm EOT of gate dielectrics [3]. In addition, logic chip groups requiring high performance of devices such as central processing units for computers also need the high-k dielectrics for boost of drain current in scaled down transistors. Secondly, memory devices such as dynamic random access memory (DRAM) and flash memory demand high-k dielectrics both for gate and capacitor regions. The future technology of flash memories such as charge trapping flash (CTF) will require several special specifications of (i) tunnel oxides and (ii) trapping oxides [10,11]. Tunnel oxides should have the thinner EOT and higher tunneling process for faster responses and longer retention time but at the same time, lower barrier height for effective tunneling process. Trapping oxides should have the high trapping efficiency which should be controlled by gate bias only. DRAM really relies on the specification of stacked metal-insulator-metal (MIM) capacitors for charge storage. The insulator should be thin enough to store an enough amount of charge (25fF/cell) while maintaining reasonable retention characteristics [3]. Therefore, high-k dielectrics are necessary for future advanced logic and memory devices.

Furthermore, high-k dielectrics are really opening a pathway for new emerging devices. There are many reported preliminary results on novel device concepts utilizing high-k dielectrics: (i) resistive RAM (ReRAM), (ii) ferroelectric RAM (FeRAM), and (iii) hetero-junction high mobility interfacial channels [3,12].

All in all, realization of high-quality and reliable high-k dielectrics is a first priority technology for continuing the evolution of microelectronic- or nanoelectronic- devices.
1.2 Reliability Issues of High-k Dielectric Gate Stacks

Although significant efforts have been made to integrate high-k dielectric into advanced devices for the last 10 years, the introduction of high-k gate dielectrics has been delayed from the initial roadmap projection since they have several inferior intrinsic properties compared to SiO$_2$ which turned out to deteriorate the device performance and reliability [12,13]. Major problems for the integration of high-k dielectrics to MOSFETs are listed as (i) leakage current levels which is not solely dependent on physical oxide thickness, (ii) surface dipoles or defects present close to the interface of poly-Si gate/high-k gate dielectrics invoking Fermi level pining, (iii) lowered channel mobility compared to the universal mobility, and finally (iv) fast charge trapping and trap creation resulting in threshold hysteresis and threshold voltage instability. These problems are considered to be very closely related to the presence of defects in high-k gate dielectrics after many studies.

The observed problems raised serious reliability concern for poly-Si gated devices employing high-k dielectrics. Frequently, one might be told things: “simple replacement of high-k dielectrics to SiO$_2$ never works at all” and “only one good thing about high-k dielectrics is its high k value”. Later, however, high-k dielectrics in the gate stacks were used with new material integration, metal gate electrodes [13]. The use of metal gate was really effective to achieve more reliable novel gate stacks with high-k dielectrics than poly-Si/high-k gate stacks although it created other issues such as flat band voltage tuning (specially for pFETs) and metal/gate stack interface transformation after anneal [14,15].

One particularly important reliability issue of novel high-k gate stacks is long term reliability since this is based on the extrapolation-based-prediction for extraction of “10-year
life time”. Several critical studies in this specific topic reported multiple effects of metal gate on long term reliability: (i) metal gates reduce the delay between soft and hard breakdown of gate stacks and (ii) metal/oxide interfaces are subject to the severe degradation by the re-growth or chemical reactions after thermal processing. Thus, interfaces of metal/high-k gate stacks are recently being considered as a main issue on the reliability [16].

However, the ultimate interest on reliability of high-k dielectrics is to understand the physical origin and properties of intrinsic defects present in oxides and to obtain the engineering pathway for suppression of defects. For this specific study on high-k dielectrics, the basic review on the intrinsic physical and chemical characteristics is essential.

1.3 Intrinsic Chemical and Physical Properties of TM/RE Oxides

The effective way to describe the intrinsic properties of TM/RE high-k oxides is to compare their electronic band structures to SiO₂ as shown in Fig 1.1. The electronic states in Fig. 1.1 were constructed by molecular orbital (MO) theory. SiO₂ has a large band gap at 9 eV and the valence band (VB) and the conduction band (CB) edge are composed of bonding- and anti-bonding 3s and 3p states mixed with O₂p states. The local bonding structure is well known as tetrahedral Si-O₄ in amorphous structure. On the other hand, ZrO₂ has a smaller band gap at 5.8 eV than SiO₂ and VB and CB edge states are associated with the bonding and anti-bonding Zr 4d states mixed with O₂p states. The various unique features of TM/RE oxides are due to d-states [17]. Firstly, the mixed orbital states of TM/RE d- and oxygen p-orbitals have a lower local symmetry and therefore, contribute localized exited states with respect to the ground states under electric field. These excited states
result in an asymmetric charge distribution between metal and oxygen which invokes additional ion off-center displacement arising increase in (i) polarizability and (ii) k values [18]. Because of this ionic interaction/overlapping between metal d-states and oxygen p-states, bandgaps of high-k dielectrics are typically lower than other amorphous oxides such as SiO₂ and Si₃N₄ and tend to be decreased for TM/RE oxides with higher k values [19].

Another crucial physical property of TM/RE oxides is the sensitivity of d-states to the local bonding environments [17]. Thin film structures of TM/RE in high-k dielectrics of interest for device applications suffer from crystal structure transformation with anneals at different temperature. This is because d-states are sensitive to the changes and distortions in local bonding which will be discussed in the next section. The Inherent strong localization of electron distribution in d-states tends to be susceptible to the bonding distortion associated with the global structure changes that occur with thermal energy and mechanical strain at grain boundaries so that asymmetric bonding configurations are very common in thin film nanocrystalline TM/RE oxides.

Therefore, in contrast to the conventional amorphous gate dielectrics such as SiO₂ and Si₃N₄, TM/RE high-k oxides are subject to crystallization, bonding distortion and defects, and, therefore, intrinsic VB/CB band edge energy states tend to change which sometime induce band gap changes, as in LaScO₃ thin films [20].

1.4 Crystal-Field and Jahn-Teller Term Splitting

The electronic band diagram in Fig. 1.1 was derived from state assignments under MO theory. In definition, a MO specifies the spatial distribution and energy of one (or one pair of)
electron(s) in diatomic molecule environment [21]. Most commonly, an MO is represented as a linear combination of atomic orbitals (the LCAO-MO method). Because of such nature of MO theory, it is more effective to explain strongly localized bonding types [17,22]. This is the reason that MO theory is regarded as the best model to describe the electronic band structures of TM/RE oxides since they have the localized MO states between partially filled TM/RE d-states and oxygen 2p states. Figure 1.2 represents the schematic CB and VB band edge MO states in TiO₂. In CB edge, there are triply degenerate T₂g states (dₓᵧ, dᵧz, and dₓz) in π anti-bonding characteristic and doubly degenerate E₉ states (dₓ² - y² and d₂) in σ anti-bonding characteristic respectively. In the VB edge, these MO states are located in mirror symmetry but the top of the valence band edge is dominated by non-bonding oxygen 2p states. Depending on bonding structures, the energy locations of T₂g and E₉ are reversed. For example, HfO₂ has the lower-lying E₉ and higher-lying T₂g states in energy.

A very crucial aspect of TM/RE oxides is the evolution of MO states (known as crystal field and Jahn-Teller term splitting) associated with d-orbitals, depending on a local bonding environment affecting symmetry of metal-oxygen bonding coordination in a unit cell. Figure 1.3 schematically displays d-state evolution in CB edge states of TiO₂ and HfO₂. This assignment can be done by ab initio calculation guided by molecular orbital (MO) theory. In the center of figure, all of five d-states are degenerate in spherical symmetry but, as the coordination number of metal-oxygen bonds increases, degeneracy of d-states is removed and splitting of those states occur. In case of HfO₂, going to the higher bond coordination from 4-fold (tetrahedral) to 7-fold (cubic), the T₂g and E₉ states are separated into two groups of states. This phenomenon is called crystal field term splitting (C-F) and arises from
electrostatic perturbation of the transition metal d orbitals and the surrounding anions (e.g. oxygen atoms) [17, 23]. The previous case is applied to local structures having all equivalent bonding lengths between metal and oxygen. There can be asymmetric distortion in unit cells. In the case of HfO2, the distorted cubic bonding at asymmetric bonding lengths (i.e., $a_x \neq a_y \neq a_z$) leads to multiplicities of d-states with complete degeneracy removal with the larger term split energies. This is called Jahn-Teller distortion (J-T) according to which a non-linear molecule in an electronic state with orbital degeneracy will distort so as to lower its symmetry and remove the degeneracy [24]. This case for HfO2 is described by evolution in the left hand side direction in Fig. 1.3. The evolution for right hand side direction corresponds to the octahedral (6-fold) metal-oxide bonding environment of TiO2, LaScO3, and LaTiO3.

As discussed in later sections, the observation of C-F and J-T splitting is very important for the nano-crystalline TM/RE high-k oxides used for gate dielectric applications. The J-T splitting detected by spectroscopic techniques is an indication that oxide morphology is subject to nanocrystalline since J-T splitting primarily occurs at grain boundaries of nanocrystalline oxides where the significant local distortion is concentrated [20]. This grain boundary is an intrinsic bonding defect source of oxygen vacancies. In most cases, the physical dimension of gate dielectrics is extremely small at several nm’s range, so that the conventional analysis methods such as X-ray diffraction (XRD) are not effective, instead, several unique spectroscopic techniques (as listed in next section) can probe J-T splitting and localized defects in nano-scale TM/RE oxides. Therefore, this experimental approach to detect C-F and J-T is very useful as a preliminary study of the intrinsic properties of TM/RE
oxides before device integration of high-k dielectrics.

1.5 Spectroscopic techniques: X-ray absorption spectroscopy (XAS) and spectroscopic ellipsometry (SE)

In this section, several spectroscopic techniques employed in this study are addressed. XAS and SE techniques can probe the empty states by the transition from occupied states (core level for XAS and top of valence band for SE) to empty states in conduction bands. The schematic schemes of spectroscopic measurements on TM/RE oxides are shown in Fig 1.4. Although not discussed here, the occupied states in VB can be traced by Soft X-ray photoemission spectroscopy.

1.5.1 XAS

XAS is an element-specific technique to probe the local structure of elements in a material. The species of the material are determined based on its unique local structure. An important advantage to this technique is that it can be used to directly examine a wide variety of solid and liquid samples non-destructively. This method results from the absorption of a high energy X-ray by an atom in a sample. The absorption occurs at a defined energy corresponding to the binding energy of the electron in the material. The ejected electron interacts with the surrounding atoms to produce the spectrum. Occasionally, the electron can be excited into vacant bound electronic states near the valence band, and distinct absorptions will result at these energies.

X-ray absorption spectroscopy is commonly divided into two spectral regions, the X-ray
absorption near-edge structure (XANES) spectral region and the extended X-ray absorption fine structure (EXAFS) region. In the current study, measurements of XAS spectra on XANES spectral region are mainly conducted.

The XANES spectra are unique to the oxidation state and species of the element of interest, as such are used to determine the oxidation state and coordination environment of materials. In the current study, there are two types of transition of interest: (i) the inter-atomic transition from occupied core level of OK₁ edge to empty conduction band states of metal d-, s-, and p- states mixed with oxygen p- states and (ii) intra-atomic transition from metal core p- states to empty conduction band states [20].

There are two important factors to be considered in interpretation of XANES spectra on TM/RE oxides. Firstly, the intensity of a transition is strongly governed by matrix elements as a function of ground and final states. This means that spectral features such as intensities of same final states are remarkably different depending on the ground states (i.e., either TiL₂,₃ edge or OK₁ edge). This matrix element affects both of inter- and intra-atomic transition but proper quantum calculations based on matrix elements between MO states make assignments of unknown spectra to specific transitions. Secondly, line width broadening effects also affect the intra-atomic transition spectra resolution in energy. Following Slater's empirical rule, core hole lift time decreases or, stated differently, the line width is expected to increase as $Z^n$ where $Z$ is atomic number of element and $n$ is 2~3. Therefore, this line width broadening effect makes it impossible to resolve the doublet character of the 5d-state in HfO₂ in the intra-atomic N transition while TiO₂ (smaller Z than Hf) has the line width (< 0.5 eV) narrow enough for resolving J-T split Ti 3d states in TiL₂,₃ edge intra-atomic transition.
spectra [25].

In the current study, XAS measurements were performed at the National Synchrotron Light Source (NSLS) at the Brookhaven National Laboratory (BNL), and at the Stanford Synchrotron Radiation Laboratories (SSRL) at the Stanford Linear Accelerator Center (SLAC) using total photo-electron yield to determine the relative absorption strength of the spectral features associated with transitions from TM, RE, and O-atom core level states to empty conduction band-states [26]. The current research proved that the XAS technique is very effective to detect a length of nanocrystalline less than 4 nm, a physical detection limit of XRD that can determine the size of crystalline.

1.5.2 SE

It is crucial to investigate the energy band structure of high-k materials since it has a direct relationship to the tunneling current and trap level in the gate dielectrics. Several optical measurements, such as transmission, and reflection spectroscopy have been employed for this kind of research. Among these optical measurement tools, SE is a very effective tool to achieve dielectric function of material [27]. SE is optical characterization technique that is used to determine the complex reflectance ratio, \( \rho = r_s r_p^{-1} \) where \( r_p \) and \( r_s \) are the complex reflectance of the light polarized parallel (p) and perpendicular (s) to the plane of incidence, respectively. Visible ultra violet (VUV) light having energy range from 1.5 eV: 8267 Å to 10eV: 1240Å as an optical source is used to excite electrons from the top of valence band to conduction band in the overlayer material. From \( \rho \), optical constants are determined. Those are index of reflection \( n \), extinction coefficient \( k \), and dielectric function \( \varepsilon \).
These are related each other by electromagnetic characteristics. Figure 1.5 depicts the procedure of SE measurements.[29]

The material system that we consider for this research is the ideal 3 layer system of which the uppermost layer is the ambient, the middle layer is the thin film high-k dielectric in nm $(10^{-9} m)$ range, and the lower layer is the substrate, normally Si wafer. This application of SE requires the conversion of measured quantities associated with microscopic polarization phenomenon into the macroscopic sample properties of interest: thin film thickness, optical constant, compositions, properties, etc. In other words, we can not use ellipsometry to directly measure much of the information of interest. As a result, we need an “optical model” to bridge the gap. This model is an ideal mathematical representation of the sample that allows us to calculate its polarization state change in terms of physical properties like thickness, refractive index, and composition. For each sample, $\rho$ is calculated to match the experimental data, using multilayer mathematical models that contain parameters, such as layer thickness or composition, which are independent of the parameters varied in the measurement.

For the theory of analysis on data from SE measurements on high-k dielectrics on substrates, it is needed to go over (i) two- and three-phase models and (ii) effective medium approximation.

(i) Two phase and three phase model

Reflection is a result of an impedance mismatch, that is, of different values of n on opposite sides of a (planar) boundary. The boundary value problem is completely defined by the requirement that normal D and B and tangential E and H are continuous across the
boundary, that the projection of k onto the boundary is the same for each medium, and dispersion equation, \( \varepsilon = c^2 k^2 / \omega^2 \). Reflection at a boundary usually involves the participation of 4 waves, since in general both leftward- and rightward-propagating waves exits on either side of the boundary. As it is more efficient mathematically to represent these waves by single amplitude components only, reflection is described in terms of electric field for s-polarized light and the magnetic field for p-polarized light [27,28].

If no overlayer are present on the substrate or if the uppermost overlayer is optically thick, then no back reflectance occurs from deeper within, and only the two materials denoted by subscripts s and a (substrate and ambient) are involved. This is a 2 phase situation. In this case, reflectances can be expressed in the analytic form:

\[
\begin{align*}
    r_{s,sa} &= \frac{E_s^o}{E_s^r} = \frac{n_{appd} - n_{appd}}{n_{appd} + n_{appd}}; \\
    r_{p,sa} &= \frac{E_p^o}{E_p^r} = \frac{\varepsilon_s n_{appd} - \varepsilon_a n_{appd}}{\varepsilon_s n_{appd} + \varepsilon_a n_{appd}};
\end{align*}
\]

which give the s- and p-polarized complex reflectances for the two-phase model.

The ellipsometrically measured complex reflectance ratio can be also given analytically in the two-phase model:

\[
\rho = \frac{r_{p,sa}}{r_{s,sa}} = \frac{\sin^2 \phi - n_{appd} \cos \phi}{\sin^2 \phi + n_{appd} \cos \phi};
\]

where \( \phi \) is the incident angle.

This can be inverted to give \( \varepsilon_s \) directly in terms of the measured quantity \( \rho \).
If there is a very thin overlayer on substrate, the situation is different from 2 phase case. In principle this becomes simply a matter of starting at the just inside the substrate at the boundary between the substrate and first overlayer, where the boundary conditions $E'_s = H'_s = 0$ meaning no back reflection inside substrate apply, then calculate the field amplitudes just across the boundary in the first overlayer, then applying the appropriate exponential factors to calculate the amplitudes at the other boundary of the first overlayer, the repeating process until the wave emerges into the ambient. Considering in addition propagation across the layer $(j+1)$ assuming a thickness $d_{j+1}$, if only three phases (substrate, overlayer, ambient) are present, the generic form of reflectance for either s-or p-polarized light is therefore given by:

$$r_{sao} = \frac{r_{sso} + Zr_{rso}}{1 + Zr_{roa}r_{soa}},$$ \hspace{1cm} 1.8

where $Z = \exp(2ik_{j+1,pdd}d_{j+1})$.

If the overlayer is extremely thin so that $d << \frac{4\pi}{\lambda}$, then analytic results can again be obtained.

$$r_s = r_{s,sa}[1 + \frac{4dn_o\cos\phi}{\lambda}\frac{\varepsilon_a - \varepsilon_o}{\varepsilon_s - \varepsilon_a}];$$ \hspace{1cm} 1.9

$$r_p = r_{p,sa}[1 + \frac{4\pi n_o\cos\phi}{\lambda}\frac{\varepsilon_s - \varepsilon_o}{\varepsilon_a - \varepsilon_s}(\frac{1}{\varepsilon_a} + \frac{1}{\varepsilon_s})\varepsilon_a \sin^2\phi];$$ \hspace{1cm} 1.10

$$\rho = \rho_{sa}[1 + \frac{4\pi \varepsilon_o n_o\cos\phi}{\lambda}\frac{\varepsilon_s(\varepsilon_s - \varepsilon_o)(\varepsilon_a - \varepsilon_o)}{\varepsilon_o(\varepsilon_s - \varepsilon_a)(\varepsilon_s \cot^2\phi - \varepsilon_a)}].$$ \hspace{1cm} 1.11

The last equation can also be put in pseudodielectric function form, where a
pseudodielectric function $<\varepsilon>$ is that quantity that would be calculated from the direct ellipsometric data using $\rho$ using the two phase model, that is, by ignoring the existence of possible overlayers. The advantage of $<\varepsilon>$ is that it represents the data in a form more nearly related to the quantity of interest for materials analysis; the original data $\rho$ can always be recovered by reapplying the two-phase model to calculate it form $<\varepsilon>$. The result is

$$<\varepsilon> = \varepsilon_s + \frac{4\pi idn_a}{\lambda} \frac{\varepsilon_s(\varepsilon_s - \varepsilon_a)(\varepsilon_o - \varepsilon_a)}{\varepsilon_o(\varepsilon_s - \varepsilon_a)} \left[ \frac{\varepsilon_s}{\varepsilon_o} - \sin^2 \phi \right]^{1/2}; \quad 1.12$$

Therefore, $<\varepsilon>$ is a measured quantity and all parameters except $\varepsilon_o$, can be known so that $\varepsilon_o$, dielectric function of thin film overlayer can be achieved by iteration.

(ii) Effective medium approximation (Bruggeman mixing)

So far, we have assumed the ideal 3-phase case which is ambient-overlayer-substrate. However, in reality the actual phase is not mathematically abrupt 3 phase model since there are “interfaces” and “void” between each medium as shown in Fig. 1.6 [27,28].

Thus, we need to consider the effective medium approximation (EMA) to take the microscopic inhomogeneous phases into account for approaching a more realistic model. In the most widely used EMA, the effective dielectric constant $\varepsilon$ is given by the Bruggeman expression

$$0 = f_a \frac{\varepsilon_a - \varepsilon}{\varepsilon_a + K\varepsilon} + f_b \frac{\varepsilon_b - \varepsilon}{\varepsilon_b + K\varepsilon}; \quad 1.13$$

This assumes two randomly mixed phases with dielectric functions $\varepsilon_a$ and $\varepsilon_b$ with fractions $f_a$ and $f_b$ respectively ($f_a + f_b = 1$), and it is straightforwardly extended for more than
two phases. K=2 assumes spherical microstructure.

In this study, two types of SE machines were used depending on the energy range of incident beam. One is visible-UV SE having an incident polarized beam generated by a xenon lamp with energy between 1.5 and 6 eV. This machine is working in ambient condition. The other machine is vacuum-UV SE covering higher energy range, from 4 to 10 eV, where deuterium UV lamp and 256-channeled Si based photomultiplier are used for a light source and detector. Also, the medium range vacuum (~ 10 mTorr) is maintained to minimize the scattered lights with particles in ambient at the higher energy above 6 eV. Both of SE machines are working in rotating compensator configuration [29].

1.6 Electrical techniques: Current-Voltage (I-V) and Capacitance-Voltage (C-V)

For electrical measurements, metal-electroded capacitors were fabricated using shadow masks on mid $10^{17}$ to low $10^{18}$ cm$^2$ n- and p-type Si and Ge substrate. Capacitors were prepared in class-100 cleanroom located at North Carolina State University (NCSU). The overall process steps include surface cleaning, sacrificial thermal oxide and high-k oxide growth, post deposition rapid thermal anneal (RTA), and dot metal electrode (Al) formation using evaporation. In the process included forming gas anneal (FGA) for 30 minutes in a mixture of 10% H$_2$ in N$_2$ at 400°C was used to minimize D$_{it}$. This step was done before metallization in order to prevent reactions between the Al gate metal and the dielectric films.

Electrical measurements of Si- and Ge-capacitor devices were performed on a Material Development Corporation system. An HP 4284A LCR meter with a frequency range of 10 kHz to 1 MHz was used to perform capacitance-voltage measurements for capacitance
dispersion. Current-voltage measurements were done on an HP 4140B voltage source with a pico-ammeter. Voltage-ramp rates were varied from \( \frac{dV}{dt} = 0.001 \text{ V/sec} \) to \( \frac{dV}{dt} = 0.05 \text{ V/sec} \). A slower ramp rate is preferred to reduce the displacement current, ensuring that the current measured is actually tunneling current. The temperature of the sample was maintained at 25°C and all measurements were performed in a light-tight box.

The focus on analysis on I-V measurements is to investigate the trap level’s role in injection and transport mechanism in leakage current process. This was possible from in-depth analysis of I-V traces based on the basic relation of possible transport mechanisms in oxides such as direct tunneling (DT), Poole-Frenkel (PF), trap assisted tunneling (TAT), and Folwer–Nordheim tunneling (FN) to the governing parameters such as temperature, trap depth, electric field, and dependence on trap density [30-32].

The focus on analysis on C-V measurements is to quantify trapped charges at defects in oxides. The specific methods for this are (i) trapped charge density extracted from C-V hysteresis and (ii) frequency dispersion of C-V traces giving information about dominant trap location (e.g. interface or bulk oxide region) [32,33].

1.7 Overview of dissertation

The purpose of this research is to investigate (i) physical origin of intrinsic defects in TM/RE high-k oxides, (ii) relation of defect behavior to a length scale (or crystalline size) of nanocrystalline high-k oxides, (iii) correlation of bonding defects to the electrical activity in devices, and finally, (iv) to find the efficient engineering pathway to suppress or control defects in oxides satisfying required levels in both for materials and electrical point of views.
In order to achieve this goal, the main approach is a spectroscopic characterization on various TM/RE elemental/complex oxides in the context of thin films and correlation of those results to the electrical data on devices using the same oxides as gate dielectrics. However, analysis on data was not limited to the intrinsic properties of oxide itself but reached to the interfacial reaction to other materials such as substrate and metals. The main focus on this dissertation study is quantification of pre-existing defects from spectroscopic measurements and correlation of pre-existing defects to the trapped charges in device operation.

Chapter Two addresses the intrinsic bonding defects inherently existing in the nanocrystalline high-k dielectrics associated with the discrete asymmetric defect energy levels near the conduction and valence band edge. This study demonstrates the spectroscopic measurement techniques and analysis approaches to quantification of the defect density and energy states.

Chapter Three reports the relation of length scale of LaScO$_3$ nanocrystalline to the conduction band changes driven by J-T distortion and localized defect behavior affected by grain growth with anneal and dimensional constraints.

Chapter Four presents the pathway to suppress the pre-existing defects in BaSrTiO$_3$ by Ni-doping. This study proves that doping of a proper metal into a perovskite oxide can successfully stabilize the local structure distortion and provide a enhancement of oxide reliability for device applications (i.e., metal-insulator-metal capacitor).

Chapter Five and Chapter Six provide the novel process approach to minimize trapping in Ge MOS capacitors. Results strongly suggest that it is necessary to (i) eliminate the interfacial oxide layers to prevent conduction band well charge trapping and (ii) minimize
interfacial defects. The results propose the engineering solution for elimination of Ge-
interfacial layers by post deposition anneal with thermally stable HfSiON.

Chapter Seven concludes the dissertation with a summary and suggestions for future
work in these research areas.

1.8 References


[27] N. V. Edwards, Status and Process for VUV ellipsometry, Characterization and
Metrology for ULSI Technology: 2003 International Conference

[28] Irving P. Herman, Optical diagnosis for thin film processing, Academic process, 1996


Fig 1.1. Electronic band edge diagrams of SiO$_2$ (left) and TM/RE high-k oxides (ZrO$_2$, right) constructed by molecular orbital (MO) theory.
Fig 1.2. Schematic CB and VB band edge MO states in TiO$_2$. 
Fig. 1.3. Schematic d-state evolution in TiO$_2$ and HfO$_2$ consisting of CB edge states.
Fig. 1.4. Schematic scheme of spectroscopic measurements on TM/RE oxides.
Fig. 1.5. Schematic diagram of the ellipsometry (top) and the ellipsometric modeling process.
Fig. 1.6. (a) Schematic diagram of the pseudodielectric function. (b) On left, model assumptions (electromagnetically sharp interface). On right hand side, what is encountered in reality (interface layers, contamination, surface roughness).
2 Spectroscopic Defection of Defects present in TM/RE Elemental/Complex High-k oxides

Abstract
This paper identifies localized defects of nanocrystalline TM-oxides; TiO$_2$ and HfO$_2$. The combined spectroscopic measurements of near edge X-ray absorption spectroscopy, spectroscopic ellipsometry and soft-X-ray photoelectron spectroscopy revealed the asymmetric and discrete localized defects in nano-crystalline TM-oxides, typically after annealing. This approach provide an unambiguous way to distinguish between these two technologically important regimes of nano-crystalline order, yielding significant information on electronic structure of intrinsic band edge states and intrinsic electronically-active defects. Engineering solution for defect reduction is also reported. Non-crystalline Hf/Ti Si-oxynitrides with high content Si$_3$N$_4$ showed enhanced thermal stability up to 1100°C, and spectroscopic evidence confirms that these pseudo-ternary complex oxides have the greatly decreased defect density at least one order lower than nanocrystalline Ti/HfO$_2$ or chemically phase separated Ti/Hf-silicates.
2.1 Introduction

The densities of interfacial and bulk traps, and fixed interfacial charge in complementary metal–oxide–semiconductor (CMOS) devices with high-k dielectrics are typically about two orders of magnitude higher ($\sim 10^{12}$ cm$^{-2}$) than those in Si–SiO$_2$ devices [1]. A crucial issue is whether these high-k oxide defects are intrinsic and associated with bonding on a particular nanocrystalline length scale, or whether they are derived from chemical impurities introduced during processing. These bonding defects have been confirmed as electrically active defects which are asymmetry trapping sources for holes and electrons. Many reports revealed that trapping kinetics in high-k dielectric gate stacks represent a potentially significant limitation for the operation and reliability of Si CMOS devices and circuits [2,3].

Although many studies on defects in high-k dielectrics have employed theoretical calculations such as local density approximation (LDA) and density functional theory (DFT), the energy location and charge status of defects (i.e., oxygen vacancies and interstitials) deviated from the experimentally observed results which might be due to the incorrect basis set ignoring the severe local distortion driven defect formation [4,5].

This chapter presents spectroscopic studies of high-k gate dielectrics, with an emphasis on (i) identification of spectral features associated with intrinsic defects of various transition metal/rare earth such as TiO$_2$ and HfO$_2$ and (ii) suppression of defects in Hf- and Ti-Si oxynitrides.

2.2 Experimental Procedures

Thin films of TM oxides of 10-100 nm thickness were deposited on films onto Si (100) substrates at 300 °C by remote plasma enhanced chemical vapor deposition (RPECVD).
The Si, Hf/Ti source gases, 2% SiH₄ in He, and Hf (IV)/Ti (IV) t-butoxide respectively, were delivered directly into the substrate region of a remote plasma reactor through two different injectors. An N₂/N₂O/He mixture was subjected to remote plasma excitation at 30 W and 13.56 MHz and was used to initiate RPECVD process. Prior to the Hf/Ti oxynitride-alloy deposition, a thin nitridation layer approximately 0.6 nm thick was deposited on the Si substrate by RPECVD to provide chemical passivation to suppress further unwanted reaction between the deposited Hf/Ti Si oxynitride alloys and the Si substrate. Upon deposition, heat treatment of samples was done by rapid thermal annealing (RTA) at 900 and 1100 °C.

Soft X-ray photoelectron spectroscopy (SXPS on beam-line U4A at the National Synchrotron Light Source), near edge X-ray absorption spectroscopy (NEXAS on beam line 10-1 at the Stanford Synchrotron Research Laboratory), and visible- and vacuum ultra-violet spectroscopic ellipsometry (VUV SE) have been performed on nano-crystalline transition metal (TM) elemental/complex oxides.

2.3 Results and Discussion

Two sub-sections on TM (i) elemental and (ii) complex oxides will be addressed here.

2.3.1 Defects in TiO₂ and HfO₂

Figs. 2.1(a) and 2.1(b) display respectively O K₁, (often designated as simply O K), and Ti L₃ core level near edge X-ray absorption spectroscopy (NEXAS) results for nanocrystalline TiO₂ thin films. Unless otherwise indicated, the group IVB TM oxide spectra introduced explicitly in the figures, and/or discussed in this paper are for nanocrystalline thin
films: 4 – 6 nm thick, and annealed after deposition in inert non-oxidizing ambient (N₂/Ar) at temperatures between 700 and 900 °C. The Ti O K₁ and L₃ spectra for TiO₂ are for transitions that originate in the respective O 1s and Ti 2p₃/₂ states, and terminate in final and normally empty states that display the same d-state average crystal-field (C-F) energy splittings, and the same Jahn-Teller (J-T) term splittings that are also present in optical transitions between the O-atom 2p \(\pi\) non-bonding states at the top of the valence band, and normally empty conduction band states, as e.g., revealed by the analysis of SE spectroscopic ellipsometry (SE) results [6]. The relative d-state energies are the same in the O K₁ and Ti L₃ spectra, whilst the final states are qualitatively different. The final states for O K₁ transitions are anti-bonding O 2p molecular orbital states localized on the same O-atoms, and are mixed with anti-bonding Ti d-states on their neighboring Ti atoms. Therefore, these transitions display spectral features at the energies of the spatially and energetically localized Ti 3d states. In contrast, the final states for the Ti L₃ transitions are the anti-bonding Ti d-states localized on the same Ti atoms, where the average C-F, and J–T term splittings reflect the local site symmetry of the Ti atoms with respect to their O atom neighbors. The photon energies identified using the minima obtained from the second derivatives of the O K₁ and Ti L₃ spectra identify the expected five d-state features, and these are addressed in Fig. 2.2(a). The x-axis values in Fig. 2.2 (a) are from the Ti L₃ differentiation, and the y-axis values, from the O K₁ differentiation. The five spectral features in Fig. 2.2 (a) are assigned to J–T d-state term splittings, i.e., the removal of the threefold and twofold degeneracies from the C-F split \(T_{2g}\) and \(E_g\) states, respectively. The energy spacing between the average values of these two symmetry group transitions yields a C-F field splitting of 2.6 ± 0.2 eV.
The J–T energy differences for the T_{2g} and E_g states are 0.7 \pm 0.2 eV, which are smaller by about a factor of about four than the average C-F splitting. The linearity of the relationship in Fig. 2.2 (a), particularly the slope at \sim 1 supports this interpretation in terms of C-F and J–T splittings.

Figures 2.3 (a) and (b) respectively display the epsilon 2 (\epsilon_2) spectrum for TiO_2, obtained by i) the analysis of VUV-SE measurements and ii) the valence band spectrum for TiO_2 by the analysis soft X-ray photoelectron spectroscopy (SXPS) measurements. The d-states have been extracted from the minima in the second derivative of the \epsilon_2 spectrum, and their relative energies in Fig. 2.2(b) are compared with those of the d-state features obtained from the differentiation of the O K_1 spectrum. This plot is also linear with a slope \sim 1, the same slope as in Fig. 2.2(a). However, the equally important SXPS valence and \epsilon_2 conduction band edge spectra in Figs. 2.3(b) and 2.3(a), respectively, show additional spectral features as (i) a doublet structure at the valence band edge and (ii) a broad spectral feature at the conduction band edge. These are respectively attributed to the occupied bonding and unoccupied anti-bonding states of intrinsic bonding defects associated with an O-deficient TiO_2 stoichiometry, TiO_{2-x} [6]. For TiO_2, these defect states are consistent with the electronic states of Ti^{3+} atomic species associated with local Ti_2O_3 bonding, or equivalently O-atom vacancies at the grain boundaries of these nanocrystalline films [6-8].

The spectroscopic data for HfO_2 is qualitatively similar to that of TiO_2. Figs. 2.4(a) and 4(b) display the S-XPS and VUV SE spectra on nano-crystalline HfO_2. In Fig. 2.4(a), the higher lying occupied state is less than 2 eV above the top of the valence band edge, and the lower defect state in the upper half of the band gap is at least 4 eV above the same
valence band edge. Comparing to SXPS spectra of TiO$_2$, the higher lying valence band edge
defect state and broad defect state feature below the conduction band edge are at
essentially the same energy relative to the valence band edge, $\sim 2.3\pm 0.2$ eV, suggesting that
they are associated with a partially occupied state of the same bonding defect.

From those spectroscopic measurements on HfO$_2$ and TiO$_2$, the model on band edge
and pre-existing paired defect states are suggested in Fig 2.5 (a) and (b) respectively.
Similarly to other calculation models on defect states in HfO$_2$, spectroscopically resolved
defect states are indeed discrete and paired. Nevertheless, those calculations have inherent
limitation in explaining the origin of defects by using incorrect wave basis sets and
generating hypothetical combination of oxygen vacancies and interstitials which will be
subject to the serious recombination in a real situation.

In contrast, our model constructed from spectroscopic measurements explains the origin
of defects with molecular orbital states of oxygen deficient Ti$^{3+}$ or Hf$^{3+}$ in sub-oxides in
stoichiometric TiO$_2$ or HfO$_2$. Therefore, it can be quantified by describing O-deficient TiO$_{2-\delta}$
and HfO$_{2-\delta}$ as mixtures that contain respectively Ti$_2$O$_3$/Hf$_2$O$_3$ and TiO$_2$/HfO$_2$ bonding fractions.
This is equivalent to O deficient mixtures including local bonding arrangements with both
tetravalent Ti$^{4+}$ and Hf$^{4+}$ and trivalent Ti$^{3+}$ and Hf$^{3+}$ species. If $\delta$ is the relative concentration of
defects ($\sim 10^{20}$ cm$^{-3}$, or $\sim 0.003$) for any one of these O-deficient oxides, e.g., HfO$_{2-\delta}$, then
HfO$_{2-\delta}$=$(1-2\delta)$ HfO$_2 +2\delta$ Hf$_2$O$_3$.

2.3.2 Defect suppression in Ti- and Hf-Si oxynitrides

An engineering pathway to suppress defects has been studied by increasing the
thermal stability of high-k dielectrics using pseudo-ternary alloys. The stability of high-Si$_3$N$_4$ content TM Si oxynitride alloys, (SiO$_2$)$_x$(Si$_3$N$_4$)$_y$(Ti/Zr/HfO$_2$)$_{1-x-y}$, against a chemical phase separation (CPS) has been established by spectroscopic studies [7,9,10]. TM Si oxynitride alloys were deposited at 300 °C by RPECVD and annealed in Ar at temperatures up to 1100 °C. The alloys with approximately equal SiO$_2$ and Ti/Zr/HfO$_2$ contents (~40 to 45%) and a low-Si$_3$N$_4$ content (<15–25%) exhibited CPS into noncrystalline SiO$_2$ and nanocrystalline Ti/Zr/HfO$_2$ after annealing at temperatures up to 900 °C, where those alloys with a high-Si$_3$N$_4$ content (~40%) and approximately equal SiO$_2$ and TM oxide contents (~30%) did not exhibit spectral features indicative of CPS.[7,9] This behavior with respect to CPS is qualitatively different from that obtained for Zr and Hf silicate alloys [11,12]. These alloys are unstable with respect to CPS at ~900 °C, regardless of the alloy composition, i.e., the relative i) SiO$_2$, and ii) ZrO$_2$ or HfO$_2$ alloys fractions. Since the stable IVB TM Si oxynitride alloys are noncrystalline, they do not include grain boundaries at which high densities (>10$^{13}$ cm$^{-3}$) of O-vacancies could cluster; therefore, they represent a possible engineering solution for producing high-k dielectrics with inherently lower defect densities for advanced Si devices.

Figure 2.6 shows a comparison of O K1 NEXAS and band edge $\varepsilon_2$ spectra for Ti Si oxynitride alloys. The NEXAS spectra for the low-Si$_3$N$_4$ content alloy show CPS with a change in Ti atom coordination from fourfold after deposition to six-fold following the 900 °C anneal. The comparison between the $\varepsilon_2$ spectrum from vis–VUV SE measurements, and O K$_1$ edge spectra for the 40% high-Si$_3$N$_4$ content alloy indicates no spectroscopic evidence for a coordination increase associated with CPS, i.e., the C-F splitting is indicative of fourfold coordinated Ti bonding after the film deposition and after the 900 °C annealing as well.
Consistent with the corresponding behavior of TiO$_2$ noted above, the spectra in Fig. 2.6 also establish that the d-state features in the O K$_1$ spectrum terminated in the same anti-bonding d-states as in $\varepsilon_2$ spectra. However, it should be noted that each spectrum also displays a significant tailing of states into the forbidden band gap suggestive of intrinsic defects associated with the inherent noncrystallinity of these films. Since these states are energies less than 5.5 eV, they may be associated with the Si–N bonding of these alloys, and in particular band-tail defects localized on the nitrogen atoms.[13]

Figure 2.7 represents the similar $\varepsilon_2$ spectra of Hf-Si oxynitride showing the strong dependence of thermal stability onto Si$_3$N$_4$ composition ratios. Although differences in spectral features before and after an annealing are not severe as in Ti-Si oxynitride, lower Si$_3$N$_4$ content alloys revealed the additional states at about 6.5 eV and more pronounced edge states which might be partially due to CPS driven local bonding defects. In contrast, there are no noticeable spectra changes in 40% Si$_3$N$_4$ alloy both for edge and higher energy states in $\varepsilon_2$ spectra. The much softer edge of $\varepsilon_2$ spectra in 40% Si$_3$N$_4$ alloy indicates its non-crystalline character, and this was confirmed in a previous XPS study on Zr-Si oxynitrides revealing no changes in oxygen bonding states before and after anneal [10].

The physical reason for observed thermal stability enhancements in high Si$_3$N$_4$ content TM-Si oxynitrides is explained by bond constraint theory. A schematic representation of the local bonding in the group IVB TM atoms in the optimized TM Si oxynitrides has been presented in Fig. 2.8. The application of bond constraint theory (BCT) to this bonding group includes broken bonding constraints on the Si atom, and yields an average number of bonding constraints per atom, $C_{av} \sim 3.05$, for an alloy with equal concentrations of Si$_3$N$_4$,.
SiO$_2$ and the TM elemental oxide, e.g., ZrO$_2$ [14]. Alloys with $C_{av}$ in the range between 2.9 and 3.2 generally form intermediate phases in which defects and defect precursors are minimized making them ideal candidates for device applications. $C_{av}$ increases modestly to $\sim$3.15 when the Si$_3$N$_4$ concentration is increased to 40%, and the SiO$_2$ and TM elemental oxide concentrations are reduced proportionally to $\sim$30%. This higher Si$_3$N$_4$ content creates regions of local rigidity associated with the Si$_3$N$_4$ alloy fraction being greater than the SiO$_2$ fraction. However, this local rigidity cannot percolate throughout the sample, and does not change the intermediate phase properties of these alloys. The bonding arrangements in these alloys results from a chemical bonding self-organization that optimizes bonding properties, reducing configurational entropy associated with random bonding, but reducing bond strain to compensate for the entropy reduction.

2.4 Summary

The spectroscopic data in this paper have indicated that: (i) defect state features are at the valence band edge in TiO$_2$ and HfO$_2$ as determined by SXPS and below the conduction band edge as determined by NEXAS, vis–VUV SE, and (ii) on the basis of the results of comparisons with intrinsic d-state features, these defect state densities can be $>10^{13}$ cm$^{-2}$ [or equivalently $> (3 - 5) \times 10^{19}$ cm$^3$]; (iii) defect states in HfO$_2$ are quantitatively different from those in TiO$_2$; (v) qualitatively similar defect bonding arrangements are assigned to Ti$^{3+}$ bonding in TiO$_2$, and to Hf$^{3+}$ bonding in HfO$_2$; (iv) these defects are in suboxide bonding arrangements with (TM)$_2$O$_3$ compositions clustered at nanocrystalline grain boundaries, however, the bonding coordinations at the Ti, and Zr and Hf sites may be different; (v) a connection between intrinsic bonding arrangements and grain boundary defects is
supported by the results of studies on noncrystalline group IVB TM Si oxynitrides; and finally (vi) even though discrete Ti$^{3+}$ and Hf$^{3+}$ valence and conduction band edge defects have not been observed in thin film dielectrics identified in (vii), these dielectrics show band edge tailing, indicative of pre-existing defects at order of magnitude lower concentrations than the grain-boundary-associated defect densities in the nanocrystalline.

2.5 References


Fig. 2.1. NEXAS spectra for TiO$_2$: (a) O K$_1$ and (b) Ti L$_3$ edges.
Fig. 2.2. Photon energies of Ti d-state features: (a) O K$_1$ edge vs Ti L$_3$ edge and (b) $\varepsilon_2$ vs O K$_1$ edge.
Fig. 2.3. (a) VUV SE $\varepsilon_2$ spectrum and (b) SXPS VB structure versus photon energy for TiO$_2$
Fig. 2.4. (a) SXPS VB structure versus binding energy and (b) VUV SE $\varepsilon_2$ spectrum versus photon energy for HfO$_2$. 

- PVD HfO$_2$ (30 nm) 900°C annealed
- Hf$^{3+}$ defects
- $\Delta E_g \sim 1.4$ eV
- 1st $E_g$
- 2nd $E_g$
Fig. 2.5. Band edge and pre-existing defects determined by spectroscopic studies for (a) HfO$_2$ and (b) TiO$_2$. 
Fig. 2.6. O K$_1$ and $\varepsilon_2$ spectra for low and high Si$_3$N$_4$ content Ti Si oxynitride alloys.
Fig. 2.7. $\varepsilon_2$ spectra for (a) low- and (b) high-Si$_3$N$_4$ content Hf-Si oxynitride alloys before and after annealing.
Fig. 2.8. Schematic representation of local bonding arrangement in optimized Zr(Hf)-Si oxynitride alloy with ~33-40 % Si₃N₄, and 30-33 % SiO₂ and HfO₂.
Abstract

This paper uses (i) spectroscopic measurements; X-ray absorption and vacuum ultraviolet spectroscopic ellipsometry, (ii) high resolution transmission electron microscope, and (iii) internal photoemission spectroscopy to distinguish between non-crystallinity, and the suppression of Jahn-Teller splittings that identify a scale of order metric, $\lambda_s$, of $\sim$3 nm for distinguishing between i) nanocrystalline-order that can be detected by x-ray diffraction for $\lambda_s >$ 3-4 nm, and ii) reduced nanocrystalline order that can be detected by atomic-scale imaging and extended X-ray absorption spectroscopy for $\lambda_s < \sim$2.5 nm. The coherent $\pi$-bonding coupling is strongly associated to J-T split driven localized oxygen bonding defects at grain boundary in LaScO$_3$ and the incoherent $\pi$-bonding coupling is related to oxygen vacancies at very thin hetero-interfacial region of LaAlO$_3$ on SrTiO$_3$ at $\sim$ 0.4nm.
3. 1. Introduction

There has been much debate and interest in the possible existence of a non-crystalline phase for transition metal (TM) and rare earth (RE) atom elemental and complex oxides. TM and RE silicates, and TM Si oxynitride alloys can be deposited as noncrystalline thin films; however, this does not apply to elemental and complex TM and RE atom elemental and complex oxides having fairly high dielectric constants. The absence of line features in conventional X-ray diffraction (XRD) measurements has often been used to label a material as being X-ray amorphous, a designation which lacks any substance. In marked contrast, this paper uses X-ray absorption and vacuum ultra-violet spectroscopic ellipsometry (VUV-SE) to distinguish between noncrystallinity, and the suppression of Jahn-Teller (J-T) splittings that identify a scale of order of ~3 nm for distinguishing between two distinct and different regimes of nanocrystallinity: i) nanocrystalline order that can also be detected by X-ray diffraction for $\lambda_s > 3-4$ nm, ii) reduced nanocrystalline order that can only be detected by atomic-scale high resolution transmission electron microscope imaging (HRTEM) and extended X-ray absorption spectroscopy (EXAFS) for $\lambda_s < \sim 2.5$ nm [1,2], and iii) finally physical correlation of empty energy state changes of J-T driven intrinsic d-states and localized defects to the length scale of order in oxides.

3. 2. Experimental Procedures

Nanocrystalline LaScO$_3$ films were deposited at room temperature by the molecular beam deposition on p-type Si (001) substrate at Pennsylvania State University. The native SiO$_x$ (x=1~2) on the silicon wafer was thermally removed in ultrahigh-vacuum at 900 °C.
before the film deposition. Deposited samples were respectively annealed for 1 min from 700 to 1000 °C in an inert ambient. The film thickness analyzed by SE is about 40nm. Films were studied by HRTEM (UCSB), VUV SE and X-ray absorption spectroscopy (XAS). MOS capacitors consisting of transparent Ag electrodes/LaScO₃/Si were fabricated for internal photoemission spectroscopy (IPS) measurements at KU Leuven and photoconductivity (PC) spectra under the voltage bias were measured with the exposure of UV light swept from 1.5 and 6 eV.

XAS and SE spectra have also been obtained for 0.38 nm LaAlO₃ films on single crystal SrTiO₃.[2] These were prepared by reactive sputtering. XAS measurements were made the Stanford Synchrotron Research Laboratory (SSRL).

3.3 Results and Discussion

Figures 3.1, 3.2 and 3.3 present core level XAS spectra for as-grown and 1000 °C annealed nanocrystalline LaScO₃ thin films. These spectra include the transitions from Sc L₂,₃ (Fig 3.1), O K₁ (Fig. 3.2), and La M₂,₃ (Fig 3.3) core levels to the conduction level. Sc L₂,₃ spectra for all samples clearly show the multiplicity of five well-resolved states. This multiplicity of d-states originates from the fundamental d-orbital characteristics produced by bonding to a common O-atom in TM/RE complex oxides [3,4].

If TM/RE complex oxide has symmetric bonding environments such as six-fold octahedral with all equivalent bonding length between metal and coordinated six oxygen atoms, crystal field (C-F) spitting occurs which reserves the three- and two-fold degeneracies of d-states. However, as the structure of TM/RE complex oxides changes to
the distorted bonding environments, the degeneracy of constituent atom valence and conduction band d-states with spherical symmetry is removed [5]. Therefore, as the structure evolves from symmetric structure to distorted one, a distinction between i) J-T term splittings and ii) C-F splitting can be a clear reference to determine either symmetric bonding environment or asymmetric one with localized bonding distortion.

Figure 3.4 displays the evolution of C-F and J-T term splitting for TiO$_2$ d-states from i) a regular octahedral and then to ii) distorted octahedral and finally to iii) additional distortions that occur at grain boundaries in nanocrystalline films. LaScO$_3$ has the same octahedral bonding environment as TiO$_2$ so that the evolution of LaScO$_3$ d-state splittings is almost same as TiO$_2$ but with a slight difference in energy of term-splittings. From *ab initio* calculation guided by molecular orbital (MO) theory, the three lower states and two higher states have been assigned as T$_{2g}$ in $\pi$ anti-bonding characteristic and E$_g$ in $\sigma$ anti-bonding characteristic respectively [6]. The J-T term splitting becomes larger as bonding environments are subject to more aggressive distortions and therefore decreases the conduction edge level to the lower energy. The physical reason for the presence of J-T distortion in TM/RE oxides has been regarded as the electrostatic stabilization of localized metal-oxygen bondings [5].

The d-state splittings in Fig. 3.1 thus imply that as-deposited LaScO$_3$ thin film has the distorted octahedral bonding environment in contrast to the previous reports which have declared an amorphous structure for as-deposited LaScO$_3$. [7] These term-splittings are also evident in the O K$_1$ edge spectra. Both of Sc L$_{2,3}$ and O K$_1$ edge spectra show the systematic decrease in spectra line-width of the d-state features between as-deposited film and those
annealed at 700 °C and 1000 °C. The change of d-states also reveals the overall energy shift of $T_{2g}$ states to the lower energy in Sc L$_{2,3}$ edge spectra and the significant change of edge states in O K$_1$ spectra. In Fig. 3.1 (b), The $T_{2g}$ term splitting are 0.8±0.5 eV, and the average $T_{2g}$-$E_g$ is about 2.7 eV. This term-splitting is approximately the same as the Ti L$_3$ edge spectra for TiO$_2$ thin film which has the same local bonding environment as LaScO$_3$, i.e., 6-fold octahedral Ti-O bonding [6]. XRD studies have detected crystallinity after an 850°C anneal, but not in as-deposited or 700°C annealed samples. This implies that the XAS spectra are more sensitive to nanocrystalline films than XRD [8]. Since XRD can detect the nano-crystallites at a scale greater than 4 nm but can not distinguish between i) amorphous films, and ii) nanocrystalline films with grain size smaller than 4 nm, as-deposited and 700°C annealed thin films are considered to have the 1 ~ 2 nm nanocrystallites.

The La M$_{2,3}$ spectrum for thin films as-grown and those annealed at 1000 °C are shown in Fig. 3.3. There is only one 5d feature in each of the spin-orbit split spectra indicating the absence of J-T term splitting. The combination of spectroscopically resolved J-T term splitting in the Sc L$_{2,3}$ spectrum in Fig. 3.1 and the absence of J-T distortion in the La M$_{2,3}$ spectrum in Fig. 3.3 is consistent with a nanocrystalline morphology based on the orthorhombic perovskite structure.[8] In this structural model, there are asymmetric x, y and z displacements of the Sc atom respect to six O-neighbor atoms, but the La atom remains in a symmetric environment with twelve nearest-neighbor O-atoms. The crystalline nature of this film has been confirmed by x-ray diffraction. In contrast, J-T splittings are evident for the both the Al 3p- and La 5d-states in LaAlO$_3$ arising from the rhombohedral unit cell distortion.
of the perovskite structure.

Figure 3.5 represents the linear scaling plot correlating Sc L₃ and O K₁ edge spectra for thin film annealed at 1000 °C. This O K₁ edge spectrum for the 1000 °C annealed film is consistent with the previous assignments made for Gd and Dy scandate O K₁ spectra since they also have similar bonding environments in the crystallinity [9,10]. Two strongest features at ~ 399.4 eV and ~ 401.4 eV in Sc L₃ edge spectrum corresponds to features at ~ 530.6 eV and ~ 532.6 eV in O K₁ edge spectrum. Although the empty MO states are essentially same, the relative intensities of absorption are different for each core level transition because strong matrix elements are involved.

SE measurements have been made on LaScO₃ thin films to investigate intrinsic changes of optical band gap and conduction level edge states with annealing.

SE measurements probe the complex dielectric constant, ε₁+iε₂ where ε₁ is the real part and ε₂ is the imaginary part of complex dielectric function. The energy states in ε₂ spectra reflect the feature of the joint density between valence band and conduction band states, their relative amplitudes, and the energy dependence of the optical transition matrix element. The complex dielectric constant can be directly converted to the optical absorption coefficient, α and the energies of features in α and ε₂ are approximately same. However, the energies of the feature in α also are affected by the dispersion in ε₁, so that determination of the energy position based on ε₂ has been done in this study.

Figure 3.6 plots the imaginary dielectric constants for as-deposited and annealed thin films. These ε₂ spectra show the rapid decrease in the line width of strongest features with a peak at around 6.8 eV for thin films annealed at above 900 °C and also systematic changes
of steepest edges depending on annealing temperatures similar to the Sc L\textsubscript{2,3} and O K\textsubscript{1} edge XAS spectra. Several previous works defined this steepest edge of the strongest feature as the optical band gap of LaScO\textsubscript{3} thin film which shifts from \(~ 5.5\) eV for amorphous to \(~ 6\) eV for the crystallized thin film. These results have been used as general definition for optical band gap, but there must be an additional sophisticated interpretation based on empty MO state changes consistent with nano-crystallinity of thin films to define band offset energy thresholds between the dielectrics and Si.

In XAS and SE spectra, the line width sharpening with anneal relates to the length of scale in nanocrystalline. In order to verify this, HRTEM images on as-grown and 1000 °C annealed LaScO\textsubscript{3} were taken (Fig. 3.7). TEM Images indicates crystalline order in even as-grown, but only a scale of \(~ 2\)nm but much larger order range for annealed samples showing the clear grain boundaries. Therefore, it is obvious that length scale of nanocrystalline forces the changes in spectral line widths.

Figure 3.8 presents the PC spectrum of as-deposited LaScO\textsubscript{3} thin film [11]. In this spectrum, the strong feature is \(~ 5.6\) eV, which has been occasionally declared as the band gap. However, there are weak states at \(~ 4.6\) and \(~ 5.1\) eV which also appear at the absorption coefficient plot in Fig. 3.6. It is regarded that the physical origin of these three features as they appeared in both PC and absorption coefficient measurements are same. As discussed earlier, these features are due to J-T term splittings of Sc \(T_{2g}\) states acting as the final state for the transitions from Sc \(\pi\) bonding d-states in the valence band to Sc \(\pi^*\) anti-bonding d\(^*\)-states in the conduction band. These Sc d-states are also coupled to O\(_{2p}\) states in the valence and O\(_{2p}^*\) states in the conduction band [6].
Again, the previous assignment that defined the conduction band edge at ~ 5.6 eV based on this PC edge features is not correct but should be corrected to ~ 4.6 eV. This argument can be equally applied to the crystalline Sc$_2$O$_3$ having the strong absorption onset at about 6 eV but the absorption tail extending to about 4.6 eV. These tail states in Sc$_2$O$_3$ are inherently the same states as edge states of LaScO$_3$, i.e., $T_{2g}$ term splittings of Sc d-states. These features of the crystalline Sc$_2$O$_3$ are well coincident with features of 1000°C annealed LaScO$_3$ thin films with larger nano-crystallite size. Furthermore, the overall edge features in the conduction level of LaScO$_3$ or Sc$_2$O$_3$ are qualitatively similar to TiO$_2$ since it also has octahedral bonding environment between Ti and six neighboring O atoms and suffers from the J-T distortion of those bondings.

As a result, the correct reinterpretation of PC spectra confirms the significant decrease of the conduction band offset by the re-definition of absorption onset energy from 5.6 or 6 eV to 4.6 eV. This decrease results in a conduction band offset between the these kinds of scandinate oxides and Si smaller than 1 eV so that the significant direct tunneling can occur at the target operation gate voltage, 1V proposed by roadmap projections for device at EOT of 1 nm [12]. Additionally, the PC below 4.5 eV may be partly assigned to the intrinsic defect states, some of which can be derived from J-T term split states at the internal grain boundaries [13,14]. This defect state has been suggested as one of the paths contributing to the gate leakage current by trapping or Frenkel-Poole hopping process through high-k gate dielectrics [15,16]. These states are also observed in absorption coefficients or $\varepsilon_2$ spectra but are not clearly resolved because they are overlapped with weak $T_{2g}$ features at relatively weak amplitudes and wide spectral line width like Ti$_3^+$ defect states in TiO$_2$ thin films [17].
From all of the spectra evidence on LaScO$_3$ so far, it can be concluded that the larger length scale of nanocrystalline resulted in J-T term split. Between as-deposited and 1000 °C annealed films, a systematic grain size expansion is observed and pronounced J-T term split is observed at temperature no less than 800 °C where the crystallinity is detectable by XRD. Based on HRTEM images and the detection limit of XRD on crystallinity, the transitional length of scale, $\lambda_s$, is between 3 and 4 nm. This is coincident with a lower border limit for coherent $\pi$-bonding coupling between TM d states (i.e., Sc 3d) and oxygen 2p states across neighboring TM-oxygen unit cells (i.e., octahedral Sc-O unit cells) through oxygens requiring at least three or four unit cells. If $\lambda_s$ of specific TM/RE oxides is less than $\sim$ 3.5 nm, it will be subject to the incoherent $\pi$-bonding coupling. This length of scale, $\lambda_s$, is universally applied to other TM/RE elemental/complex oxides having nanocrystalline structure, so another very thin complex oxide interface at 0.38 nm, LaAlO$_3$ on SrTiO$_3$ was studied.

Figures 3.9 (a) and (b), respectively, display the O K$_\text{I}$ XAS and SE absorption ($\alpha$) spectra for heterointerface structures with 0.38 nm of LaAlO$_3$ deposited on single crystal SrTiO$_3$ substrate. This interface structure has been of great interest because the very high mobility two dimensional electron gas has been observed but the origin of this phenomenon was not clear. However, one of major process factors is that the oxygen concentration in LaAlO$_3$ deposition turned out to play a major role on the occurrence of high mobility electron gas at this interface.

Sample 0728 is a non-conducting sample deposited at an O$_2$ pressure of $10^{-5}$ Torr, whilst sample 0802 has the same physical thickness of LaAlO$_3$ and is a conducting sample deposited at a reduced O$_2$ pressure of $10^{-6}$ Torr. The Ti 3d and 4s features are significantly
stronger relative to the La 5d features; in addition the half-width-at-half-maximum (hwhm), at the low energy side of the Ti T_{2g} feature relative to TiO_2 is smaller for the 0728 sample compared with the 0802 sample. This is indicative of a decrease in the density of O-atom vacancies, or alternative Ti^{3+} bonding. The absorption constant spectra support the interpretation of the O K\textsubscript{1} spectra. The band edge defect state features between 2.3 and 3.5 eV are stronger in the sample deposited at the lower O\textsubscript{2} pressure consistent with a higher concentration of O-atom vacancies, or equivalently Ti^{3+} defect sites. The O-vacancies in the SrTiO\textsubscript{3} surface region that borders the metallurgical boundary between the SrTiO\textsubscript{3} substrate and the La\textsubscript{2}O\textsubscript{3} over-layers has its origin in incoherent π-bonding at this interface [18].

3.4 Conclusions

In the nanocrystalline TM/RE atom elemental and complex oxides, there are two critical size effects: films with nano-grains less than 3 nm do not have coherent grain boundaries, but instead have about two atomic layers of disordered bonding interconnecting the grains, whereas films with nanograins greater than about 3 nm, there are coherent grain boundaries [1,4]. These two length scales of nanocrystalline order are differentiated by XAS and SE spectra that reveal intrinsic band edge states; either J-T splitting, or different spectral widths of the band edge features. Band edge defects in nanocrystalline TM/RE oxide films are qualitatively different in these two length scale regimes. For nanocrystalline grain size >3-4 nm, there are discrete band edge states associated with O-atom vacancies clustered at grain boundaries [1], whereas in as-deposited films, and films with a physical thickness of ~2 nm, they are band-tail states.
3.5 References


Fig. 3.1. Sc L$_3$ edge XAS spectra for (a) as-deposited and (b) 1000 °C annealed nanocrystalline LaScO$_3$. 

59
Fig. 3.2. O K$_1$ edge XAS spectra for (a) as-deposited and (b) 1000 °C annealed nanocrystalline LaScO$_3$. 
Fig. 3.3. La M$_{2,3}$ edge XAS spectra for (a) as-deposited and (b) 1000 °C annealed nanocrystalline LaScO$_3$. 
Fig 3.4. Calculated conduction band edge d-states for TiO$_2$: the crystal field (C-F) splitting for
i) a regular or undistorted octahedral distribution of O neighbors, ii) a geometric distortion
with the same nearest neighbor bonding as rutile and iii) a grain boundary distortion.
Fig 3.5. Linear scaling between features of the Sc L₃ edge, and O K₁ edge spectrum for 1000°C annealed LaScO₃ thin film.
Fig. 3.6. Imaginary part of the complex dielectric constant versus photon energy for as-deposited and annealed LaScO$_3$ thin films between 700 and 1000 °C.
Fig. 3.7. HRTEM images of (a) as-deposited and (b) 1000°C annealed LaScO₃.
Fig. 3.8. Band edge PC for nano-crystalline as-deposited LaScO$_3$ film.
Fig. 3.9. (a) XAS O K$_1$ edge spectrum and (b) VUV SE spectra for 0.38 nm of LaAlO$_3$ on SrTiO$_3$ for different oxygen pressure in film deposition.
4 Defect Band Engineering of BaSrTiO$_3$ Dielectrics in Metal Insulator Metal Capacitor by Ni Doping

Abstract

The transition from direct to trap-assisted Fowler-Nordheim tunneling in metal-insulator-metal capacitors is suppressed in metal-insulator-metal (MIM) capacitors when Ni-doped barium strontium titanate (BST) thin film dielectrics are substituted for undoped BST. For Ni-doping at the one percent level, the spectral dependence of the imaginary part of the complex dielectric constant, $\varepsilon_2$, obtained from spectroscopic ellipsometry (SE), shows significant differences in the band edge trap depth relative to undoped BST. There is direct correlation with these changes in defect state energies relative to the conduction band edge and improved electrical performance for MIM capacitors with the Ni-doped BST dielectrics.
4.1 Introduction

Barium strontium titanate, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ (hereafter, BST) has been investigated as a high-k dielectric for storage capacitors for gigabit dynamic random access memory (DRAM), organic devices, and microwave tunable devices as well [1-4]. Thermally annealed, ferroelectric BST has a dielectric constant $>200$-300, that is a function of domain size as determined by film thickness [1]. Previous studies have indicated significant reliability issues associated with BST devices [5-9], and major problems are attributed to the metal contact interface when using ultra-thin oxides [5]. These problems are present as asymmetric high current leakage under moderately high bias voltages [7]. There are other issues associated with long-term reliability under both constant positive and negative voltage stress [9]. Previously published studies have suggested that oxygen vacancy defects distributed within BST films play a major role in the high leakage current and charge trapping [1,2]. This study identifies changes in band edge defects states for Ni-doped BST that correlate with improved electrical performance. Changes in leakage current are correlated with spectroscopic detection of changes in conduction band (CB) edge defect states in as-deposited nonferroelectric films, as well as annealed ferroelectric films.

4.2 Experimental Procedures

Undoped and 1% Ni-doped $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Ti}$ targets, two inches diameter in diameter, were prepared by a conventional ceramic powder process. BST and 1% Ni-doped BST thin films 200 nm thick were deposited directly onto Pt (150 nm)/Ti (50 nm)/$\text{SiO}_2$/Si substrates at room temperature using an rf magnetron sputtering system. The final schematic device structure
is shown in Fig. 4.1 (a). For electrical measurements, Pt top electrodes 100 nm thick (A=4x10^-4 cm^2) were deposited through a shadow mask in a dc magnetron sputtering system. Leakage current density-voltage (J-V) characteristics were obtained with a semiconductor parameter analyzer (HP4155A). The dielectric constants were obtained from the impedance measurements (Fig. 4.1 (b)) at 1MHz using a HP4192A impedance analyzer; the relative dielectric constants (k) were 28 for as-deposited and undoped BST and 26 for as-deposited and Ni-doped BST. These smaller dielectric constants compared with bulk BST are due to the small grain size in Ni-doped and undoped BST films as-deposited at room temperature (RT). Measurements on as-deposited films present an opportunity to identify local bonding changes responsible for differences in J-V characteristics between undoped and Ni-doped BST. The real and imaginary parts of the complex dielectric constant, \( \varepsilon_c = \varepsilon_1 + i\varepsilon_2 \), for undoped BST and Ni-doped BST were determined by visible- and vacuum-ultra violet SE in a rotating compensator configuration spectrometer [10]. The spectral dependence of \( \varepsilon_2 \), extracted from measurements indicates significant increases in band edge defects in the undoped BST after annealing in Ar, but essentially the same smaller band edge defect densities in Ni-doped BST, thereby a potential pathway for improving thin BST films for DRAM and other applications.

4.3 Results and Discussion

Figure 4.2 compares J-V curves of MIM capacitors with as-deposited BST and Ni-doped BST dielectrics. The applied voltage was swept to 40 V to determine the relative stability of Ni-doped BST under at relatively high bias voltage, and also to reveal any asymmetry in the J-V characteristics. The J-V curves in Fig. 4.2 show markedly different
behavior with, and without Ni-doping in the BST. Asymmetries in J-V plots for undoped BST devices have been assumed to be related to differences in native defects at the top and bottom interfaces consistent with anticipated differences in interface bonding between i) Pt and deposited BST, and ii) the BST as-deposited surface and a deposited Pt electrode. Our focus will be on positive gate bias results. For a positive applied bias to the top electrode, the undoped BST display a rapid increase of current at ~2-3 V, and multiple random dielectric breakdowns at applied voltages >14 V. The rapid increase in current of undoped BST is attributed to a combination of trap assisted tunneling (TAT) and Folwer-Nordheim (F-N) tunneling out of these traps [11]. In contrast, the Ni-doped BST films show no significant increases in J for applied bias voltages of up to 40 V, indicating a significant reduction in the TAT process. While there is a marked asymmetry in the J-V curves for the undoped BST MIMs, the J-V curves for the Ni-doped BST MIMs are symmetric with no indications of TAT or a transition to F-N tunneling.

Differences in conduction band edge defect states between undoped and Ni-doped BST have been determined directly by spectroscopy, visible and VUV SE, rather than by indirect extraction of defect state properties from modeling the temperature dependence of J-V measurements [11-13]. Figure 4.3(a) presents the spectral dependence of the imaginary part of the complex dielectric constant, $\varepsilon_2$, for updoped and Ni-doped BST, including traces for as-deposited films, and films annealed at 800°C. The Ni-doped and undoped BST display strong absorption threshold at ~3.3 eV associated with band gap transitions from occupied O-atom non-bonding 2p states at the top of valence band to the lowest empty Ti$^{4+}$ 3d-states which, based on a local MO description, are Jahn-Teller (J-T) term-split 3d-states
with a $t_{2g}$ symmetry [14]. The relatively broad, and weaker $\varepsilon_2$ features between 2.8 and 3.2 eV in undoped BST spectra are due to intra-d state transitions at native defects. They are between occupied Ti$^{3+}$ non-bonding $e_g$ states near the valence band edge, and empty anti-bonding $t_{2g}$ states in the upper half of the band gap of BST [14,15]. These states are assigned to O-atom defects, and are consistent with O-deficient Ti-O bonding with a Ti$_2$O$_3$ stoichiometry and are clustered at grain boundaries (GB) in nano-crystalline transition metal oxides [16]. Figure 4.3(b) indicates the spectral dependence of $\varepsilon_2$ for BST and Ni-doped BST in a more limited spectral regime from 2.6 to 4 eV to highlight a difference in photon energy of $\sim$0.26$\pm$0.15 eV between the threshold for trapping in undoped BST, $\sim$2.65 eV, and Ni-doped BST, $\sim$2.91 eV.

The resonance energies of the Ti 3d state features in the as-deposited films have been obtained by differentiation of the respective $\varepsilon_2$ spectra [14], and are displayed in Fig. 4.3. Based on spectroscopic studies of band edge states in TiO$_2$, spectra features at photon energies $> 3.3$ eV are assigned to Ti$^{4+}$ $t_{2g}$ empty conduction band states, and features below 3.5 eV to Ti$^{3+}$ band edge defects [14,15]. The 3-fold degeneracy of the $t_{2g}$ states is removed in undoped BST indicating a distorted octahedral bonding environment between Ti and its six O-atom neighbors; e.g., an orthorhombic unit cell structure with different distortions in the x, y and z directions as shown in Fig 4.4. Band edge defects are assigned to Ti$^{3+}$ bonding that is compensated by O-atom vacancy defects clustered at grain boundaries [14]. Transitions giving rise to defect feature are from occupied Ti$^{3+}$ $e_g$ occupied d-states at the valence band edge, to unoccupied Ti$^{3+}$ $t_{2g}$ d-states at the conduction band edge. There are also two weaker features in the derivative spectra at 4.0 eV in the Ti$^{4+}$ $t_{2g}$
region of the spectrum, and ~2.80 eV in the Ti$^{3+}$ t$_{2g}$ region of the defect states.

Figure 4.5 identifies a significant difference between the Ti 2tg empty states in undoped and Ni-doped BST. As noted above the 3 fold degeneracy of the Ti 3d t$_{2g}$ state is completely removed in the undoped BST, while the degeneracy is only partially removed in the Ni-doped BST. The partial removal is consistent with a change in the local bonding geometry at the Ti$^{4+}$ sites from either orthorhombic or monoclinic in the undoped BST to tetragonal in the Ni doped BST. Based on the two-fold degeneracy of the higher lying t$_{2g}$ state in Ni-doped BST, the centroids of the t$_{2g}$ states in undoped and Ni-doped BST are effectively the same, and equal to 4.15±0.15 eV, consistent with the six-fold coordination of Ti by O-atom neighbors.

Figure 4.5 summarizes differences in spectroscopic features attributed to band edge O-atom vacancies for undoped and Ni-doped BST. The basis for these assignments derives from previously published studies of TiO$_2$ band edge intrinsic defects attributed to Ti$^{3+}$ bonding in divacancy defects clustered at grain-boundaries between nano-grains [14]. There are several important properties of these band edge defects in the 2.6 to 3.3 eV regime: i) the thresholds for absorption into empty defects are (a) independent on the processing temperature, and (b) there is increased absorption in the annealed undoped BST, but not in the Ni-doped BST, and most importantly, ii) the threshold for absorption in the Ni-doped BST is upshifted by 0.26 eV; i.e., it is closer the conduction band edge in Ni-doped BST. This change in the defect state energy in Ni-doped BST correlates with the change in symmetry of the Ti atom empty t$_{2g}$ states, and the energy shift is about the same as the average of the combined shifts for the change from two states higher lying t$_{2g}$ states in undoped BST to a
single state in Ni-doped BST.

The changes in the band edge defects are consistent with the substitution of divalent Ni$^{2+}$ for tetravalent Ti$^{4+}$. To maintain local charge neutrality, the divalent Ni$^{2+}$ atoms must be part of the divacancy structure, so that it can no longer be characterized as a Ti$^{3+}$ defect, but rather must instead be characterized as a divacancy that includes both Ni$^{2+}$ and Ti$^{3+}$ atomic species [16]. The correlated spectral changes in both the empty conduction $t_{2g}$ states, and the band edge defect, suggests that the change in symmetry for the Ti$^{4+}$ atoms is driven by an effect associated with the local dipoles at the divacancies which include a significant dipole concentration for the Ni$^{2+}$ bonding state [16]. This will be addressed in more detail in a more comprehensive study that addresses symmetry driven changes in transition metal oxides in a more general way [17].

Figure 4.6 is an interfacial band alignment diagram in which: i) the BST-Pt conduction band energy difference is 1.4 eV, ii) the trap depth for undoped and Ni-doped BST are indicated respectively by solid and dashed lines, and ii) three tunneling pathways are indicated: (a) TAT for Ni-doped BST by dashed arrows, (b) TAT for undoped BST by solid arrows, and (c) a DT mechanism in which the electrons are supplied from occupied Pf 5d states [11,18]. The relative trap depths and the lower density of traps in Ni-doped BST relative to undoped BST are consistent with the following assignments: i) the TAT/F-N tunneling is responsible for the rapid rise in current for the undoped BST MIM at ~ 2-3 V [18], ii) the reduced trap density and position of the trap in the biased MIM do not support a TAT/F-N tunneling process for MIMs with Ni-doped BST, so instead, a symmetric direct tunneling mechanism prevails, and iii) the asymmetry between + and - gate biases is due to
differences in interfacial bonding for the deposition of BST on Pt, and the deposition of Pt on
BST. These results suggest an approach for improve BST MIM devices for gigabit DRAM
applications that is based on the changes in defect state energies between undoped and Ni-
doped BST, and the observation that the band edge defects in Ni-doped BST did not
increase annealing at elevated temperature, 800°C in Figs 4.3(a) and 4.3(b).

4.4 Conclusions

In conclusion, a significant suppression of leakage current in MIM capacitors with the Ni-
doped BST insulator was observed. The Ni-doping improved the leakage current
characteristics of MIM cells by achieving a several order reduction of current by suppressing
the trap assisted tunneling injection processes. It also provided a more symmetrical J-V
characteristic for positive and negative gate bias conditions. A physical model for explaining
the leakage current differences between Ni-doped and undoped BST has been developed
by correlating J-V characteristics with the spectroscopically detected pre-existing oxygen
vacancy defects revealed by SE measurements. Changes in these defect states in both
energy and density with Ni doping are responsible for the control of injection to traps in the
BST insulator. This study therefore identifies a novel band edge state engineering approach
based on transition metal doping which should be applied to other oxides with perovskite
structures, e.g., PbTiO₃ and PbZrO₃.
4.5 References


Fig. 4.1 (a) schematic representation of MIM (Pt/Ni-BST/Pt) capacitor. The bottom Pt electrode is placed on Ti/SiO₂/Si stack which emulates the actual layers in DRAM storage cell and (b) Dielectric constants of MIM capacitor extracted from high-frequency (1 MHz) C-V analysis with Ni-doped and undoped BST dielectrics. The undoped BST showed the slightly higher dielectric constant. There was no significant dielectric loss across the applied voltage.
Fig. 4.2. J-V Characteristic of Ni-doped and undoped BST MIM cells at room temperature. Traces are included for both positive and negative gate bias in a spectral range from –20 V to + 20 V. The physical thicknesses of two dielectrics are 200nm so that the equivalent oxide thickness is 28 nm for undoped BST and 30 nm for Ni doped BST.
Fig. 4.3. Epsilon 2 ($\varepsilon_2$) extracted from SE measurements of undoped and Ni-doped BST. (a) The solid circle points are as-deposited films (room temperature), and the open circles films annealed in Ar at 800°C. (b) $\varepsilon_2$ for as deposited in undoped and Ni-doped BST in a narrower spectral regime from 2.6 to 4.0 eV. This regime emphasizes changes in the spectral character of the band edge defect states.
Fig. 4.4. Local bonding of Ti-atoms (gray) and O-atoms (black) in i) undistored octahedral arrangements in which all bond lengths, $a_x$, $a_y$, and $a_z$ are equal, ii) orthorhombic arrangements in which all bond lengths are unequal, and iii) in tetragonal arrangements with two equal bond lengths.
Fig. 4.5. Schematic energy band diagram for conduction band empty anti-bonding states, and band edge defects states for undoped and Ni-doped BST obtained from analysis of $\varepsilon_2$ spectra. Solid lines, and bold face energy level positions, and energy differences reflect strong features in $\varepsilon_2$, whereas, dashed lines, and plain text indicate significantly weaker spectral features,
Fig. 4.6. Band alignment for that includes band edge defects in undoped (heavy solid line) and Ni-doped (dashed line) BST MIM capacitors. The Pt 6s state Fermi level is indicated and metal gate Fermi levels are indicated, as well as the Pt 5d state filled band. Transport processes are indicated by arrows beginning in the Pt electrodes of the cathode (negative) and differentiated by the character of these arrows.
5 Preparation of Native Oxide and Carbon Minimized Ge surface by NH₄OH based Cleaning for Deposition of High-k Dielectrics

Abstract

The native oxide and carbon contaminant minimized Ge surface and interfacial oxide layer preparation with NH₄OH based cleaning for deposition of high-k dielectrics is reported. The native oxide thickness on Ge surface before and after different cleaning methods are compared by optically equivalent oxide thickness of GeO₂ determined by spectroscopic ellipsometry measurements. The HF rinsing step in cyclic hydrofluoric acid (HF)/deionized water (DIW) cleaning was not effective for a removal of native GeO₂ since it can not form the soluble species by a chemical reaction in low pH-HF solution but rather, DIW rinsing step removed GeO₂. A cyclic cleaning in a sequence of H₂O, H₂O₂, methanol, NH₄OH, and H₂O results in a minimum residual GeO₂ at 4 and 8 Å on Ge (111) and (100) respectively. The fast regrowth of GeO₂ on cleaned Ge surface in the ambient revealed 15 Å of GeO₂ after 7 min. exposure to the air regardless of the cleaning methods. However, in-situ Auger electron spectroscopy spectra showed the much less amount of carbon on Ge surfaces with NH₄OH based cleaning than with HF based cleaning. The small amount of residual carbon after NH₄OH based wet cleaning was completely removed by O₂ plasma for very thin (~20 Å) surface oxidation in remote plasma enhanced chemical vapor deposition chamber.
5.1 Introduction

The necessary step for successful integration of Ge/high-k gate stacks for future metal oxide field effect transistor (MOSFET) is Ge surface preparation without native GeO$_2$ and other possible contaminants (i.e., carbon) [1-3]. Initial major efforts on the task of Ge surface preparation have been made by hydrofluoric acid (HF) based cleaning [4,5]. Although HF solution is very effective for Si surface preparation since it provides an oxide free and H-terminated Si surface, many studies proved that it is not applicable to Ge surface passivation with limited GeO$_2$ removal and instable passivation layer [6]. Therefore, the alternative surface preparation method using different chemicals instead of HF solution have been extensively investigated.

In order to achieve a good Ge surface for MOSFET application, the removal of native oxides and formation of a high quality interfacial oxide layer is of great importance since the native oxide has considerable amount of carbon species as well as high interfacial roughness [7]. More importantly, the relatively thick native GeO$_2$ (> 2.5 nm in ambient) on bare Ge surfaces, if not removed effectively, makes EOT control more difficult.

In this study, the removal efficiency of HF and ammonium hydroxide (NH$_4$OH) based treatments and the resistance to oxide re-growth after treatment were evaluated by real-time visible ultra-violet spectroscopic ellipsometry (SE) measurements. Residual chemical elements for (i) each surface treatment method and (ii) O$_2$ plasma exposure for ultra thin Ge oxide formation were also measured by in-situ Auger electron spectroscopy. From results in this study, we report the enhanced surface preparation of NH$_4$OH based treatments.
5.2 Experimental Procedures

The bare n-type Ge (100) or (111) wafers (Sb doped, 0.01 Ω·cm) are treated by either HF-based or NH₄OH-based cleaning. For HF-based treatment, wafers are dipped into diluted (10%) HF for 10 sec followed by deionized water (DIW) for 20 sec. This process has been repeated six cycles. Another experiment set of HF-based treatment is DIW dip for 2 min, H₂O₂ dip for 10 sec, 10 min diluted HF dip, and final DIW rinsing. This cleaning combination was reported to produce H-terminated Ge surface [8]. Cleaned surfaces were evaluated by SE for comparison to other treatment methods. NH₄OH-based treatment includes DIW dip for 5 min, and rinsing wafer surfaces with diluted hydrogen peroxide (H₂O₂, 6%), methanol (CH₃OH), NH₄OH (10%), and finally DIW. This cycle was repeated two times.

For in-situ SE measurements, chemical solution treatments are carried out directly in the sample stages of the SE, specially designed for measurements on etching experiments, which is connected to a drain hose and filtered chemical waste bottle. N₂ purge on the wafer was done between each chemical rinsing step and all the time during measurement to prevent oxide regrowth by water absorption on surface. The oxide removal efficiency in all the treatment processes and oxide regrowth in ambient after treatment were real-time monitored by SE.

Cleaned wafers were introduced to a loadlock chamber (base pressure at 1x10⁻⁸ Torr) which is in-situ connected to AES analysis chamber (1x10⁻¹⁰ Torr) and remote plasma enhanced chemical vapor deposition chamber (RPECVD). Two kinds of wet solution (either HF or NH₄OH) were used and subsequent O₂ plasma exposed wafers were analyzed by AES for identification of chemical elements. In O₂ plasma oxidation, Ge wafers were
exposed to a remote O$_2$ plasma at the process condition of 300 °C of substrate temperature, 30 W of plasma power, and 0.3 Torr of O$_2$ pressure.

5.3 Results and Discussion

Imaginary pseudo dielectric function spectra of bare and cleaned (100) Ge wafers extracted by SE measurements are shown in Fig 5.1. The best rule for distinguish a clean Ge surface from a overlayer such as native oxide is from the peak height of direct transition states in Ge observed at 2.3 and 4.2 eV. These peak heights should be a maximum when the native oxide is thinner based on heterogeneous medium optical model. The dielectric function of best clean Ge surfaces so far has been measured by a previous study on Ge [1]. Based on this reference data from a previous study, we extracted the optically equivalent GeO$_2$ thickness by using three phase model calculation.

Before any cleaning, the native oxide thickness on bare Ge wafer was 20 Å. The first cyclic HF/DIW treatment on Ge wafers resulted in 17 Å of GeO$_2$ while the second combination of DIW/H$_2$O$_2$/HF showed 45 Å of GeO$_2$ thicker than bare Ge wafer. From these data, HF is not effective for removal of GeO$_2$ but rather DIW is plays a role for GeO$_2$ removal since GeO$_2$ is water soluble. An H$_2$O$_2$ dip of Ge rapidly forms a chemical oxide like it does with; however, HF dip does not remove GeO$_2$ effectively so that the resultant GeO$_2$ thickness is almost entirely due to the chemical oxide formed by H$_2$O$_2$ since the DIW dip prior to H$_2$O$_2$ step removed most of native GeO$_2$. These results on a HF/DIW combination often obscure the real removal efficiency of HF on GeO$_2$ because GeO$_2$ dissolution in DIW causes misinterpreted as the ability of HF to remove GeO$_2$. Based on the reported
electrochemistry of reactions of Ge surfaces in wet solutions, acid solutions having lower pH are essentially not effective to solubilize products formed by liquid reactions because the solubility dramatically drops as the pH is lowered. On the other hand, higher pH base solutions actively form soluble reaction products [9].

The enhanced GeO₂ solubility in the base solution is confirmed from the minimum 2 Å of GeO₂ thickness on Ge (111) surfaces treated by NH₄OH based cycles. Because this thickness value is not physical thickness but the optical equivalent thickness (OET), the actual overlayer may not be a uniform layer covering the whole surface but rather, it could be an island type phase of GeO₂ or less than monolayer on average. NH₄OH is a strong base chemical solution and therefore, it etches the chemically grown (by H₂O₂) GeO₂ very effectively down to Ge surfaces. It should be noted that this very thin GeO₂ layer was observed only when the N₂ purge is maintained on the Ge surfaces thereby blocking oxidizing agents in ambient such as water vapor. Although regrowth of GeO₂ occurs even for NH₄OH treated Ge surface because it does not passivate surface, it is very crucial to observe the complete GeO₂ removal during the treatment since this complete etching of native oxide is essential to achieve the removal of carbon species in oxide layer and to provide a smoother Ge surface by chemical oxide induced reconditioning, an important factor to minimize fast interfacial states arising from channel surface roughness [10].

Although continuous N₂ purge allowed a GeO₂ removal efficiency, by excluding regrowth of oxide in ambient, the real condition in device manufacturing inherently requires the evaluation on the stability of surfaces in ambient that are exposed to air. For this purpose as well as to determine specific chemical solution’s role on surface treatment, real time SE
measurements for NH$_4$OH-based treatment were done.

Figure 5.2 represents GeO$_2$ OET evolution under N$_2$ purge condition for each chemical agent in the NH$_4$OH based treatment both on (111) and (100) Ge surfaces. A starting point is Ge wafer dip in DIW for 5 min. This first step removes GeO$_2$ for both orientations significantly, but the initial thickness was different: 6 Å for (111) and 12 Å for (100). The chemical solution is applied by a downstream rinsing from a bottle between 5 and 10 sec and then a N$_2$ blowing purge was done for removal of residual solution on surfaces. This combined step, solution rinse and N$_2$ blow is defined as each chemical treatment step which is indicated with dotted lines in Fig. 5.2.

From Fig 5.2 (a), it is obvious that the chemical etchants for GeO$_2$ are NH$_4$OH and water. As expected, a H$_2$O$_2$ rinsing step oxidizes the surface very quickly (only in 5 sec) by forming 38 Å of GeO$_2$. Methanol is involved in neither oxidation or oxide etching but is supposed to remove organic residues such as hydrocarbon. An important observation on the GeO$_2$ evolution plot is GeO$_2$ regrowth rate right after etching agents, NH$_4$OH and water rinse. The lower GeO$_2$ thickness after etching, the faster a GeO$_2$ regrowth rate is observed. For an example, the GeO$_2$ regrowth rate after a final H$_2$O rinse starting when thickness of GeO$_2$ is only 2.5 Å is 1.5 Å GeO$_2$ per 1 min even with a N$_2$ purge.

As observed in Fig. 5.2 (b), (100) Ge has much a lower GeO$_2$ removal efficiency with same NH$_4$OH-based surface treatment compared to (111). The starting thickness of GeO$_2$ is already twice of that of (111) Ge, the lowest one during treatment cycle is 6.4 Å. Although trends for GeO$_2$ removal are the same for (100) as (111), uneven etching of GeO$_2$ surfaces occurs for (100). Plots in Fig. 5.2 confirm that GeO$_2$ removal efficiency has a strong
dependence on Ge orientation.

Figure 5.3 compares the GeO$_2$ regrowth rate for different orientations in ambient without N$_2$ purge. Before turning the N$_2$ purge off, same NH$_4$OH-based treatment was done for both (111) and (100) Ge wafers. Analysis of oxide regrowth kinetic gives three different growth domains. For (111) Ge, right after stopping N$_2$ purge, GeO$_2$ starts to grow spontaneously up to 7 Å after 9 sec (0.3 Å/sec) and then keep growing to 9.4 Å after 46 sec at the fast rate (3.8 Å/min) and then, regrowth rate becomes rapidly lower and saturated at 12 Å after 460 sec (0.2 Å/min). As a result, although NH$_4$OH removed GeO$_2$ completely, the aggressive oxide regrowth results in10 Å of GeO$_2$ after only 1 min ambient exposure. In fact, real GeO$_2$ thickness should be 1 or 2 Å less than this OET value since we confirm from SE measurements that the water vapor physisorbed on top surface contributes some thickness to a total measured OET without N$_2$ purge. Therefore, the real physical GeO$_2$ thickness on a Ge (111) surface which is introduced in vacuum chamber within 1 min after current NH$_4$OH-based treatment is about 7 to 8 Å.

The same analysis can be made on Ge (100) surface. The initial GeO$_2$ thickness is already 8 Å after treatment reached at 14 Å 1 min after the N$_2$ purge was turned off and finally saturated at 17 Å after 410 sec exposure to the ambient. Similarly, if water vapor on the surface is considered, the resultant physical GeO$_2$ thickness on (100) Ge surface is about 12 to 13 Å if introduced to vacuum chamber in 1 min. This thickness in the vacuum chamber is equivalent to the pre-device processing condition: i.e., interface condition prior to high-k dielectric deposition.

From real-time SE measurements on cleaned Ge surfaces, oxide regrowth of Ge
regardless of wafer orientation is common even after the complete GeO₂ removal during the chemical treatment. Nevertheless, this surface treatment based on NH₄OH is very promising for effective Ge surface preparation for devices since it removes not only native and but also chemical oxide completely to produce Ge surface conditioning and smoothened surfaces. The observed oxide regrowth on cleaned Ge surface is higher than on H-passivated Si (3 or 4 Å OET right after HF cleaning measured by SE) but still stays at a reasonable level of half of the native oxide thickness seen on bare Ge (100) wafer (~20 Å).

For comparison, the re-grown oxide thickness for Ge (100) surface with HF/DIW cyclic treatment was 15 Å OET after 8 min exposure to the air without N₂ purge which is almost the same as the NH₄OH treated surface. Therefore, the resultant oxide thickness in the ambient after treatment is not largely different depending on chemicals but rather, there is an apparent difference in the residual carbon amount in the oxide and Ge top surface conditioned by complete GeO₂ etch during the treatment. In this regard, NH₄OH based treatment is proved to be superior to HF/DIW combination based on SE and AES analysis to be discussed as following.

So far, the oxide removal efficiency of different chemical treatments has been discussed based on the analysis of SE measurements. Although this methodology is one of great interest, characterization of residual chemical species is equally crucial. Therefore, AES analysis on cleaned and plasma oxidized Ge wafers were made.

Figure 5.4 represents AES wide and narrow scan spectra for several different Ge surfaces. In Fig 5.4 (a), there are energy peak states associated to germanium (45~50 eV), carbon (268 eV) and oxygen (509 eV) species. Particularly, Ge peaks are related to two
different bonding states, Ge-O (44 eV) and Ge-Ge (48 eV) and the narrow scan AES spectra between 40 and 60 eV is shown in Fig 5.4 (b). For relative comparison of each chemical element amount, every spectrum has been normalized to Ge-Ge peak intensity in spectra of bare Ge wafers.

Oxygen contents are significantly reduced in AES spectra by both surface treatment methods compared to the bare wafer but HF-based treatment has the lower oxygen peak intensity. This smaller oxygen amount on HF cleaned surfaces is due to the residual carbon in oxide. AES data in Fig. 5.4 (a) indicated that carbon species are not effectively removed from the level of bare wafer with the cyclic HF/DIW treatment but considerably reduced by NH₄OH based treatment. The reduced carbon amount after NH₄OH-based treatment is completely removed by O₂ plasma for surface oxidation below AES detection limit because reactive atomic O radicals form volatile CO and CO₂ gas products.

In HF-based treatment, HF is not a GeO₂ etchant as confirmed in SE analysis but the DIW rinse step etches oxides. Therefore, repeated cyclic DIW rinse steps removed GeO₂ almost to the same level as NH₄OH-based treatment but has the limitation for surface carbon removal. Therefore, this residual carbon species may act as a barrier for chemical reaction of Ge with O. This is supported by the lower AES peak ratio of Ge-O (44 eV) to Ge-Ge (48 eV) for HF (0.2) than NH₄OH (0.3) treated surface.

As a result, the combined SE and AES results suggest several crucial aspects on Ge surface preparation. The fast regrowth rate of Ge surface results in the native GeO₂ saturated at about 1.5 nm for both of cyclic HF/DIW and NH₄OH based surface treatment but there is a meaningful advantage of NH₄OH based treatment on (i) the efficiency of
carbon removal in oxide layers and (ii) complete native GeO$_2$ liftoff ensuring Ge surface conditioning even for the short period time during the treatment.

In particular, the final O$_2$ plasma step for the very thin GeO$_2$ growth (~1 nm for 15s) is able to remove the residual carbon completely so that provides the possible pathway for carbon-free interfacial oxide layer preparation before high-k dielectric deposition in Ge MOSFET gate stacks.

5.4 References


Fig. 5.1. The plot for Imaginary parts of pseudo dielectric function for (100) Ge surfaces with and without different surface treatment: NH$_4$OH-based, HF-based, H$_2$O$_2$/HF, and No treatment (Bare wafer). $E_1$ and $E_2$ are peaks associated to Ge direct optical transition. Note that $E_2$ peak height is directly related to the oxide thickness.
Fig. 5.2. The plot for GeO$_2$ thickness evolution during the NH$_4$OH-based surface treatment for (a) (111) and (b) (100) Ge surfaces. The GeO$_2$ thickness was extracted from the real-time SE measurements with cleaning process.
Fig. 5.3. The plot for GeO$_2$ regrowth evolution during the air exposure of the cleaned (a) (111) and (b) (100) surface as a function of exposure time. Both of surface orientations show the similar regrowth feature in the ambient.
Fig. 5.4. AES (a) wide and (b) narrow scan spectra for (100) Ge surface with and without surface treatments: Bare, HF-, and NH₄OH-based cleaning. For wide energy scan, there are energy peak states associated to germanium (45~50 eV), carbon (268 eV) and oxygen (509 eV) species. For narrow energy scan, there are Ge peaks related to two different bonding states, Ge-O (44 eV) and Ge-Ge (48 eV).
6 Correlation between Defects identified by Spectroscopic Measurements and Charge Trapping at Ge/HfO₂ and HfSiON Interfaces with GeON layer

Abstract

This paper reports the physical identification of processing induced defects (i) at Ge-Hf high-k dielectric interfaces, and (ii) in the bulk of these dielectric thin films as determined from spectroscopic studies, primarily X-ray absorption spectroscopy (XAS), spectroscopic ellipsometry and medium energy ion scattering (MEIS), and the correlation of defects to electrical properties evaluated by capacitance-voltage (C-V) and leakage current density-voltage (J-V) measurements. The XAS and MEIS comparisons between as-deposited and annealed films indicate that two physically distinctive defects are increased with post deposition anneal controlling the combined effects of (i) Ge oxynitride interface decomposition and (ii) diffusion of Ge species from the substrate. Both for HfO₂ and HfSiON, these electrically-active defects are introduced during the initial deposition process, and their relative densities are increased during subsequent rapid thermal anneals in Ar at temperatures between 600°C and 800°C. C-V and J-V data revealed that test capacitor devices annealed at the optimized temperature (650 °C for HfSiON and 600 °C for HfO₂) showed the minimum oxide trapped charge density and highest positive (substrate injection) breakdown voltages as well as lowest leakage current level compared to other annealed and as-grown devices. The band alignment model for suppression of electron trapping at the...
6.1 Introduction

There have been considerable research efforts in order to achieve Ge-based metal-oxide-semiconductor field effect transistor (MOSFET) since Ge channel provides higher and symmetric intrinsic mobility for both electrons and holes as compared to Si. Previous studies revealed that Ge-based MOSFETs really exhibit 2× higher hole mobility than Si, leading to a corresponding increase in the pFET drain current [1]. Nevertheless, Ge-based MOSFETs usually suffer from inferior interfacial properties between the Ge channel, the interfacial oxide and the high-k gate dielectrics [2,3]. This interfacial problem is mainly responsible for the large capacitance-voltage (C-V) hysteresis, and extremely low nFET mobility.

In this regard, several approaches to achieve high quality Ge interfaces have been investigated, using various interfacial passivation layers, such as GeOₓ, GeOₓNy and Si [3-6]. Although the physical reason for the degraded interfacial quality is still vague, one recent study reported that the fast interface state density (Dᵢn) of a high-k/GeOₓ-passivated Ge gate stack was fairly low, e.g., the order of 10¹¹ cm⁻²eV⁻¹ [7]. In contrast, other studies have reported that Ge devices still have relatively high defect densities inferred from oxide trapped charge densities (N_tot) at the order of ~10¹² cm⁻² [8,9]. Therefore, these defects in the interfacial region do function as electrical traps both at the interface and in the film, leading to inferior device performance although providing a reasonably good Ge surface passivation with low Dᵢn.

This fact strongly illustrates the need for in-depth studies focusing on the pronounced
degradation that occurs at interfaces between Ge-O and Ge-N interfacial layer and high-k gate dielectrics, studies to date have not yet assigned a specific origin to these defect states.

In this study, we focused on the physical identification of processing induced defects (i) at Ge (100)-Hf high-k dielectric (pseudo-ternary N-rich (> 40%) HfSiON and HfO₂) interfaces, and (ii) in the bulk of these dielectric thin films as determined from spectroscopic studies, primarily X-ray absorption spectroscopy (XAS) and medium energy ion scattering (MEIS), and the correlation of defects to electrical properties evaluated by capacitance-voltage (C-V) and leakage current density-voltage (J-V) measurements. The combined results from spectroscopic and electrical measurements unambiguously indicate that post-deposition anneal (PDA) temperature is a very sensitive factor to control (i) the interfacial Ge-N and Ge-O bond removal and (ii) behavior of two specific types of defects in both high-k materials. XAS and MEIS data clearly show the behavior of those two thermal events relying on PDA process and more importantly, provide physical grounds for the charge trapping and leakage current level changes in C-V and J-V analysis.

6.2 Experimental Procedures

An n-type Ge wafer was sequentially rinsed with de-ionized water, H₂O₂ (6%), methanol, NH₄OH (15%), and de-ionized water again, removing the native oxide layer and producing a flat Ge surface [10,11]. Immediately following this surface treatment, the Ge wafer was introduced into the vacuum load lock of a remote plasma-enhanced metalorganic chemical vapor deposition (RPE-MOCVD) chamber. A sacrificial, interfacial GeON layer and high-k oxide films (pseudo-ternary HfSiON for a high Si₃N₄ concentration > 40% and HfO₂),
respectively, were then deposited by RPE-MOCVD at 300°C.[11] The sacrificial layer had a thickness of 0.7 ± 0.1 nm and was grown in order to prevent direct reaction between the Ge substrate and the high-k film, as well as to prevent substrate oxidation during the high-k film deposition process. However, this interfacial GeON layer could (i) limit the attainable down scaling of equivalent oxide thickness (EOT) owing to the lower dielectric constant of the GeON layer and (ii) contribute to the high-level of charge trapping as discussed later. As an alternative approach in this study, a one minute PDA treatment in Ar from 575 to 800°C has been done in order to remove the interfacial GeON layer, which transferred enough thermal energy to the material to decompose it either partially or fully [12]. The spectroscopic analysis by XAS, SE and MEIS, compared the defect states of the high-k film with the compositional changes in the film, both before and after PDA for all temperature range. The test capacitor devices are fabricated by Al evaporation for the front side metal electrode dot formation. H₂/N₂ forming gas annealing at 400°C was performed before Al evaporation to prevent the additional interfacial reaction between Al and high-k dielectrics. For the back side contact, Al metal typically does not provide the good ohmic contact to n-type Ge. In this study, the good backside contact was achieved by applying InₓGa₁₋ₓ eutectic paste to the scratched backside of wafer.

6.3. Spectroscopic identification on defects: MEIS, SE, and XAS results

Figure 6.1 shows the compositional depth profile for HfO₂ and HfSiON films as a function of PDA temperature, as obtained through MEIS, using H⁺ ions with incident energy of 100 keV. For detailed information, MEIS energy spectra were simulated by the Kido program [13]. An interfacial GeON layer approximately 0.7 - 0.8 nm thick is observed in the
as-deposited films of both HfO$_2$ and HfSiON and is subsequently eliminated after PDA treatment. In the HfO$_2$ films, the width of the Hf peak (not shown here) is slightly decreased after PDA treatment, which means that the density of the HfO$_2$ films was changed as a result of crystallization [14]. Another interesting finding involves the behavior of Ge in the films after PDA treatment. The areal density of Ge in the HfO$_2$ layer, which corresponded to the amount of Ge in the entire film, is $3.65 \times 10^{15}$ Ge atom/cm$^2$ and $6.04 \times 10^{15}$ Ge atom/cm$^2$ for as-deposited (except an interfacial GeON layer) and annealed films, respectively. Similarly, the areal density of Ge in the HfSiON films is $2.56 \times 10^{15}$ Ge atom/cm$^2$ and $3.35 \times 10^{15}$ Ge atom/cm$^2$ for as-deposited and annealed films, respectively. HfO$_2$ films have a higher Ge concentration than both the as-deposited and the annealed HfSiON films. Moreover, the Ge concentration in the HfO$_2$ films is markedly increased after PDA; whereas, the corresponding concentration of Ge in the HfSiON films is increased by a much smaller amount. Evidently, Ge diffusion is inhibited more effectively by HfSiON films. The relative ease with which Ge diffused into the HfO$_2$ films during annealing is suspected to have been caused by the disappearance of the interfacial GeON layer and by HfO$_2$ film crystallization during the PDA treatment.

Imaginary dielectric function ($\varepsilon_2$) spectra for HfO$_2$ and HfSiON films on Ge(100) substrates are shown in Figure 6.2. These spectra were extracted from a simple four-phase model, which was comprised of a Ge substrate, a GeON overlayer, a high-k overlayer, and an ambient layer [15]. The best fit to this model was determined to be the one which minimized artifacts in the dielectric function below the conduction band edge caused by the strained Ge substrate. The imaginary dielectric function spectra clearly depict two distinct
types of energy states below the Hf 5d e\textsubscript{g} conduction band edge states, which are located at approximately 6 eV. D\textsubscript{1} and D\textsubscript{2} are regarded as sub-band gap defect states because they are observed at 1.7 ± 0.1 eV and 2.7 ± 0.1 eV, respectively, below the conduction band edge states. Both defect states are observed in as-deposited HfO\textsubscript{2} films and significantly increased after PDA. The defect states are both observed in as-deposited HfSiON films as well; however, they show a much less substantial change upon PDA. In fact, though the D\textsubscript{2} state shows a minor increase, the D\textsubscript{1} state shows almost no change at all. From previous MEIS results, we could observe Ge diffusion into both HfO\textsubscript{2} and HfSiON films, as well as structural changes in the HfO\textsubscript{2} films. Thus, when the \( \varepsilon \textsubscript{2} \) spectra are coupled with the MEIS data, it is reasonable to conclude that D\textsubscript{1} is related to the structural evolution of the high-k films, and D\textsubscript{2} is related to Ge diffusion into the high-k films. More specifically, D\textsubscript{1} is the result of empty Hf\textsuperscript{3+} states in oxygen di-vacancies, which are clustered at grain boundaries in these high-k films. D\textsubscript{2} is a di-vacancy defect related to the incorporation of Ge into oxygen vacancies or at grain boundaries [16]. The defect states of as-deposited films originated from intrinsic oxygen di-vacancies in the high-k and from Ge in the interfacial region between the high-k film and the GeON layer. The rise in the quantity of HfO\textsubscript{2} defect states after PDA is attributed to increased Ge diffusion and to HfO\textsubscript{2} crystallization. In the HfSiON films, however, only the increased Ge diffusion seems to play a significant role during PDA.

Figure 6.3 shows XAS spectra over a narrow energy region below the Hf 5d e\textsubscript{g} conduction band edge states of the O K\textsubscript{1} feature in both HfO\textsubscript{2} and HfSiON films. In order to qualitatively analyze the defect states, the spectra also include Gaussian fits, which were
performed within the detection limit of XAS, following background subtraction and peak normalization. The Gaussian fits are composed of i) band edge defect states below the Hf 5d e₉ states, ii) Hf 5d e₉ states from which two-fold degeneracy has been removed by a static Jahn-Teller distortion, iii) Hf 5d t₂g states for which three-fold degeneracy has been removed similarly, and iv) two features that correspond to Hf 6s and Hf 6p states. Consequently, the peak intensities of the Gaussian fits in one sample could be compared to those in the other samples in order to determine the relative quantities of the energy states. Figure 6.3 shows only the narrow energy region relevant to the defect features located below the conduction band edge. Like the ε₂ spectra, the Gaussian fits identify two different types of defect states, and they are located at similar energies below the Hf 5d e₉ conduction band edge; 531.8 ± 0.2 eV. Relative changes in the intensities of the two defect states after PDA also coincide with the Ge diffusion and HfO₂ crystallization previously discussed with respect to the MEIS data. As a result, the defect state (D₁) located near 530 eV is assigned to transitions that terminated in empty Hf³⁺ states in di-vacancy defects, clustered at grain boundaries. Upon correlating the XAS spectra with the MEIS and SE results, the defect state (D₂) located near 528.7 eV is assigned to a di-vacancy defect that included simultaneously a Hf³⁺ di-vacancy and the incorporation of Ge into the films. An increase in the number of HfO₂ defect states following PDA is clearly observed, though similar effects in HfSiON are only very slight. Therefore, HfSiON films prevent effectively an increase in these di-vacancy defects, which is critical because such defects can function as sources for both fixed and oxide trapped charges.

Based on XAS spectra analysis using by Gaussian fitting, the relative strength of two
kinds of defect features with respect to PDA temperature determined from OK₁ edge spectra is shown in Fig. 6.4. The overall strength of both of D₁ and D₂ defect states are much higher for HfO₂ than HfSiON over the whole anneal temperature range. In addition, the notable rise in defect absorption of HfSiON at 650 °C is more or less delayed in temperature compared to HfO₂ at 600 °C. Therefore, this reinforces the observation that HfSiON more effectively prevents defects and Ge diffusion in the film.

The increase of defects at the higher PDA temperature in Fig 6.4 is closely related to the decomposition of Ge oxynitrides where Ge-N and Ge-O bonds are present. Figure 6.5 (a) and (b) represents NK₁ edge XAS spectra for HfSiON and HfO₂ as a function of PDA temperature. The spectra for as-grown samples are mostly due to N at the buried interfacial Ge oxynitrides and the states becomes weaker as N is released from the interfaces during annealing. However, HfSiON shows the delayed N release at the same PDA temperature compared to HfO₂. The nearly complete removal of N states is observed at 750 °C for HfSiON and 700 °C for HfO₂ respectively. The complete removal of Ge-N at the buried interfaces causes another possible mixture interface formation in the high-k film such as germanate by the aggressive Ge diffusion from substrate since there is no blocking layer anymore. This N release dependence on PDA temperature is another cooperative driving force for the increase in defects shown in Fig 6.4 along with more thermal energies for activated Ge diffusion.

6.4 Electrical properties of Hf based high-k on Ge

Figure 6.6 and 6.7 compare C-V traces for 5nm thick HfSiON and HfO₂ films (equivalent
oxide thickness (EOT) at ~2 and ~1.2±0.1 nm respectively) on n-type Ge (100) substrates for as deposited, 650 and 700°C annealed HSiON and as deposited, 600 and 650 °C annealed HfO₂ respectively. C-V traces are swept from 0.0 to negative bias, and then reversed to positive gate bias. The frequency dependence was also considered by two separate low-(100 kHz) and high-(1 MHz) frequency measurements.

The primary interest on C-V traces in Fig 6.6 and 6.7 is the effectively trapped charge density ($N_{EFF}$) extracted from flat band voltage ($V_{FB}$) difference between gate voltage ramping down and up traces. In similar trend for both high-k dielectrics, the $N_{EFF}$ level is decreased to a minimum level at the optimum PDA temperature (650°C for HfSiON and 600°C for HfO₂) and then, increased back to a larger level at higher temperature. The absolute $N_{EFF}$ value ranges from low- to mid-$10^{12}$ cm⁻² but only HfSiON annealed at 650°C revealed the lowest $N_{EFF}$ value at $5\times10^{11}$ cm⁻². The analysis on C-V traces in Fig. 6.6 and 6.7 leads to the following interpretation of the hysteresis traces. For tracing from 0.0 to negative bias, there is a positive component in voltage shift associated with trapped electrons that are released as the gate bias becomes increasingly negative. Therefore, the larger $dV_{FB}$ hysteresis is due to the more trapped charge in gate oxide stack, yielding a larger $N_{EFF}$.

Because the charge trapping efficiency is strongly affected by several factors such as charge screening depending on the dielectric constant, charge injections, and kinetics of bias sweep, it is needed to compare the charge trapping for different gate stacks under the identical condition. For the purpose of this, the plot of $N_{EFF}$ as a function of $N_{inj}$ is shown in Fig. 6.8. $N_{inj}$ is defined as $J_g/qdt$ where $J_g$ is the leakage current at the positive turnaround voltage bias (1V) in the C-V trace and $dt$ is the average hold time for C-V measurement at
each voltage. Therefore, $N_{\text{inj}}$ is the average upper limit of injected charge density. The plot shows (i) the much dramatic change in $N_{\text{inj}}$ of HfSiON between as deposited and annealed samples and (ii) the lower $N_{\text{EFF}}$ corresponds to the lower $N_{\text{inj}}$. On the other hand, HfO$_2$ has the systematic $N_{\text{inj}}$ changes between as deposited and annealed samples but $N_{\text{EFF}}$ stays at the similar level. Except HfSiON sample annealed at 650°C, HfO$_2$ shows the more suppressed $N_{\text{EFF}}$ in the same $N_{\text{inj}}$ range. This means that the bulk defect is not the only determinant for the charge trapping but the interface effect is another crucial factor as well.

The anticipated flat-band voltage for these gate stacks is ~0 V based on the work function of Al, and the energy of the Ge conduction band with respect to vacuum; however, $V_{\text{FB}}$ obtained from the retrace from negative to positive volts is subject to the large deviation from -1.5 V to -0.9±0.1 eV for HfSiON depending on the PDA temperature. $V_{\text{FB}}$ for HfO$_2$ is more stable at about -0.9V. This $V_{\text{FB}}$ indicates a significant positive fixed charge, ~mid-10$^{12}$ cm$^{-2}$. It is very interesting to correlate $N_{\text{EFF}}$ to $V_{\text{FB}}$ for high-k dielectrics as a function of PDA temperature. This is shown in Fig. 6.9. For HfSiON, PDA at 650°C resulted in minimum $N_{\text{EFF}}$ but HfSiON exhibited the largest negative $V_{\text{FB}}$ at the highest PDA temperature, it showed higher $N_{\text{EFF}}$ but smaller negative $V_{\text{FB}}$. The $V_{\text{FB}}$ variation with PDA temperature in HfO$_2$ is also generally similar to HfSiON but with less total variation.

We suppose such differences of $V_{\text{FB}}$ are related to the boundary properties between interfaces and high-k dielectrics. As confirmed in spectroscopic results, HfSiON is more chemically robust so that it does not give a chance to chemical reconstruction to elements in the buried interfaces or diffused Ge at the elevated temperature. Therefore, it essentially causes the higher fixed oxide charges derived from non-optimized chemical properties at the
boundary. However, if thermal energy from PDA (>650°C) is high enough to overcome the barrier, chemical intermixing (i.e., PDA induced interfacial germanate) occurs at the some region of the bulk HfSiON near the boundary and $V_{FB}$ shift toward positive direction with less fixed oxide charges. As re-stated based on Fig. 6.4, the increased defect density is also a result from the chemical intermixing across boundary but make opposite effects on $N_{EFF}$ (increase) and $V_{FB}$ shift (less negative). If extending this argument to the optimum PDA temperature of 650°C, this temperature is a cross point where the substantial decomposition of interfacial Ge-O-N occurs while it maintains the low defect density as functions as a blocking layer to Ge diffusion.

On the other hand, Ge amount intermixed in HfO$_2$ is already substantial even in as deposited films as shown in MEIS data in Fig. 6.1 (a) and chemical driving force for intermixing across oxide stacks is high. Chemical intermixing is believed to relieve the strain at the boundary so that HfO$_2$ has the less fixed oxide charge. Because there is no significant barrier to this chemical intermixing and high-level defect formation, both $V_{FB}$ and $N_{EFF}$ changes for HfO$_2$ in Fig. 6.9 are not sensitive to PDA temperature and there is a slight positive $V_{FB}$ shift as $N_{EFF}$ is decreased between 575 and 650 °C. The enhancement of both of $V_{FB}$ and $N_{EFF}$ at the optimum PDA temperature for HfO$_2$ is different from HfSiON where $V_{FB}$ shift is worse but $N_{EFF}$ is minimized.

As a result, HfSiON gate stack shows less $N_{EFF}$ but larger $V_{FB}$ shift. Nevertheless, it might be necessary to engineer $V_{FB}$ with deeper work function metal gate while maintaining the $N_{EFF}$ suppression to the lowest level at mid-$10^{11}$ cm$^{-2}$ achieved from the current approach.

Figure 6.10 shows J-V plots for HfSiON and HfO$_2$ films, as-deposited and, after
annealing at the optimum PDA temperature. The applied voltage bias in the plot has been set to a net gate bias with respect to $V_{FB}$ to produce a measure of the actual band bending. The J-V curve in gate injection mode (negative $V_G-V_{FB}$) is similar before and after PDA. However, the pronounced difference with PDA is observed for substrate injection mode (positive $V_G-V_{FB}$); Both in HfSiON and HfO$_2$, PDA lowers the current and increases the breakdown voltage ($V_{BD}$). The average leakage current at +1 V bias is $\sim$3x10$^{-4}$ A cm$^{-2}$ for the 650 °C annealed stack, essentially the same as for 50% SiO$_2$-50% Si$_3$N$_4$ Si oxynitride alloy with the same EOT, ~1.5 nm, and ~3,000 less than for SiO$_2$ leakage at the same oxide bias.

In order to explain the leakage current mechanism, it is helpful to compare the results on a Ge substrate with those on the same HfSiON on SiON/Si gate stack. Figure 6.11 presents the J-V curve of HfSiON on SiON/Si gate stack (EOT at 1.5 nm) before and after anneal at 900 °C. It shows two-orders of magnitude lower J level (2x10$^{-6}$ A cm$^{-2}$ at 1V) for the annealed sample and much more symmetry with respect to the gate bias polarity. This implies that the interfaces of the HfSiON/Ge gate stack are dissimilar to those with Si, and they play a major role in the asymmetric J-V characteristics.

The schematic band alignment of as-deposited HfO$_2$-Ge and Si and annealed HfO$_2$-Ge under zero and positive gate bias condition is proposed in Fig. 6.12. This alignment diagram was based on the previous XAS, SE and ultra violet photoemission spectroscopy measurements. X-ray absorption spectroscopy gives band edge differences between i) of 3.4 eV for GeO$_2$ and SiO$_2$, and ii) 0.9 eV for Ge$_3$N$_4$ and Si3N4, yielding band gaps of 5.5±0.1 eV for GeO$_2$ and 4.4±0.1 eV for Ge$_3$N$_4$, in agreement with published results [18,19] and SE dielectric function results (not shown here). The valence band offset energy between Ge and
GeO$_2$ was determined by ultra-violet photoemission spectroscopy, UPS, and is 3.3±0.15 eV [8]. Combined with a GeO$_2$ band gap of 5.5±0.1 eV, this gives a conduction band offset energy (CBOE) between Ge and GeO$_2$ of 1.5±0.15 eV. The same CBOE is obtained for Ge and Ge$_3$N$_4$. Combining these CBOEs with a 2 eV CBOE between HfO$_2$ and Ge, yields the gate stack structures in Fig. 6.12 (a). Figure 6.12 (b) compares injection from an i) n-type Ge substrate for a Ge/GeO$_2$/HfO$_2$/Al metal gate stack, in which the CBOE between Ge and GeO$_2$ is less than that between Ge and HfO$_2$, with ii) an n-Si/SiON/HfO$_2$/Al metal stack, in which the CBOE between Si and SiON is greater than that between Si and HfO$_2$. Under positive gate bias, a potential well is formed in the GeO$_2$ film between the n-type Ge substrate and HfO$_2$ that acts as an electron trap. Therefore, substrate current injection is qualitatively different for the band alignment in the n-Si/SiON/HfO$_2$/Al metal gate stack for which the interfacial layer band gap is greater than that of HfO$_2$. The alignment for HfSiON/GeON is basically similar except that (i) HfSiON band gap is ~0.2 eV larger than HfO$_2$ and (ii) GeON band gap is 0.5 eV smaller than GeO$_2$, therefore, the well depth becomes 0.7 eV deeper than GeO$_2$. Consequently, interfacial dielectrics on Ge are the origin of the electron trapping with the larger $N_{EFF}$ above mid-10$^{12}$ cm$^{-2}$ addressed in Refs. 7,8.

The schematic band alignment in Figure 6.13 describes Ge/HfSiON gate stacks where the interfacial GeON was eliminated by PDA. The description of the Si/SiON/HfSiON gate stack is also displayed for comparison. The band alignment shown in Fig 6.13 (a) is simply equivalent to Ge devices without electron trapping at the interfacial layer potential well. Compared to Fig. 6.13 (b), there is no more sequential F-N transport enhanced leakage current through the potential well at the GeON interface region but rather, direct tunneling
dominant leakage current through high-k dielectric is observed and thus, the elimination of interface suppresses leakage current level as well as enhances positive $V_{BD}$ in substrate injection mode.

6.5 Summary

The correlation between spectroscopic and electrical analysis on Ge-Hf high-k gate stacks was studied. XAS and MEIS comparisons between as-deposited and annealed films indicate that two physically distinctive defects are increased with post deposition anneal controlling the combined effects of (i) Ge oxynitride interface decomposition and (ii) diffusion of Ge species from the substrate. For both HfO$_2$ and HfSiON, these electrically-active defects are introduced during the initial deposition process, and their relative densities are increased during subsequent rapid thermal anneals in Ar at temperatures between 600°C and 800°C. C-V and J-V traces revealed that test capacitor devices annealed at the optimized temperature (650 °C for HfSiON and 600 °C for HfO$_2$) showed the minimum $N_{EFF}$ and highest positive (substrate injection) breakdown voltages as well as the lowest leakage current level compared to other annealed and as-deposited devices. The band alignment model proposes that suppression of electron trapping at the conduction band well by the elimination of Ge oxynitride interfaces is directly responsible for the enhancement of leakage current characteristics.
6.6 References


Fig. 6.1. Compositional depth profile obtained by simulating MEIS energy spectra for as-deposited and annealed (a) HfO$_2$ films and (b) HfSiON films on Ge(100) substrates. Dotted line and arrow indicate the Ge substrates and the direction of the films. The spot with the error bar represents the fitting error in the depth direction and the relative concentration.
Fig. 6.2. Imaginary dielectric function ($\varepsilon_2$) spectra from SE measurement for as-deposited and annealed HfO$_2$ and HfSiON films on Ge(100) substrates. $D_1$ and $D_2$ indicate the defect states located below the conduction band edge.
Fig. 6.3. XAS spectra below the absorption edge of the O K$_1$ feature for (a) HfO$_2$ and (b) HfSiON films on Ge(100) substrates. Two deconvoluted peaks, labeled D$_1$ and D$_2$, indicate the defect states determined by Gaussian fitting of the XAS O K$_1$ edge spectra.
Fig. 6.4. Relative strengths of defect features determined from Gaussian fits to O K$_\epsilon$ edge spectra. The error bar is related to the uncertainty of Gaussian fit parameters to the OK1 XAS spectra. The overall uncertainty is 5 to 10 % of the resolved peak intensity.
Fig. 6.5. XAS spectra below the absorption edge of the NK₁ feature for (a) HfSiON and (b) HfO₂ films on Ge(100) substrates as a function of PDA temperature.
Fig. 6.6. C-V hysteresis traces for (a) as-deposited, (b) 650 °C, and (c) 700 °C annealed HfSiON. The oxide trapped charge density is extracted at $V_{FB}$. 

- (a) Oxide trapped charges = $3.6 \times 10^{11}$ cm$^{-2}$
  \[ \Delta V = 0.8 V @ V_{FB} = -1.4 V \]

- (b) Oxide trapped charges = $4.5 \times 10^{11}$ cm$^{-2}$
  \[ \Delta V = 0.1 V @ V_{FB} = -1.5 V \]

- (c) Oxide trapped charges = $1.9 \times 10^{12}$ cm$^{-2}$
  \[ \Delta V = 0.27 V @ V_{FB} = -1 V \]
Fig. 6.7. C-V hysteresis traces for (a) as-deposited, (b) 600 °C, and (c) 650 °C annealed HfO₂. The oxide trapped charge density is extracted at $V_{FB}$. 

121
Fig. 6.8. Plot of $N_{\text{EFF}}$ as a function of $N_{\text{inj}}$ for as deposited and annealed HfO$_2$ and HfSiON.
Fig. 6.9. The relation between the effective trapped charge density, $N_{\text{EFF}}$ and $V_{\text{FB}}$ extracted from C-V hysteresis as a function of PDA temperature for (a) HfSiON and (b) HfO$_2$. 
Fig. 6.10. J-V plots for test devices with (a) as deposited and (b) 650 °C annealed HfSiON and (c) as deposited and (c) 600 °C annealed HfO₂. There is an enhancement of leakage current characteristics for each annealed device compared to the as deposited.
Fig. 6.11. J-V plot for test devices with as deposited and 900 °C annealed HfSiON on SiON/Si. The HfSiON was deposited in the exactly same recipe as high-k/Ge devices.
Fig. 6.12. (a) Band alignments between (i) n-type Ge, GeO$_2$ and HfO$_2$ and (ii) n-type Ge, Ge$_3$N$_4$ and HfO$_2$ and (b) substrate injection for an n-type Ge, GeO$_2$ and HfO$_2$ stack in (a), with and Al gate electrode, for which the conduction band offset energy between Ge and GeO$_2$ which is less than that between Ge and HfO$_2$, and for a gate stack on n-Si and with an SiON ITR, which is greater than that between Si and HfO$_2$. 
Fig. 6. 13. Energy band alignment between an substrate/high-k gate dielectric stack and Al metal gate electrode for substrate injection: (a) HfSiON on an SiON ITR on Si(100) for the J–V plot in Fig. 6.9 and (b) HfSiON in direct bonding contact with Ge for the J–V plot in Fig. 6.8 (b).
7 Concluding Remarks and Future Work

This dissertation study primarily focused on investigation of transition metal and rare earth elemental/complex high-k dielectrics in the effort to understand the physical origin of intrinsic and extrinsic defects, and to achieve the enhanced reliability of advanced electronic devices such as Si- and Ge-high-k MOSFETs and MIM capacitors.

The summary of study on intrinsic properties of high-k materials and interfaces is following:

Intrinsic bonding defects inherently exist in nanocrystalline high-k dielectrics associated with the discrete asymmetric defect energy levels near the conduction and valence band edges. Therefore, this thesis work investigated the engineering pathways for defect minimization of high-k dielectrics by (i) nano-crystalline length scale control, (ii) TM doping, and (iii) pseudo-ternary alloying. Nanocrystalline LaScO$_3$ has the coherent pi-bond interaction between Sc and O in Sc-O octahedron which is responsible for J-T term splitting and localized defects when the nanocrystalline size is larger than the 3-4 nm, scale of order for this phi-bond interaction. Ni-doping to BaSrTiO$_3$ successfully stabilized the local structure distortion by Ni$^{2+}$ replacement of divacancies related to Ti$^{3+}$ defect states and therefore, resulted in an enhancement of MIM capacitor reliability by the suppression and recovery of the symmetry in the leakage current.

As a second part of this thesis, we utilized the knowledge on the intrinsic properties, gained from the first part, to enhance Ge/high-k gate stacks.
This study proposes the engineering solution for suppression of charge trapping by the elimination of interfacial layer. Anneal from 600 to 800 °C of (100) and (111) Ge substrates eliminated the interfacial transition layer by removing Ge-N and possibly Ge-O bonds. With NH₄OH cleaning, this interfacial oxide free Ge/HfSiON gate stack suppressed (i) the charge trapping at defects in germanate of high-k/GeOₓ and (ii) band well trapping at GeOₓ or GeON and therefore, provides a possible solution for Ge n-FETs.

As a suggestion for future study, more accurate engineering tuning on doped BST and Ge/high-k gate stacks is required for future application.

Ni-doped BST showed the great reduction of leakage current characteristics, but it is achieved only at room temperature (RT) condition. Although some applications such as organic devices are restricted to this RT condition, other important applications such as memory capacitor cells require ultra high-k values (> 100) of BST after the doped BST is annealed. Therefore, further study on anneal effects of Ni-doped BST for increased k values as well as on achievement of the good thermal stability at doped-BST/metal electrode interfaces will provide the greatest opportunity for application of BST in the future devices such as a charge trapping layer in charge trapping flash memory. In addition, other TM (e.g., Mn) doping into the perovskite is another interesting option for study.

The results for Ge/high-k stacks provide an excellent understanding on charge trapping at the interfacial region between Ge and high-k dielectrics. However, this charge trapping becomes more severe Ge/high-k MOSFET is scaled to lower EOT while taking advantage of the carrier mobility enhancement in Ge. Therefore, the optimized interfacial removal and
suppression of defects under lower EOT (<1.5 nm) is required as well as the flat band voltage tuning. The annealed Ge/HfSiON stack in this thesis work is satisfactory for the charge trapping suppression but has some issues related to the relatively large negative flat band voltage shift. This should be investigated further by applying different metal gate electrodes (i.e., deep work function metal such as TiN) and/or more stable interfaces passivation (i.e., SiNₓ/Si) rather than GeOₓNy, providing enough energy barrier to Ge. Some of previous works for Si passivation on Ge has achieved good surface passivation on p-FET but n-FET still showed the much lower electron mobility which might be due to the charge transport through Si surface not Ge based on interfacial band-bending. Therefore, it would be interesting to study SiNₓ/Si/Ge stacks for passivation on Ge n-FET.