ABSTRACT

NIU, DONG. Interface reactions during processing of chemical vapor deposited yttrium oxide high-k dielectrics. (Under the direction of Dr. Gregory N. Parsons)

High dielectric constant (high-k) insulators are important for advanced MOS devices to limit gate leakage and increase gate capacitance. Reactions between high-k’s and the substrate during deposition or post-deposition processing lead to an increase in the equivalent oxide thickness, and the mechanisms that control the changes need to be well understood. We investigate yttrium-based high-k dielectrics formed by oxygen plasma assisted CVD on Si(100), using two different yttrium diketonate precursors. Characterization techniques include IR, XPS, TEM, EELS, AES, and IV and CV electrical analysis. During deposition and post-deposition anneals a thin Y-O-Si (silicate)/SiO₂ structure due to intermixing of Y, O and Si and substrate oxidation is formed at the interface, between the Y₂O₃ and silicon. The extent of the intermixing depends on substrate surface preparation, process conditions, and annealing conditions. As-deposited Y₂O₃ films show evidence for O-H bond due to water absorption. With in-situ deposited Si capping layers, water pickup is significantly reduced, and interfacial SiO₂ layer after annealing is less than 5 Å. Analysis of reaction mechanisms suggests that Si diffusion is attributed to silicate formation, and water absorption, catalytic dissociation of residual O₂, and O₂ plasma may account for SiO₂ formation.

Nitridation of chemical vapor deposited yttrium oxide using N₂ plasma during deposition and post-deposition treatments is investigated. The use of N₂ instead of O₂ during deposition minimizes the substrate oxidation. Similar activation energies for post-deposition anneals of O₂ and N₂ films indicate substrate oxidation processes are likely the
same. Bulk properties including chemical bonding, concentration and distribution of N are also studied for as-deposited and annealed films.
INTERFACE REACTIONS DURING PROCESSING OF CHEMICAL VAPOR DEPOSITED YTTRIUM OXIDE HIGH-K DIELECTRICS

by

DONG NIU

A dissertation submitted to the Graduate Faculty of North Carolina State University
In partial fulfillment of the Requirements for the Degree of Doctor of Philosophy

CHEMICAL ENGINEERING

Raleigh, North Carolina

2002

APPROVED BY:

Dr. H. Henry Lamb

Dr. Gerald Lucovsky

Dr. Veena Misra

Dr. Gregory N. Parsons
Chair of Advisory Committee
This thesis is dedicated to my wife, Jian Zhou,
my parents, Changren Niu and Guiqin Guo,
and my little sister, Yan Niu, for all their love.
DONG NIU was born in Daqing City, Heilongjiang, northeastern China on December 2, 1971. He moved to Zhongmu, Henan, a small town in central China, with his parents and younger sister in 1978. In 1986, he attended Kaifeng High School in Kaifeng City. One and half years later, he won the first place in a chemistry contest in Henan Province and attended the Olympic chemistry class at the Affiliated High School of Peking University in Beijing. In 1989, he was accepted, exempt of National College-Entrance Examination, to the Department of Chemical Engineering at Tsinghua University, where he received his bachelor’s and master’s degrees in 1994 and 1997, respectively. In March 1997, he was married to Jian Zhou after having studied in the same class for almost 8 years, and 5 months later, they moved to Raleigh together continuing their graduate studies in the Department of Chemical Engineering at North Carolina State University. On the way to his Ph.D., he received his second Master’s degree in Electrical Engineering in May 2001. He will join Novellus as a Process Development Engineer after graduation.
ACKNOWLEDGEMENTS

I am grateful to my advisor Dr. Parsons for his guidance and support throughout this work. He also has been a great mentor and a true friend to me. I am thankful to the past and present members in Dr. Parsons’ group, Dr. Tom (Chien-Sheng) Yang for encouraging me to choose the field of electronic materials, Dr. Tonya M. Klein for training me on the CVD system, Dr. Ashfaqual Chowdhury, Dr. Jim Chambers, Dr. Atul Gupta, Dr. Gougousi Theodosia, Kevin Bray, Jason Kelly, Dr. Laura Smith, Kiejin Park, and David Terry for thoughtful discussions and collaborations. Special thanks go to Robert Ashcraft who has made excellent contributions to the research and reactor maintenance.

I would like to acknowledge my committee members, Dr. Henry Lamb, Dr. Gerry Lucovsky, and Dr. Veena Misra for their support and excellent mentoring. I would also like to thank my collaborators, Dr. Stemmer, Dr. Garfunkel, Dr. J.-P. Maria, Dr. Marc Ulrich, Dr. Osburn, Dr. Israel Baumvol, Z. Chen, Bruce Rayner, Chris Hinkel, and Sunkee Han for performing various analysis.

Special thanks to Kit Yeung for being a good friend and helping me repair and maintain of the CVD system. Also thanks to the cleanroom staff personnel including Joan O’Sullivan and Dr. Ginger Yu. Thanks to all the people at AIF, especially Dr. John Phillips and Dr. Dieter Driffis, for helping obtain the XPS data.
# TABLE OF CONTENTS

LIST OF FIGURES .......................................................................................................................... VIII

CHAPTER 1 ........................................................................................................................................ 1

INTRODUCTION ................................................................................................................................. 1

1.1 ISSUES OF SCALING OF ULTRA-THIN GATE OXIDE ............................................................ 1
1.2 SELECTION OF HIGH-K DIELECTRIC CANDIDATES ............................................................. 3
1.3 PROPERTIES OF YTTRIUM OXIDE AND YTTRIUM SILICATE ............................................. 4
1.4 SELECTED CURRENT ISSUES OF HIGH-K DIELECTRICS .................................................. 5
1.4.1 Dielectric/Si Interface Stability ....................................................................................... 5
1.4.2 Dielectric/Si Interface Quality ....................................................................................... 6
1.4.3 Film Morphology .......................................................................................................... 6
1.4.4 Thermal Stability of Metal Silicates ............................................................................... 7
1.4.5 Gate Electrode Compatibility ....................................................................................... 7
1.5 OBJECTIVE OF THIS WORK ............................................................................................... 8
1.6 OVERVIEW OF DISSERTATION ......................................................................................... 9
1.7 REFERENCES ....................................................................................................................... 13

CHAPTER 2 .................................................................................................................................... 19

ELEMENTARY REACTION SCHEMES FOR PHYSICAL AND CHEMICAL
VAPOR DEPOSITION OF TRANSITION METAL OXIDES ON SILICON FOR
HIGH-K GATE DIELECTRIC APPLICATIONS .................................................................................. 19

2.1 INTRODUCTION ..................................................................................................................... 21
2.2 MATERIAL PREPARATION AND ANALYSIS ...................................................................... 22
2.3 RESULTS ................................................................................................................................ 23
2.3.1 PVD Yttrium Silicate ..................................................................................................... 23
2.3.2 CVD Aluminum Oxide .................................................................................................. 28
2.3.3 CVD of Y₂O₃ .................................................................................................................. 30
2.4 PROPOSED ELEMENTARY REACTION SCHEMES .............................................................. 31
2.5 SUMMARY ............................................................................................................................ 36
2.6 ACKNOWLEDGEMENTS ....................................................................................................... 37
2.7 REFERENCES ....................................................................................................................... 38

CHAPTER 3 .................................................................................................................................... 53

WATER ABSORPTION AND INTERFACE REACTIVITY OF YTTRIUM
OXIDE GATE DIELECTRICS ON SILICON .................................................................................. 53

3.1 INTRODUCTION AND EXPERIMENTAL APPROACH ........................................................ 55
3.2 RESULTS ................................................................................................................................ 56
3.3 DISCUSSION AND CONCLUSION ....................................................................................... 58
3.4 ACKNOWLEDGEMENTS ....................................................................................................... 59
3.5 REFERENCES ....................................................................................................................... 60
CHAPTER 4.................................................................................................................... 66
ELECTRON ENERGY LOSS SPECTROSCOPY ANALYSIS OF INTERFACE
STRUCTURE OF YTTRIUM OXIDE GATE DIELECTRICS ON SILICON ...... 66
4.1 INTRODUCTION ........................................................................................................ 68
4.2 EXPERIMENTAL ........................................................................................................ 68
4.3 RESULTS ..................................................................................................................... 69
4.4 DISCUSSION AND CONCLUSIONS ....................................................................... 71
4.5 ACKNOWLEDGEMENTS ......................................................................................... 73
4.6 REFERENCES ............................................................................................................ 74

CHAPTER 5.................................................................................................................... 81
REACTION-RATE LIMITED SUBSTRATE OXIDATION DURING
ANNEALING OF Y₂O₃ ON SILICON ........................................................................ 81
5.1 INTRODUCTION ........................................................................................................ 83
5.2 EXPERIMENTAL ........................................................................................................ 84
5.3 RESULTS ..................................................................................................................... 85
5.4 DISCUSSION AND CONCLUSIONS ....................................................................... 87
5.5 ACKNOWLEDGEMENTS ......................................................................................... 89
5.6 REFERENCES ............................................................................................................ 90

CHAPTER 6.................................................................................................................... 96
CHEMICAL, PHYSICAL, AND ELECTRICAL CHARACTERIZATIONS OF
OXYGEN PLASMA ASSISTED CHEMICAL VAPOR DEPOSITED YTTRIUM
OXIDE ON SILICON .................................................................................................... 96
6.1 INTRODUCTION ........................................................................................................ 98
6.2 EXPERIMENTAL ........................................................................................................ 99
6.3 RESULTS ..................................................................................................................... 101
6.3.1 Y₂O₃ Deposition Using Y(HF₃AA)₃ ........................................................................ 101
6.3.2 Y₂O₃ Deposition Using Y(TMHD)₃ .................................................................... 103
   6.3.2.1 Deposition On Clean Silicon (100) ............................................................. 103
   6.3.2.2 Deposition On In-Situ Pretreated Silicon ................................................. 106
   6.3.2.3 Macroscopic Silicon Substrate Consumption ....................................... 107
6.4 DISCUSSION ............................................................................................................. 108
6.5 SUMMARY AND CONCLUSIONS ......................................................................... 112
6.6 ACKNOWLEDGEMENT ......................................................................................... 113
6.7 REFERENCES ............................................................................................................ 114

CHAPTER 7.................................................................................................................. 139
REACTIONS OF Y₂O₃ FILMS WITH (001) SI SUBSTRATES AND WITH
POLYCRYSTALLINE SI CAPPING LAYERS .......................................................... 139
7.1 INTRODUCTION AND APPROACH ................................................................. 141
7.2 RESULTS ................................................................................................................ 142
7.3 DISCUSSION AND CONCLUSIONS .................................................................. 144
7.4 ACKNOWLEDGEMENTS .................................................................................... 145
7.5 REFERENCES ........................................................................................................ 146
CHAPTER 8
NITRIDATION OF YTTRIUM OXIDE GATE DIELECTRICS USING N$_2$ PLASMA

8.1 INTRODUCTION
8.2 EXPERIMENTAL
8.3 RESULTS
8.3.1 Comparison of Yttrium Oxide Deposited with O$_2$ and N$_2$ Plasma
8.3.2 Chemical Structure and Properties of Y$_2$O$_3$ Films Deposited with N$_2$ Plasma
8.3.3 Effects of Diluted N$_2$ Plasma
8.4 DISCUSSION
8.4.1 Effects of O$_2$ and N$_2$ Plasma on Water Absorption and Substrate Oxidation
8.4.2 Chemical Structure and Properties of Nitried Yttrium Oxide
8.4.3 Effects of Diluted N$_2$ Plasma
8.5 CONCLUSIONS
8.6 ACKNOWLEDGEMENTS
8.7 REFERENCES

CHAPTER 9
EVIDENCE OF ALUMINUM SILICATE FORMATION DURING CHEMICAL VAPOR DEPOSITION OF AMORPHOUS AL$_2$O$_3$ THIN FILMS ON SI(100)

9.1 INTRODUCTION
9.2 EXPERIMENTAL
9.3 RESULTS AND DISCUSSION
9.4 REFERENCES

APPENDICES
APPENDIX A
ELECTRICAL PROPERTIES OF NMOS TRANSISTORS USING Y$_2$O$_3$ GATE DIELECTRICS
APPENDIX B
COMPARISON OF PROPERTIES OF CHEMICAL VAPOR DEPOSITED YTTRIUM OXIDE WITH AND WITHOUT IN-SITU CAPPING POLY-SI LAYERS
LIST OF FIGURES

CHAPTER 1. INTRODUCTION

Figure 1.1  Experimental (dots) and simulated (solid lines) tunneling currents as a function of gate voltage in ultra-thin SiO₂ poly-silicon-gate MOS devices. The dashed line shows a tunneling current level of 1 A/cm²……………….17

Figure 1.2  Calculated band offsets for various oxides on Si..............................18

CHAPTER 2. ELEMENTARY REACTION SCHEMES FOR PHYSICAL AND CHEMICAL VAPOR DEPOSITION OF TRANSITION METAL OXIDES ON SILICON FOR HIGH-K GATE DIELECTRIC APPLICATIONS

Figure 2.1  XPS Si 2p spectra for various thicknesses of yttrium layers on Si(100) after various processes……………………………………………………………40

Figure 2.2  TEM for four yttrium silicate films formed with ~8 Å initial yttrium on silicon, followed by oxidation at 900°C for various times: (a) 6 seconds; (b) 15 seconds; (c) 1 minute; (d) 20 minutes……………………………..41

Figure 2.3  XPS results for yttrium silicide films oxidized at various temperatures to form Y₂O₃/SiO₂ films…………………………………………………………..42

Figure 2.4  Si-O/Si integrated area ratio determined from the Si 2p XPS data in Figure 2.3c vs. 1/T. The MEIS Si fraction is also plotted vs. inverse oxidation temperature…………………………………………………………..43

Figure 2.5  Narrow Resonant Nuclear Reaction Profiles for two Al₂O₃ films deposited on Si(100)……………………………………………………………..44
Figure 2.6  XPS results for Al₂O₃ films on Si(100) after anneals at various temperatures.................................................................45
Figure 2.7  XPS results for “Y₂O₃” films deposited by CVD.................................46
Figure 2.8  CV results for thin films on clean and nitrided surfaces.....................47

CHAPTER 3. WATER ABSORPTION AND INTERFACE REACTIVITY OF YTTRIUM OXIDE GATE DIELECTRICS ON SILICON

Figure 3.1  (a) Si 2p XPS spectra after annealed at various temperatures for 1 minute. (1) as-deposited; (2) 600°C; (3) 700°C; (4) 800°C; (5) 900°C.  (b) Si-O/Si peak area ratio vs. 1000/T.  An activation energy of 0.33 eV was obtained.................................................................62
Figure 3.2  FTIR OH peak growth over time.  (a) Capped films show slower OH absorption; (b) Annealed films without capping layers show slower OH absorption.................................................................63

CHAPTER 4. ELECTRON ENERGY LOSS SPECTROSCOPY ANALYSIS OF INTERFACE STRUCTURE OF YTTRIUM OXIDE GATE DIELECTRICS ON SILICON

Figure 4.1  XPS Y 3d spectra of CVD “Y₂O₃” films with various thicknesses............75
Figure 4.2  (a) TEM of the film deposited at 400°C for 3 min and annealed at 900°C for 1 min. The thickness is about 65 Å; (b) Si L-edges measured across the film. The locations correspond to those on the TEM image. The inset is the ADF image.................................................................76
Figure 4.3  XPS Y 3d spectra of CVD “Y₂O₃” films on (1) bare Si; (2) nitried Si
Figure 4.4  (a) TEM of Y₂O₃ on nitried Si; (b) Si L-edges of the same film: (1) Si bulk; (2) 1 nm from Si interface; (3) 2.3 nm from Si interface; (4) 5.5 nm from Si interface

CHAPTER 5. REACTION-RATE LIMITED SUBSTRATE OXIDATION DURING ANNEALING OF Y₂O₃ ON SILICON

Figure 5.1  XPS Si 2p spectra of films with different thicknesses
Figure 5.2  Illustration of the substrate consumption. (a) Film was deposited at 400°C. Part of the film was etched by HF; (b) Film was annealed at 900°C in N₂; (2) part of the annealed film HF was etched by HF
Figure 5.3  Oxidation of HF-last bare Si at 900°C in N₂

CHAPTER 6. CHEMICAL, PHYSICAL, AND ELECTRICAL CHARACTERIZATIONS OF OXYGEN PLASMA ASSISTED CHEMICAL VAPOR DEPOSITED YTTRIUM OXIDE ON SILICON

Figure 6.1  Schematic of remote plasma enhanced CVD system
Figure 6.2a  XPS O 1s spectra for films from fluorinated precursor: (1) “thin sample” (~50 Å) deposited with plasma power 5 W; (2) “thick sample” (~1000 Å) with plasma power of 5 W; (3) “thick sample” (~1000 Å) with plasma
Figure 6.2b  XPS Y 3d spectra for films from fluorinated precursor: (1) “thin sample” (~50 Å) deposited with plasma power 5 W; (2) “thick sample” (~1000 Å) with plasma power of 5 W; (3) “thick sample” (~1000 Å) with plasma power of 10 W; (4) “thick sample” (~1000 Å) with plasma power of 25 W………………………………………………………………………..118

Figure 6.2c  XPS Si 2p spectra for films from fluorinated precursor: (1) “thin sample” (~50 Å) deposited with plasma power 5 W; (2) “thick sample” (~1000 Å) with plasma power of 5 W; (3) “thick sample” (~1000 Å) with plasma power of 10 W; (4) “thick sample” (~1000 Å) with plasma power of 25 W……………………………………………………………………….121

Figure 6.3  C-V result of a film from fluorinated precursor Y(HFAA)₃. Large hysteresis (~0.9 eV) indicates the presence of oxide-trapped charges………………………………………………………………………………..120

Figure 6.4a  XPS O 1s spectra for films with different thicknesses from hydrogenated precursor………………………………………………………………………………..122

Figure 6.4b  XPS Y 3d spectra for films with different thicknesses from hydrogenated precursor………………………………………………………………………………..123

Figure 6.4c  XPS Si 2p spectra for films with different thicknesses from hydrogenated precursor………………………………………………………………………………..124

Figure 6.5a  TEM image of the film deposited at 400°C for 3 min and annealed at 900°C for 1 min. The thickness is about 65 Å……………………………………124
Figure 6.5b  ADF image of the film deposited at 400°C for 3 min and annealed at 900°C for 1 min. The thickness is about 65 Å……………………125

Figure 6.5c  EELS shows Si L-edges measured across the film. The locations correspond to those on the TEM image……………………………….126

Figure 6.6  C-V results of a film from hydrogenated precursor Y(TMHD)₃. Negative flatband shifts indicate the presence of positive fixed charges. Flatband voltage V_fdb does not change with film thickness…………………….127

Figure 6.7  Mid and Far IR spectra of as-deposited and annealed films. As-deposited film shows significant OH and C and broad feature of Y-O. The OH and C peaks are almost completely removed after anneal. Y-O triplet peaks become very sharp, indicating crystallization of the film…………..128

Figure 6.8  XRD results of films from hydrogenated precursor. (1) After anneal at 900°C in N₂, clear features of crystallized Y₂O₃ observed; (2) as-deposited, no clear features……………………………………………..129

Figure 6.9a  AFM image of the as-deposited sample with roughness ~3.9 Å……….130

Figure 6.9b  AFM image of the annealed sample with roughness ~7.6 Å…………….131

Figure 6.10a  XPS O 1s spectra for films deposited using from hydrogenated precursor on: (1) bare Si; (2) nitrided Si; (3) oxidized Si…………………………132

Figure 6.10b  XPS Y 3d spectra for films deposited using from hydrogenated precursor on: (1) bare Si; (2) nitrided Si; (3) oxidized Si…………………………133

Figure 6.10c  XPS Si 2p spectra for films deposited using from hydrogenated precursor on: (1) bare Si; (2) nitrided Si; (3) oxidized Si…………………………134

Figure 6.11a  TEM of Y₂O₃ on nitrided Si. The thickness is about 70 Å…………………135
Figure 6.11b  EELS spectra of Y$_2$O$_3$ on nitrided Si taken at various distances from the substrate: (i) the bulk of the substrate; (ii) 1.0 nm from the substrate; (iii) 2.3 nm from the substrate; (iv) 5.5 nm from the substrate..........................136

Figure 6.11c  Si concentration depth profile of Y$_2$O$_3$ on nitrided Si..........................137

Figure 6.12  Illustration of the substrate consumption. (a) as-deposited. The step from Si to Y$_2$O$_3$ is ~500 Å; (b) annealed at 900°C in N$_2$. The step from Si to Y$_2$O$_3$ is ~240 Å; (c) HF etching of part of the film deposited. The second step from Si to Y$_2$O$_3$ is ~525 Å, indicating ~285 Å Si is consumed.................................................................138

CHAPTER 7. REACTIONS OF Y$_2$O$_3$ FILMS WITH (001) SI SUBSTRATES AND WITH POLycrystalline SI CAPPING LAYERS

Figure 7.1  (a) HRTEM micrograph of the film grown on bare Si. (b) Annular dark-field image (filtered) of the film on bare Si. (c) EELS line profiles of across (b) and (e) for the Si L edge as a function of distance from the Si substrate interface. Open squares are from the film on bare Si, circles from the film on nitrided Si. Note that the films have different thickness (the position of the interfaces and layers are indicated as a guide). (d) HRTEM of the film on nitrided Si. (e) Annular dark-field image of the film on nitrided Si.................................................................148
CHAPTER 8. NITRIDATION OF YTTRIUM OXIDE GATE DIELECTRICS USING N₂ PLASMA

**Figure 8.1** FTIR Spectra of CVD Y₂O₃ thick films deposited with (1) O₂ plasma and (2) N₂ plasma and exposed to ambient for various times………………...171

**Figure 8.2** Peak area versus exposure time in ambient for CVD Y₂O₃ films; (1) O-H peak (3700-2700 cm⁻¹) for a film deposited with N₂ plasma; (2) O-H peak (3700-2700 cm⁻¹) for a film deposited with O₂ plasma………………...172

**Figure 8.3** XPS Si ₂p spectra of CVD Y₂O₃ thin films deposited with O₂ and N₂ plasma; (1) as-deposited; (2) annealed at 600°C; (3) annealed at 700°C; (4) annealed at 800°C; (5) annealed at 900°C…………………………173

**Figure 8.4** Arrhenius plot of Si-O/Si peak area ratio versus inverse anneal temperature for films deposited using N₂ plasma (top) and O₂ plasma (bottom) as determined from XPS spectra; the extracted activation energies for each film are displayed……………………………………174

**Figure 8.5** FTIR spectra of CVD Y₂O₃ films deposited with N₂ plasma; (1) as-deposited film exposed to ambient for 4 hours; (2) film annealed at 900°C and exposed to ambient for 21 days; (3) film with an a-Si capping layer and exposed to ambient for 6 days……………………………………175

**Figure 8.6** Peak area versus exposure time in ambient for a CVD Y₂O₃ film deposited with N₂ plasma; (1) C-O peaks (1700-1250 cm⁻¹); (2) C-N peaks (2250-1950 cm⁻¹)……………………………………………………..176
Figure 8.7 XPS O 1s, N 1s/Y 3s, and Y 3d spectra of CVD Y₂O₃ thick films deposited in N₂ plasma; (1) as-deposited; (2) annealed at 900°C for 1 min in N₂…………………………………………………………………….177

Figure 8.8 AES surface survey spectra of CVD Y₂O₃ films deposited with N₂ plasma. The bottom curve is the spectrum taken after the film was exposed to the air. This film was then transferred in vacuum to a nitridation chamber, and underwent a post-deposition nitridation process at 300°C for 60 minutes in N₂ plasma. The resulting spectrum is the middle curve. Finally, the film was annealed in-situ at 900°C in N₂ for 1 minute and the spectrum is shown by the top curve. ………………………………………178

Figure 8.9 AES depth profile of a CVD Y₂O₃ film deposited with N₂ plasma and annealed ex-situ at 900°C for 1 min in N₂; sputter depth is based on the sputtering rate of SiO₂………………………………………………….179

Figure 8.10 C-V characteristics of CVD Y₂O₃ films deposited with N₂ plasma (solid line) and O₂ plasma (dotted line)…………………………………………………….180

Figure 8.11 FTIR spectra of CVD Y₂O₃ films deposited with (1) helium-diluted N₂ plasma (3:1 He:N₂ ratio) and (2) N₂ plasma……………………………………….181

Figure 8.12 AES spectra of CVD Y₂O₃ films deposited in diluted N₂ plasma; the bottom spectrum is for a film annealed at 900°C for 1 minute; the top spectrum is for a film that a underwent post-annealed nitridation at 400°C in N₂ plasma for 30 minutes………………………………………………………182
CHAPTER 9. EVIDENCE OF ALUMINUM SILICATE FORMATION DURING CHEMICAL VAPOR DEPOSITION OF AMORPHOUS AL₂O₃ THIN FILMS ON SI(100)

Figure 9.1a Narrow resonance nuclear reaction profile (NRP) of 18nm Al₂O₃ on Si. Model of results (shown in inset) show 2 layers with the first layer having an Al concentration corresponding to Al₂O₃.

Figure 9.1b NRP data for a thin 3.5nm Al₂O₃ film.

Figure 9.2 Auger depth profile of a AlO / AlSiₓOᵧ film showing the appearance of Si at approximately 100 Å.

Figure 9.3 TEM image Al₂O₃ deposited on silicon at ~400°C in the as-deposited state. The total film thickness is approximately 18nm. Two distinct layers are observed with approximately equal thickness.

Figure 9.4 XPS spectrum of Al and Si region of a 3.5nm aluminum oxide film deposited on silicon, showing evidence for Al-O-Si silicate bonding.

APPENDIX A. ELECTRICAL PROPERTIES OF NMOS TRANSISTORS USING Y₂O₃ GATE DIELECTRICS

Figure A1 Schematic illustration of non-self aligned gate process; (a) Grow and pattern 100 nm thick oxide and form junction; (b) Deposit 100 nm LPCVD oxide over diffusions and pattern gate and contact regions; (c) Deposit gate dielectric and electrode; (d) Pattern and etch gate electrode/gate dielectric, and deposit and pattern contact metal.
Figure A2  Electrical characteristics of $Y_2O_3$ with poly-Si gate NMOS Devices: (a) capacitance vs. gate voltage; (b) leakage current vs. gate voltage……..202

Figure A2  Electrical characteristics of $Y_2O_3$ with poly-Si gate NMOS Devices: (c) drain current vs. gate voltage; (d) device mobility……………………203

Figure A3  Threshold voltage and transconductance shift of $Y_2O_3$ with NMOS devices under 1.2 V stressing………………………………………………..204

Figure A4  Effects of FGA on electrical characteristics of $Y_2O_3$ with poly-Si gate NMOS Devices: (a) capacitance vs. gate voltage; (b) leakage current vs. gate voltage…………………………………………………………………..205

Figure A4  Effects of FGA on electrical characteristics of $Y_2O_3$ with poly-Si gate NMOS Devices: (c) drain current vs. gate voltage; (d) device mobility…………………………………………………………………206

APPENDIX B. COMPARISON OF PROPERTIES OF CHEMICAL VAPOR DEPOSITED YTTRIUM OXIDE WITH AND WITHOUT IN-SITU CAPPING POLY-SI LAYERS

Figure B1a  TEM image of a sample deposited for 6.5 minutes and annealed for 1 minute in $N_2$. The total thickness is $\sim$100 Å………………….210

Figure B1b  EELS spectra of (1) the bulk of the substrate and (2) the bottom layer in Figure B1a for the same sample. The inset is the ADF image………211

Figure B2  AES depth profile of a sample deposited under the same conditions as the sample in Figure B1. The incident electron energy is (a) 3 keV and (b) 5 keV…………………………………………………………………..212
Figure B3  AES depth profile of a sample deposited under the same conditions as the sample in Figure 1 with a 200 Å poly-Si capping layer. The capping layer was deposited *in-situ* with exposing the sample to the atmosphere. The incident electron energy is (a) 3 keV and (b) 5 keV.
CHAPTER 1

INTRODUCTION

1.1 ISSUES OF SCALING OF ULTRA-THIN GATE OXIDE

Continuous pursuit for faster speed, higher packing density, and lower power consumption has driven complementary-metal-oxide-semiconductor (CMOS) devices to shrink for several decades in the integrated circuit (IC) industry. Both constant-field scaling and constant-voltage scaling have been used as guidance for design of metal-oxide-semiconductor field effect transistors (MOSFETs). In order to avoid the problems with constant-field scaling (e.g. non-scalability of inversion-layer thickness) and constant-voltage scaling (e.g. degradation of mobility due to high electric fields), generalized scaling rules have been proposed. In reality, CMOS technology has evolved in steps of mixed both scaling principles to reflect this scaling. It is worth noting that for both the constant-field scaling and generalized scaling, the gate dielectric thickness $t_{ox}$ is expected to scale in proportion with the channel length.

Scaling of the gate dielectric helps the gate control the channel and minimize short channel effects. According to the updated International Technology Roadmap for Semiconductors, an equivalent oxide thickness ($t_{ox,eq}$) of less than 1 nm is expected at the 50 nm generation, which is only a few atomic layers thick for SiO$_2$. Growing or depositing such a thin layer across 300 mm or larger wafers imposes a formidable manufacturing challenge.
As the SiO$_2$ layer shrinks below 3 nm, direct tunneling due to quantum mechanical (QM) effects through the gate oxide starts playing a significant role. Figure 1.1 shows experimental gate oxide tunneling currents for oxide thicknesses from 3.5 nm to 1.0 nm, which clearly indicates the domination of direct tunneling over the voltage range under study.\(^4\) Even though a leakage current (off-state) as high as $10^4$ A/cm$^2$ may be tolerable for high performance microprocessors, much lower leakage currents ($\sim 10^{-2}$-$10^{-3}$ A/cm$^2$) are required for low-power applications such as laptops.

Another two important issues are boron penetration and poly depletion effect. Boron diffusing into the channel through the ultra-thin oxide causes threshold voltage shifts. Depleted poly-Si gate due to finite doping density results in an additional capacitance in series to that of the gate stack and deceases the overall capacitance. According to the scaling rules, not only does oxide thickness need scaling down, but the doping concentration in polycrystalline (poly) Si also needs to increase to minimize the poly depletion effect, both of which make boron penetration effects more pronounced.

In summary, as the gate oxide scales down to 1 nm or below, various issues are expected to make ultra-thin SiO$_2$ not suitable for CMOS technology, especially low power applications. A material with higher dielectric constant than that of SiO$_2$ (k=3.9) enables use of thicker films with the same gate capacitance (the same equivalent oxide thickness, $t_{ox,eq}$), which will lead to lower leakage currents.
1.2 SELECTION OF HIGH-K DIELECTRIC CANDIDATES

Higher dielectric constant alone is insufficient for the purpose of practical MOSFET applications. The following is a discussion of requirements for alternative high-k materials.

First of all, it is important that the alternative gate dielectric is thermodynamically stable with silicon during deposition and/or subsequent high-temperature processing, since interface reactions are very likely to reduce the overall capacitance of the gate stack. Hubbard et al. have systematically investigated the thermodynamic stabilities of binary oxides with silicon. According to their study, most metal oxides are excluded from consideration. Among remaining oxides, Al₂O₃, Y₂O₃, Re₂O₃ (Re – rare earth), ZrO₂, and HfO₂ have been selected for intensive research study for the past few years. Metal silicates, such as Hf, Zr, and Y, have also attracted extensive attention due to their thermodynamic stability with Si.

Second, a band gap of > 5 eV with a conduction band offset (barrier height) > 1.0 eV is necessary to limit Fowler-Nordheim (FN) and direct tunneling for the achievement of low leakage currents. Both FN and direct tunneling depend exponentially on band offsets and film thickness. Higher dielectric constant is not necessarily sufficient in reducing tunneling current because of the general trend that barrier heights decrease with increasing dielectric constants. Robertson has conducted theoretical calculations of the barrier heights for high-k candidates under investigation, as shown in Figure 1.2. The figure shows that all the metal oxides selected according to thermodynamic calculations meet the barrier height requirement.
Third, high-k gate dielectrics are expected to be amorphous. Amorphous materials are covalently bonded and exhibit considerable flexibility in their structure. Therefore, they may provide low leakage current and low defect density interface as far as they are thermo-dynamically stable in contact with silicon. High temperature anneals of an amorphous film can cause it to be polycrystalline, leading to higher leakage currents. The issues related to the morphology will be discussed in section 1.4.3.

Single crystalline binary and ternary metal oxides that have little lattice mismatch with silicon including CeO$_2$, Y$_2$O$_3$, Gd$_2$O$_3$, Pr$_2$O$_3$, SrTiO$_3$, and BaTiO$_3$ have been investigated as gate dielectrics.\textsuperscript{14-20} Several important issues need addressing, including (1) control of the amorphous interfacial layer growth; (2) growth of a single-phase film on a certain type of the substrate; (3) presence of metal-silicide like bonding in the first few atomic layers\textsuperscript{18,19}; (4) compatibility of molecular beam epitaxy, the main method used for crystalline film growth, with standard CMOS process due to its low throughput; (5) large flatband shifts and/or hysteresis for MOS devices, a common problem for amorphous films that will be discussed in section 1.4.2. The prospective of single crystalline oxides directly on Si remains unclear.

Finally, the high-k dielectric should be an excellent diffusion barrier to prevent dopants in the poly gate from contaminating the transistor channel.

1.3 PROPERTIES OF YTTRIUM OXIDE AND YTTRIUM SILICATE

The dielectric constant of yttrium oxide (15-20) is lower than those of hafnium oxide (20-40) and zirconium oxide (20-30). However, as mentioned in the previous section, the conduction band offset is critical in reducing tunneling current. Yttrium
oxide has a higher conduction band (~2.3 eV) than hafnium oxide (1.5 eV) and zirconium oxide (1.4 eV), as evident in Figure 2.\textsuperscript{13}

Yttrium silicate has a lower dielectric constant than yttrium oxide. However, it readily remains amorphous while yttrium oxide (and most of other metal oxides) crystallizes after modest-temperature anneal (425°C for 1 h).\textsuperscript{21} Issues related to film morphology are discussed in section 1.4.3. Another advantage of yttrium silicate compared to hafnium silicate and zirconium silicate is its thermal stability. This is discussed in section 1.4.4.

1.4 SELECTED CURRENT ISSUES OF HIGH-K DIELECTRICS

Although tremendous progress has been made in both experimental and theoretical high-k studies for MOSFETs applications for the past five years,\textsuperscript{22} various fundamental issues need to be solved. Major issues include dielectric/Si interface stability, interface quality, film morphology, thermal stability, gate electrode compatibility (ploy gates and metal gates), etching of high-k materials, process compatibility, and reliability. Our work has addressed issues related to dielectric /Si interface stability, interface quality, and film morphology.

1.4.1 Dielectric/Si Interface Stability

This issue is the main focus of this dissertation. Interface reactions between metal oxide and the silicon substrate result in formation of interfacial layers in the form of metal silicate or/and SiO\textsubscript{2}, whose dielectric constant is usually lower than that for the metal oxide. Since the interfacial layer is in series with high-k dielectric, the overall
capacitance of the gate stack is reduced. Although metal oxides, such as Al₂O₃, Y₂O₃, La₂O₃, ZrO₂, and HfO₂, are supposed to be thermodynamically stable with Si, formation of interfacial layers has been observed during deposition or post-deposition anneals of all these metal oxides. To the authors’ best knowledge, there have been only 3 papers reporting interfacial-layer-free metal oxide deposition on silicon.²³⁻²⁵ On the other hand, metal silicates without SiO₂-interfacial layers have been reported.⁷⁻⁸ Detailed discussion of possible mechanisms leading to interfacial-layer-free structure of metal oxides is presented in Chapter 2.

1.4.2 Dielectric/Si Interface Quality

SiO₂/Si interface quality is excellent in that it has extremely low interface states density (~10¹⁰ states/cm²⋅eV). In comparison, most high-k’s show large interface states density (~10¹² states/cm²⋅eV or higher). Another problem is that most high-k’s show positive or negative flatband shifts which are presumably caused by fixed charges. Large interface state and fixed charge densities can cause severe degradation of channel mobility and reduction of drive current.

1.4.3 Film Morphology

A major concern about amorphous high-k materials is whether they could be compatible with subsequent processes and remain amorphous. The transformation from the amorphous state to polycrystalline state may lead to a dramatic increase of leakage current since grain boundaries inside polycrystalline materials can act as pathways for charge transport leading to high leakage and for fast diffusion of atoms (such as O and H). Crystallization may also increase the interface roughness. However, most metal
oxides crystallize at relative low temperature (<900°C) with Al₂O₃ being a notable exception. For this matter and others, metal silicates have attracted a lot of attention since they tend to remain amorphous during high-temperature processes if no phase separation occurs. Thermal stability of metal silicates is discussed below.

1.4.4 Thermal Stability of Metal Silicates

Group IV (Hf and Zr) and group III (Al, Y, and La) metal silicates have been investigated. Zr and Hf silicates with low Zr and Hf concentrations have demonstrated k≈11 and an amorphous microstructure after annealing at 1050°C for 20 seconds. However, phase separation phenomena have been observed when Zr silicate with a composition of 50% ZrO₂ and 50% SiO₂ undergoes 900°C rapid thermal anneal treatments in argon. On the other hand, yttrium silicate with a composition of up to 72% Y₂O₃ has been formed on Si(100) with no SiO₂ interfacial layer by oxidizing yttrium metal or silicide at 900°C, indicating its good thermostability. Methods to impede phase separation are under study. For instance, it has been reported that incorporation of N stabilizes Hf silicate up to 1100°C with a Hf:Si ratio (16:20).

1.4.5 Gate Electrode Compatibility

There are many issues associated with gate electrode when a high-k gate dielectric is employed. Important issues include poly-Si/dielectric interface stability, dopant diffusion, employment of one mid-gap metal or two metal gates for PMOS and NMOS, metal gate/dielectrics stability, and thermal stability of metal gates.

Due to the reluctance to use new materials in industry, compatibility of poly-Si with high-k’s is of great interest. It has been shown that ZrO₂ reacts with poly-Si to form
metallic silicide. Another group has confirmed that ZrO₂ is not stable against formation upon high-temperature anneals (1025°C), while no reaction is observed between poly-Si gate and HfO₂. The reaction of poly-Si and Y₂O₃ during anneals will be briefly discussed in Chapter 7. Similar to SiO₂ case, the dopant diffusion through high-k dielectric is a major concern. Park et al. have shown that boron can diffuse through Al₂O₃ (50-80 Å) to the channel causing flatband shift (~1.54 V). Boron diffusion in HfO₂ has also been observed. This reference also reports that nitrogen incorporation in the top layer of HfO₂ helps block boron and oxygen diffusion and improve thermal stability.

Use of metal gates to replace poly-Si has also been extensively investigated. The advantages of metal gates are elimination of poly depletion effects and sheet resistance constraints. The disadvantage is that the requirement of two different metals for NMOS and PMOS may complicate the process. Metal electrodes such as TaN, TaSiₓNᵧ, Ru-Ta alloy, and RuO₂ have been under study.

1.5 OBJECTIVE OF THIS WORK

Our primary objective is to investigate the interface reactions during deposition and post-deposition anneal of yttrium oxide (and yttrium silicate), to expand the understanding of high-k interface reactions in general. Also, we explore the possibility of developing Yttrium oxide and silicate as a replacement to SiO₂. The first goal, therefore, was to develop a chemical vapor deposition (CVD) process for yttrium oxide. The second goal was to investigate the interface properties as well as the bulk properties of deposited Y₂O₃ films before and after anneal and the effects of substrate surface
The third goal was to understand and control interface reactions between $Y_2O_3$ and silicon substrate. We hope that study of $Y_2O_3$/Si interface reactions can help us understand CVD processes of other metal oxides such as HfO$_2$, ZrO$_2$, Al$_2$O$_3$, and La$_2$O$_3$. The fourth goal was to study the electrical performance of $Y_2O_3$ and yttrium silicate to further understand the interface and bulk properties. The fifth goal was to study the nitridation of $Y_2O_3$. Areas of interest include interface structures, thermal stability, chemical structure and electrical properties of nitride $Y_2O_3$.

1.6 OVERVIEW OF DISSERTATION

This dissertation has been focused on understanding interface reaction mechanisms during processing of chemical vapor deposited yttrium-based high-k dielectrics for MOSFET gate dielectric applications. $Y_2O_3$ and yttrium silicate have been formed using oxygen plasma assisted CVD on Si(100). During deposition and post-deposition anneals a thin Y-O-Si (silicate)/SiO$_2$ structure forms due to intermixing of Y, O and Si and substrate oxidation. The extent of the intermixing depends on substrate surface preparation, process conditions, and annealing conditions. Employment of in-situ deposited Si capping layers enables better control of interface reactions and study of interface reaction mechanisms.

Chapter 2 describes the kinetics of reactions that result in substrate consumption during formation of ultra-thin transition metal oxides on silicon. Interface reactions that occur during deposition and during post-deposition treatment are compared for PVD and CVD yttrium oxides and CVD aluminum-oxide systems. Silicon diffusion, metal-silicon
bond formation, and reactions involving hydroxides are proposed as critical processes in interface layer formation.

Chapter 3 discusses the effect of atmospheric exposure on ultra-thin yttrium oxide. Significant absorption of water vapor during atmospheric exposure has been observed. After OH absorption, a thermally activated interface reaction proceeds during anneal, consistent with substrate reaction with OH present in the film. The OH absorption rate is reduced for annealed films or films with *in-situ* Si capping layers.

Chapter 4 presents the analysis of the silicon/dielectric interface structure for thin Y₂O₃ and Y silicate films deposited on clean and pre-nitrided Si(100) using high resolution transmission electron microscopy, electron energy loss spectroscopy, and X-ray photoelectron spectroscopy (XPS). The analysis shows the films to be Y₂O₃ on top and Y-silicate/SiO₂ at the dielectric/Si interface. Pre-nitridation of the silicon surface impedes the reaction between the depositing film and the substrate, promoting a Si-free Y₂O₃ structure.

Chapter 5 we demonstrate using XPS and etching experiments, that interface reactions between chemical vapor deposited yttrium oxide and silicon results in significant macroscopic consumption of the silicon substrate during post-deposition anneal. The extent of silicon consumption increases as the thickness of the deposited dielectric increases, consistent with reaction-rate limited oxidation. The possible mechanisms are discussed.

Chapter 6 presents results of thin Y₂O₃ films deposited using two yttrium diketonate precursors. Unacceptable large hysteresis in C-V data, presumably due to the incorporation of fluorine, is observed for the films from the F-contained precursor. For
films deposited with the hydrogenated precursor and exposed to air after deposition, both interface and bulk properties have been investigated by various techniques. Pre-nitridation of the silicon surface impedes the reaction with the substrate, promoting the Y$_2$O$_3$ structure. A substantial consumption of silicon substrate is directly demonstrated by a carefully designed etching experiment. Several possible mechanisms consistent with the observed results, including Si diffusion, crystallization of Y$_2$O$_3$, and reaction with absorbed OH, are discussed.

In Chapter 7, we investigate effects of \textit{in-situ} capping layers on interfacial reactions of CVD Y$_2$O$_3$ during post-deposition annealing. We find that \textit{in-situ} capping layers significantly reduce the formation of SiO$_2$ at the interface with the substrate, but silicates form at the substrate and the capping layer interfaces. Similar to films without \textit{in-situ} capping layers, pre-deposition nitridation of the Si surface can impede the reaction at the substrate interface, resulting in formation of Y$_2$O$_3$ in the film.

Chapter 8 describes the study of nitridation of chemical vapor deposited yttrium oxide using N$_2$ plasma during deposition and post-deposition treatments. Interface structures, chemical bonding, concentration, and distribution of N in Y$_2$O$_3$ films after deposition and after high-temperature anneal were analyzed. C-N is found to be the main type of nitrogen bonding in the as-deposited films, and exchange of N with O to form C-O bonds occurs during prolonged exposure to the air. Methods to increase N incorporation are also investigated.

Chapter 9 investigates the interface structures of Al$_2$O$_3$ films deposited by low temperature ($<400^\circ$C) chemical vapor deposition on Si(100) using narrow nuclear reaction resonance profiling, XPS, TEM, and AES. The results of the interface
structures on thin films are consistent with a thin aluminum silicate layer between the silicon and Al₂O₃ layer. The silicate layer is speculated to result from reactions between silicon and hydroxyl groups incorporated in the Al₂O₃ during low temperature deposition.
1.7 REFERENCES

1. Y. Taur, D. A. Buchanan, W. Chen, D. J. Frank, K. E. Ismail, S. H. Lo, G. A.

2. Y. Taur and T. H. Ning, Fundamentals of Modern VLSI Devices (Cambridge

3. S. I. Association, The International Technology Roadmap for Semiconductors,
2001 edition (Austin, TX, 2001).

209 (1997).


Figure 1.1  Experimental (dots) and simulated (solid lines) tunneling currents as a function of gate voltage in ultra-thin SiO₂ poly-silicon-gate MOS devices. The dashed line shows a tunneling current level of 1 A/cm². Taken from reference 4.
Figure 1.2  Calculated Band Offsets for Various Oxides on Si.

Taken from reference 13.
CHAPTER 2

ELEMENTARY REACTION SCHEMES FOR PHYSICAL AND CHEMICAL VAPOR DEPOSITION OF TRANSITION METAL OXIDES ON SILICON FOR HIGH-K GATE DIELECTRIC APPLICATIONS


Department of Chemical Engineering, North Carolina State University, Raleigh, NC 27695

† Texas Instruments, Dallas TX 75243

# Department of Chemical Engineering, University of Alabama Tuscaloosa, Tuscaloosa AL

ABSTRACT

This article describes the kinetics of reactions that result in substrate consumption during formation of ultra-thin transition metal oxides on silicon. Yttrium silicate films (~40 Å) with an equivalent silicon dioxide thickness of ~11 Å are demonstrated by physical vapor deposition (PVD) routes. Interface reactions that occur during deposition and during
post-deposition treatment are observed and compared for PVD and chemical vapor deposition (CVD) yttrium oxides and CVD aluminum-oxide systems. Silicon diffusion, metal-silicon bond formation, and reactions involving hydroxides are proposed as critical processes in interface layer formation. For PVD of yttrium silicate, oxidation is thermally activated with an effective barrier of 0.3 eV, consistent with the oxidation of silicide being the rate-limited step. For CVD aluminum oxide, interface oxidation is consistent with a process limited by silicon diffusion into the deposited oxide layer.
2.1 INTRODUCTION

The semiconductor industry improves performance by decreasing the gate length with each metal oxide semiconductor (MOS) device generation. The silicon dioxide gate dielectric thickness scales with gate length to promote high channel transconductance. The *International Technology Roadmap for Semiconductors* predicts that a 50 nm device generation will require the equivalent of a sub-1.0 nm silicon dioxide.¹ A variety of metal oxides, including Y₂O₃, Ta₂O₅, TiO₂, HfO₂, ZrO₂ and Al₂O₃, have been suggested as high-k (k₉₉ > k₉₉,SiO₂ = 3.9) replacements for silicon dioxide.²⁻⁵ Thermodynamic calculations have been used to evaluate the stability, with respect to no silicide or SiO₂ formation, of binary metal oxides in contact with silicon. ZrO₂, HfO₂, Al₂O₃, Y₂O₃, La₂O₃, and other rare earth oxides are the most promising binary metal oxides from using this thermodynamic analysis.⁶ However, pure metal oxides tend to crystallize at relatively low temperatures resulting in possible high conductivity pathways along grain boundaries counteracting the benefits of the high-k dielectric.

Zirconium silicate and hafnium silicate have been demonstrated as potential high-k gate dielectrics with k~11 and an amorphous microstructure after annealing at 1050°C for 20 seconds.⁵ Yttrium silicate also possesses desirable thermodynamic, dielectric and structural properties that make it attractive as a high-k candidate. The Y-O bond is quite strong, since the free energy of formation per oxygen atom (-ΔG_r) (at 25°C) is 2.40×10⁻²² kcal for Y₂O₃ compared to 1.70×10⁻²² kcal for SiO₂.⁷ Previous studies have demonstrated the formation of yttrium silicate by the oxidation of yttrium on silicon in dry air at 500-700°C.² Yttrium silicate films with the composition Y₂.₄₅Si₀.₅₅O₅ approximately 26.0 nm thick were created using this process. Capacitance measurements on MOS capacitors
with an Al/Y_{2.45}Si_{0.55}O_{5}/Si structure yielded $k \sim 12$ for the silicate layer, which should be suitably large to obtain equivalent oxide thickness (EOT) $< 1.0$ nm with low tunneling. These films also exhibited acceptable current-voltage and breakdown characteristics.

Scaling the gate insulator into the sub-1.0 nm regime requires a material with suitably high-$k$ that remains amorphous during typical annealing cycles, and is stable with respect to reaction with the substrate semiconductor. For many cases, the stability of the deposited material with the substrate limits performance and dielectric scaling. This paper will focus on recent results that highlight details of potential interface reaction mechanisms, and direct measurements of interface reaction product and reaction rates. This work focuses on oxides of the Group III metals (Al and Y) to better understand the viability of Group III metal oxides, and to understand fundamental properties common to Group III and Group IV oxide deposition.

### 2.2 MATERIAL PREPARATION AND ANALYSIS

Yttrium silicate thin films (Y-O-Si) were formed on silicon and pretreated silicon by depositing thin layers of yttrium, then oxidizing in N_{2}O at 900°C. Some deposited Y films were annealed in vacuum to form Y-silicide before oxidation. Silicon surface pretreatments studied included *in-situ* oxidation and *in-situ* nitridation. Aluminum oxide films were deposited on clean silicon by chemical vapor deposition (CVD) using metal-organic precursors. Details of the material preparation processes are described in previous articles.\(^{8-10}\) Yttrium oxide was also deposited by plasma assisted CVD using yttrium diketonate precursors.
X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), and transmission electron microscopy (TEM) were used to identify the bulk chemical structure of the films. TEM, XPS, angle resolved XPS, medium energy ion scattering (MEIS), and resonant nuclear reaction profiling (RNRP) were also used to characterize interface structure. Current vs. voltage (I-V) and capacitance vs. voltage (C-V) testing was used to determine the electrical quality of the dielectrics. Electrical thickness is described as an EOT determined from a fit of the C-V curve that includes the quantum mechanical effect. TEM and atomic force microscopy (AFM) were used to identify film morphology. For the physical vapor deposition (PVD) yttrium deposition process, films with EOT ≥ 1.1 nm are demonstrated with leakage less than 1 A/cm² at 1 V above flat band, indicating that these materials are interesting candidates for high dielectric constant insulators.

2.3 RESULTS

2.3.1 PVD Yttrium Silicate

Yttrium silicate films with ~40 Å physical thickness were formed by oxidizing ~8 Å of Y on silicon for 15 seconds in N₂O at 900°C. Electrical characterization of these materials showed low EOT (~10 Å) with dielectric constant of ~14 (based on thickness determined from TEM). Using aluminum gates, the flat band voltages (V_{fb}) were measured to be −0.74 and −1.63 V for n- and p-type substrates, respectively, indicating positive fixed charge in the dielectric. The current density for the 10-12 Å EOT was less than 1 A/cm² in accumulation at 1 V greater than V_{fb}. 
To better understand the process involved with dielectric formation, XPS analysis in the Si 2p region of various thicknesses of yttrium layers on silicon after various process steps is shown in Figure 2.1. Spectrum (i) from a thick (1000 Å) Y film deposited on silicon and annealed for several minutes at 600°C in vacuum (~10⁻⁸ Torr), and the Si 2p peak at 98.5 eV is consistent with a yttrium silicide bonding structure. Spectrum (ii) corresponds to a thick silicide film [same as in spectrum (i)] that has been oxidized in N₂O for several minutes at 900°C. The single peak at 102.2 eV is consistent with silicon bound to oxygen in a metal “silicate” (102-103 eV).¹² The term “silicate” is used here to describe an amorphous material with Y-O-Si local bonding, similar to that found in a true crystalline silicate. Spectra (iii) and (iv) correspond to much thinner initial Y depositions and much thinner oxidized layers, consistent with the intensity of the substrate Si-Si bond at ~99.3 eV. Spectrum (iii) is for a film that underwent vacuum annealing (forming a silicide) then oxidation (forming the silicate). The Si-O peak position is shifted to slightly higher binding energy compared to the thicker film in spectrum (ii), corresponding to a higher concentration of silicon in this sample. Spectrum (iv) is for a Y metal film that was subjected to only a 900°C oxidation step. This oxidation step was the same as imposed on the metal silicide sample corresponding to spectrum (iii). The Si 2p spectra (iii) and (iv) show nearly indistinguishable peak position and peak shape, and with the Y 3d and O 1s spectra (not shown), indicate the metal deposition and oxidation process results in a thin Y-O-Si yttrium silicate dielectric on silicon. The similarity between the vacuum annealed/oxidized film (spectrum iii) and the film that was only oxidized (spectrum iv) suggests that the silicide reaction proceeds
much more quickly than the oxidation step. This will be discussed below in more detail in context with other deposition results.

To characterize the kinetics of silicide oxidation, the effect of oxidation time on dielectric thickness and structure was characterized using TEM. Figure 2.2 shows TEM images of yttrium silicate formed with \( \sim 8 \) Å of yttrium and oxidation at 900°C in air for times from 6 seconds to 20 min. Figure 2.2(a), 2.2(b), and 2.2(c) show films oxidized for 6, 15 and 60 seconds that were capped with 2000 Å of Al after oxidation with no post-metallization anneal. The physical thickness of the films determined using the Si-Si bond length as a reference is 30, 42 and 42 Å respectively. In all instances, lattice fringes are observed in the silicon substrate, but not in the Y-O-Si film indicating amorphous Y-O-Si structure. The interface for the 6 seconds oxidation appears slightly roughened, perhaps due to the presence of silicide, but the interface is smooth for oxidation at 15 and 60 seconds. The images in Figure 2.2(a), 2.2(b), and 2.2(c) all indicate the presence of one layer without any SiO\(_2\) at the Y-O-Si/Si interface. Figure 2.2(d) shows a TEM image of a film oxidized for 20 min. This film was not capped with Al after oxidation, and the top layer is epoxy. The thickness is 75 Å and the contrast in the image suggests that for long oxidation times SiO\(_2\) grows beneath the Y-O-Si layer. This data is consistent with a rapid reaction between the metal and silicon followed by oxidation of the metal-silicide. The TEM results in Figure 2.2 are consistent with an under-oxidized silicide in Figure 2.2(a) and a more fully oxidized silicide (i.e. “silicate”) in 2.2(b) and 2.2(c). For extended oxidation times, the TEM results in Figure 2.2(d) are consistent with slower oxidation of the substrate silicon after formation of the silicate top layer. It is important to note that
the combined silicide formation and silicide oxidation reactions are observed to proceed more rapidly that oxidation of a control silicon surface.  

The effect of yttrium oxidation temperature for a fixed oxidation time was also characterized. Figure 2.3 shows: (a) the O 1s; (b) Y 3d; and (c) Si 2p regions of the photoelectron spectrum for Y-O-Si films formed by the oxidation of thin (25 Å) yttrium films on silicon in 1 atm. N₂O at temperatures between 500 and 900°C. The figure also shows the spectra for a 25 Å yttrium film on silicon exposed in ambient conditions (25°C, 1 atm. air) for ~1 day. Consistent with silicate bonding, the Y 3d peaks [Fig. 2.3b] for films oxidized at 25-900°C are all shifted to higher binding energy than expected for Y 3d₃/₂ and Y 3d₅/₂ (158.8 and 156.8 eV, respectively) in Y₂O₃. The Y 3d₅/₂ peaks shift from 158.0 eV for oxidation at 25°C to 159.3 eV for oxidation at 900°C. The Y 3d spectrum for the film oxidized at 25°C exhibits a shoulder near ~156.0 eV consistent with yttrium metal (156.0 eV) or Y₂O₃ (156.8 eV), but the spectrum does not indicate the presence of any yttrium silicide (155.8 eV). The Y 3d spectra for the Y-O-Si films oxidized at 500-700°C do not exhibit evidence for Y₂O₃, yttrium metal or yttrium silicide. The Y 3d satellite and Si 2s photoelectrons cause the small peaks at ~153 and ~151 eV. The low binding energy peak in the Si 2p spectra [Fig. 2.3c] is due to the silicon substrate and the higher binding energy peaks are assigned to metal silicate. The Si-O mode shifts from 101.8 eV for oxidation at 25°C to 103.1 eV for oxidation at 900°C. The Si-O mode also increases in intensity when the oxidation temperature is increased, and the Si-O mode for oxidation at 900°C is ~3 times the integrated area of the Si-O mode for the film oxidized at 25°C. The intensity of the silicon substrate peak is largest for oxidation at 25°C. Increasing the oxidation temperature results in an
increasingly attenuated silicon substrate peak consistent with an increase in overlayer thickness. The O 1s peak positions for oxidation from 25-900°C are measured at ~532 eV. The O 1s peaks are broad peaks resulting from a combination of oxygen bonding to yttrium and to silicon. As a result, the full-width-half-maximum (FWHM) for all the O 1s peaks is ~3.0 eV, which is considerably wider than for a binary oxide (i.e. measured FWHM for SiO₂ is 1.8 eV). The FWHM generally decreases when the oxidation is performed at higher temperature, and the measured FWHM is 3.0 and 2.6 eV for oxidation at 25 and 900°C, respectively. The spectrum for the Y-O-Si film oxidized at 25°C exhibits a shoulder at ~530.5 eV, which is consistent with an increase in O-Y-O bonding.

The MEIS proton energy spectra for Y-O-Si films oxidized at 600 and 900°C were also analyzed. Consistent with the XPS results of Figs. 2.3, the MEIS spectra (not shown) exhibit peaks for yttrium (~94 keV), silicon (~86.5 keV) and oxygen (~79.5 keV). The MEIS detects near surface silicon (i.e. silicon in the dielectric film) as a high energy (~87 keV) shoulder on the larger silicon substrate background. For the film annealed at 600°C this shoulder is much smaller than for the film oxidized at 900°C. The composition calculated from the MEIS spectrum of the film oxidized at 600°C is \((\text{Y}_2\text{O}_3)_{0.60}\cdot(\text{SiO}_2)_{0.40}\), which represents a greater metal fraction than the most metal-rich yttrium silicate, \(\text{Y}_2\text{SiO}_5\). The absence of phase separated \(\text{Y}_2\text{O}_3\) in the Y 3d XPS spectrum (Fig. 2.3a) may be due to instrument sensitivity, or dispersal of the \(\text{Y}_2\text{O}_3\) clusters within the silicate bulk. The composition calculated from the MEIS spectrum of the film oxidized at 900°C is \((\text{Y}_2\text{O}_3)_{0.45}\cdot(\text{SiO}_2)_{0.55}\), which is consistent with \(\text{Y}_2\text{SiO}_5\) \((x = 0.50)\) considering the experimental error of \(x \pm 0.04\).
The results from the XPS analysis (Fig. 2.3) and the MEIS data are shown in an Arrhenius plot in Fig. 2.4, which shows the extent of silicon oxidation vs. the inverse of the anneal temperature. From the XPS data, the ratio of the Si 2p Si-O and Si 2p substrate integrated peak areas approximates the relative amounts of silicon in the Y-O-Si, and these data points are plotted (as circles) in Figure 2.4. The integrated area of the Si 2p Si-O is a measure of the total amount of silicon in the Y-O-Si film, and the integrated area of the Si 2p substrate peak is a measure of total film thickness, which also takes into account the attenuation of the Si 2p Si-O mode with increasing film thickness. A more detailed analysis of the XPS data would need to confirm that the Si-O mode intensity was independent of thickness for a set of silicate films with uniform composition. However, the MEIS data can be used to confirm the trend observed in the current XPS data. The silicon content in the film is obtained from the MEIS data by multiplying the silicon fraction times the film thickness, and the points are included (as the triangles) in Figure 2.4. The slope gives an activation energies (E_a) for the consumption of silicon during the oxidation of yttrium to be $E_a \approx 0.3$ eV. The $E_a = 0.3$ eV for oxidation of Y/Si is consistent with the activation energy for Gd/Si, Tb/Si and Er/Si oxidation reaction (0.37, 0.35 and 0.5 eV, respectively). Interface reaction schemes consistent with the XPS, MEIS, TEM, and electrical data are presented in the discussion section below.

2.3.2 CVD Aluminum Oxide

Interface reactions during CVD of aluminum oxide were also characterized. For these experiments, thin (~50 Å) Al₂O₃ was deposited on clean hydrogen terminated
silicon from metal organic precursors using a process detailed previously. Figure 2.5 shows results of narrow resonant nuclear reaction profiling for two different Al₂O₃/Si samples. The depth distribution of ²⁷Al concentration was obtained using the narrow and isolated resonance in the cross sections of the nuclear reaction ²⁷Al(p, γ)²⁸Si at 405 keV, and a tilted sample geometry was used to obtain a depth resolution of about 0.5 nm near the film surface. Concentration profiles were obtained assuming a density of 3.8 g/cm³ for the stoichiometric Al₂O₃ film. The two films were similar physical thickness, but were grown using different reactor preparation conditions. Also, sample (a) was exposed to the ambient atmosphere for several weeks before characterization, whereas sample (b) was exposed for a shorter time. Sample (a) shows clear evidence for a mixed Al₂O₃/SiO₂ interface layer, whereas sample (b) shows an abrupt Al₂O₃/Si interface. It is important to note that Al₂O₃ differs significantly from the other metal oxides currently studied for high-k applications, in part because aluminum metal, unlike Zr, Hf, La, and Y, does not readily mix with silicon to form a silicide. This means that any reaction pathway that involves silicide intermediates (such as the process for PVD Y-silicate described above) will not be active during deposition.

After deposition, the interface between an Al₂O₃ film (~50 Å) and silicon was characterized using XPS as a function of anneal temperature for a fixed time (30 s). The effects of annealing on the Si 2p spectra are shown in Figure 2.6. The response of the Al₂O₃/Si interface to rapid thermal annealing in argon (with residual oxygen) is qualitatively similar to the yttrium silicate/silicon interface annealed in 1 atm. O₂ shown in Figure 2.3 above. The lower oxygen partial pressure for the aluminum oxide interface oxidation suggests that the active source of oxygen may be excess oxygen
present in the Al₂O₃ film, possibly bound as hydride. The Si-O feature at the interface in Figure 2.6 is observed to increase with anneal temperature, and the position of the Si-O is at a lower binding energy than expected for SiO₂, indicating that mixing has occurred between the deposited Al and the Si substrate. As described above for the data in Fig. 2.3, the extent of substrate oxidation can be estimated from the ratio of the Si-O peak area to the Si-Si peak area. The ratio values increase with temperature, consistent with a thermally activated process, but the data is not sufficient to extract a well-defined activation energy for the process.

2.3.3 CVD of Y₂O₃

Yttrium oxide layers have recently been deposited in our lab using oxygen plasma assisted CVD with yttrium diketonate precursors. For these depositions, argon carrier gas flows through a heated tube containing solid precursor, and the precursor flows into the reactor just above the substrate, below a source of plasma excited oxygen. Films were deposited on clean Si(100), and Si(100) surfaces pre-exposed in-situ to plasma excited O₂ or N₂ to produce oxide or nitrided-silicon interface layers. For deposition temperature of 400°C with typical gas flow and pressure conditions, the deposition rate is ~15-20 Å/min.

X-ray photoelectron spectra of three films deposited for 3, 6.5, and 30 minutes on clean Si(100) are shown in Figure 2.7. The thickest film shows features consistent with Y₂O₃ structure in the Y 3d spectra, consistent with a thick Y₂O₃ film. The spectra for the film deposited for 3 minutes show significant shifts in Y 3d binding energy, consistent with an oxide structure that contains significant Y-O-Si (Y-silicate) bonding.
The position of the Si 2p Si-O feature is also consistent with the thinnest films consisting of significant yttrium silicate bonding structure (spectra not shown here).

Figure 2.8 shows C-V curves for thin “yttrium oxide” films deposited on clean and pretreated Si(100). The gate metal was evaporated aluminum. The film on clean silicon was deposited under the same conditions as that shown in Figure 2.7 for the 3-minute deposition time, consistent with the films having significant yttrium silicate bonding structure. All films were annealed at 900°C for 1 minute and received a post-metallization anneal in N₂/H₂ at 400°C. Fitting the C-V data for the film on clean silicon results in EOT of ~29 Å. The flatband position of this film is shifted in the negative direction, consistent with positive fixed charge in the dielectric. Some hysteresis (~20 mV) in the C-V is also observed for this film. C-V curves for films deposited under the same conditions on in-situ pretreated silicon are also shown. For these examples, the nitridation processes do not change the net oxide thickness significantly, and the net EOT is ~30 Å. Even for these relatively thick pretreatment layers, XPS spectra (not shown) for the films on pretreated silicon show evidence for some silicon content in the deposited film, indicating that the pretreatment layers (oxynitride) and the silicon substrate mix with the deposited yttrium oxide, both during deposition and post-deposition annealing.

2.4 PROPOSED ELEMENTARY REACTION SCHEMES

The data presented above shows that a clear understanding of reactions that occur at high-k dielectric interfaces, both during deposition and during post-deposition annealing, is critically important to control electronic properties of the gate stack.
Various sets of elementary interface reactions can be proposed that are consistent with the results shown above. Comparing results from CVD and PVD experiments, and the effects of surface pretreatments, can further help define likely interface reaction schemes. The ultimate goal of this effort will be to understand, control, and minimize, or ideally avoid, interface reaction processes that lead to undesired gate stack capacitance, dielectric charges, interface trap states, etc. that degrade electronic device performance.

For the case of thermal oxidation of PVD yttrium on silicon, a reaction scheme of elementary reactions for formation of yttrium silicate can be written as follows:

\[
\begin{align*}
\text{Y} + \text{Si} & \rightarrow \text{YSi}_x & (1) \\
\text{YSi}_x + \text{O}_2 & \rightarrow \text{YSi(O)}_i + \text{O} & (2) \\
\text{YSi(O)}_i & \rightarrow \text{YSi(O)}_i^† & (3) \\
\text{YSi(O)}_i & \rightarrow \text{Y-O-Si} \quad (\text{SiO}_2: \text{Y}_2\text{O}_3) & (4)
\end{align*}
\]

Reaction (1) is the formation of yttrium silicide, which occurs through diffusion of silicon from the substrate into the yttrium metal layer.\textsuperscript{16,17} The silicon diffusion happens quickly upon annealing PVD yttrium deposited on silicon, even at moderate temperatures. Rutherford backscattering analysis of metal silicide systems has shown that silicon is the dominating diffusion species in \text{YSi}_x, and the yttrium atoms remain relatively immobile even after 1 h anneal at 1000°C.\textsuperscript{16} Step (2) is oxygen dissociation, and step (3) is oxygen diffusion through the film bulk. The above scenario assumes that oxygen diffuses as atomic oxygen, but diffusion of molecular oxygen and water as oxidizing species, as well as silicon diffusion, must also be considered in a full detailed kinetic analysis. Step (4) is oxidation of the silicide, which is presumed here to occur
upon insertion of O atoms into a Y-Si bond. Repeating this reaction leads eventually to the yttrium silicate structure. Thermodynamics indicates that the favored product in the reaction between Y, Si, and O₂ should be Y₂O₃ and Si. However, processing conditions in thin film formation are generally far from equilibrium, and kinetic intermediates (such as the proposed yttrium silicide in this case) can form and further react (in this case forming silicate) resulting in products “unexpected” from bulk thermodynamics that can dominate the resulting film. The measured activation energy of 0.3 eV shown in Figure 2.4 is a net reaction barrier (including for example forward and reverse reactions) so that it cannot precisely be ascribed to any elementary reaction in this process. However, since the silicide formation and oxygen diffusion can be presumed to occur relatively rapidly, the measured reaction barrier likely involves the silicide oxidation step, reaction (4). This barrier is small compared to the barrier of ~3.0 eV measured for reduction of SiO₂ to form transition metal oxides,¹⁸ which implies that this reaction could occur during CVD processes at typical deposition temperatures, providing there are metal-silicon bonds present at or near the deposition surface.

For the case of aluminum oxide CVD, a hypothetical set of reactions governing film deposition from a generic metal-organic precursor (Al(RHₓ)₃) are written as

\[
\text{Al(RH}_x\text{)}_3 + O_2^* + \text{Si} \rightarrow \text{Al}_2\text{O}_3/\text{Si} + [n(RO)] \quad (g) \quad (5)
\]

\[
\text{Al(RH}_x\text{)}_3 + \text{Si} \rightarrow [\text{Al(RH}_x\text{)}_3]_p \cdot \text{Si} \quad (6)
\]

\[
[\text{Al(RH}_x\text{)}_3]_p + O_2^* \rightarrow \text{Al(OH)}_y + [(\text{RH}_{x-1})_3] \quad (g) \quad (7)
\]

\[
\text{Al}_2\text{O}_3 + \text{Si} \rightarrow \text{Al}_2\text{O}_3(\text{Si})_i \quad (8)
\]

\[
\text{Al(OH)}_y + (\text{Si}) \rightarrow \text{SiO}_2: \text{Al}_2\text{O}_3 \quad (9)
\]
Reaction (5) corresponds to the (non-elementary) process of aluminum metal-organic reacting with oxygen to form an abrupt Al₂O₃/Si interface and oxidation of the organic ligand (R). This process likely involves the metal organic adsorbing on the surface in a variety of product states, including molecular physisorption, dissociative physisorption, or dissociative chemisorption. Equation (6) shows molecular physisorption as an example. In equation (7), the physisorbed molecule is oxidized, leading to a hydroxide product on the surface. Equation (8) shows diffusion of silicon into the Al₂O₃. Then, in equation (9), the hydroxide reacts with interstitial silicon (or silicon available at the substrate interface) to form the interfacial silicate. Silicate formation from Si and Al₂O₃ alone is not expected to occur, but the addition of excess oxygen (i.e. hydroxide) enables aluminum silicate formation to be favored energetically.¹⁰ This reaction scheme then can be used to understand the results shown in Figures 2.5-2.6. The fact that the interface reaction proceeds to a greater extent in some samples than in others (i.e. sample (a) vs. sample (b) in Fig. 2.5) could result from a different density of hydroxide present in the two samples. In addition to the hydroxide production route shown in reaction (7), hydroxide will diffuse into the material from exposure to atmospheric water (not shown explicitly in the reaction scheme above), so that different degrees of interface oxidation may be expected from samples with different history. It is also possible that variations in chamber history or surface preparation conditions could result in enhanced interface reactivity.

The temperature dependence of the interface oxidation observed in Figure 2.6 could also result from hydroxide present in the material, and the activation barrier could then be related to the oxidation of the interstitial silicon (reaction 9), or could relate to the
barrier for Si diffusion (reaction 8). Based on the smaller barrier observed for oxidation in the yttrium case, we can conclude that the barrier is more likely related to silicon diffusion into the deposited film.

For yttrium oxide CVD, the set of elementary equations for deposition are analogous to those for aluminum. However, an important distinction between the results presented above for Al₂O₃ and those for Y₂O₃ is that it is possible to make an abrupt Al₂O₃/Si interface by CVD methods. Atomically abrupt interfaces have not been clearly demonstrated to date in other metal oxide/silicon or metal silicate/silicon interfaces of interest for high-k applications. Therefore, it is important to consider what other possible elementary steps could be present in the Y₂O₃ system that lead to the non-abrupt interface. One such reaction that could be considered in addition to those shown above for Al₂O₃ is the formation of metal-silicon bonds during diffusion of silicon into the metal oxide structure:

\[
\text{O-(Y-R}_n\text{) + Si } \rightarrow \text{ O-Si-Y}
\]

\[
\text{O-Y-O + Si } \rightarrow \text{ O-Si-Y}
\]

where the Y-Si could be on the deposition surface, i.e. with the precursor ligands still bonded to the surface as shown in equation 10, or it could be at the interface or near surface region, as shown in equation 11. Equation 11 is likely not favored for Si in contact with a true bulk oxide, but may proceed in a deposition process at the near surface where other species are present and bonded, for example, to the oxygen. The formation of metal-silicon bonds (equations 10 and 11) could occur in the yttrium case (or for Hf, Zr, La, etc.) but is not expected in the case of aluminum because yttrium
readily forms a silicide, whereas aluminum does not. This intermediate product could then oxidize to form a silicate in a process similar to that observed in reaction (4) above. The route to interfacial silicate involving hydroxides [including those resulting from deposition products, reaction (9), and from post-deposition atmospheric exposure] is also expected to be active. This means that there are likely multiple separate kinetic routes to interface silicate formation in these material systems. Data in Figure 2.8 indicates that significant interfacial silicate results during CVD of yttrium oxide on silicon. The observed limited thickness of the silicate in Figure 2.7 suggests that the reaction is limited by diffusion of silicon into the deposited layer. The reaction scheme suggests that the degree of interface reaction could be controlled by changing growth precursor (to change adsorption process and reaction-by products) and by limiting reaction of the deposited film to ambient. The relative importance of these mechanisms in controlling substrate consumption reactions will need more studies to optimize material systems for sub-1 nm gate dielectric layers.

2.5 SUMMARY

Interface reactions that occur between transition metal oxides during deposition and during post-deposition processing have been examined, and elementary process steps consistent with the observed data have been presented. It is proposed that interface reactions for Al$_2$O$_3$ deposition are significantly different than for Hf, Zr, La, and Y-based dielectrics because Al will tend to not form stable silicide structures, whereas the other metals of interest typically do form silicide bonds, which can act as kinetic intermediate to interface layer formation. Mixed metal/silicon/oxygen interface layers can result from
reaction with hydroxides present in as-deposited films or introduced post-deposition from ambient exposure. Further understanding of interface elementary processes, including detailed differences between various precursors in how they adsorb and react, will be important to control interface structure for advanced gate stacks in high performance and low power MOS devices.

2.6 ACKNOWLEDGEMENTS

The authors thank E. Garfunkel and B.W. Busch at Rutgers University for the MEIS results, D. Maher and S. Wang at NC State for TEM, and Israel Baumvol from Instituto de Fisica, Porto Alegre, for RNRA results. Support is from the SRC/SEMATECH Center for Front End Processes and NSF # 0072784.
2.7 REFERENCES


**Figure 2.1** XPS Si 2p spectra for various thicknesses of yttrium layers on Si(100) after various processes.
Figure 2.2a  TEM for four yttrium silicate films formed with ~8 Å initial yttrium on silicon, followed by oxidation at 900°C for 6 s.
Figure 2.2b  TEM for four yttrium silicate films formed with ~8 Å initial yttrium on silicon, followed by oxidation at 900°C for 15 s.
Figure 2.2c  TEM for four yttrium silicate films formed with ~8 Å initial yttrium on silicon, followed by oxidation at 900°C for 1 min.
Figure 2.2d  TEM for four yttrium silicate films formed with ~8 Å initial yttrium on silicon, followed by oxidation at 900°C for 20 min.
Figure 2.3a XPS O 1s spectra for yttrium silicide films oxidized at various temperatures to form Y$_2$O$_3$/SiO$_2$ films.
Figure 2.3b  XPS Y 3d spectra for yttrium silicide films oxidized at various temperatures to form Y$_2$O$_3$/SiO$_2$ films.
Figure 2.3c  XPS Si 2p spectra for yttrium silicide films oxidized at various temperatures to form $Y_2O_3/SiO_2$ films.
Figure 2.4  Si-O/Si integrated area ratio determined from the Si 2p XPS data in Figure 2.3c vs. 1/T. The MEIS Si fraction is also plotted vs. inverse oxidation

$E_a \sim 0.3\text{eV}$
Figure 2.5  Narrow Resonant Nuclear Reaction Profiles for two Al₂O₃ films deposited on Si(100).
Figure 2.6  XPS results for Al₂O₃ films on Si(100) after anneals at various temperatures.
Figure 2.7  XPS results for “Y$_2$O$_3$” films deposited by CVD.
Figure 2.8  CV results for thin films on clean and nitrided surfaces.

CHAPTER 3

WATER ABSORPTION AND INTERFACE REACTIVITY OF YTTRIUM OXIDE GATE DIELECTRICS ON SILICON

D. Niu, R. W. Ashcraft, G. N. Parsons

Department of Chemical Engineering, North Carolina State University, Raleigh, NC

27695

ABSTRACT

High dielectric constant insulators deposited at low temperatures rapidly absorb water during exposure to the atmosphere, and the resulting OH leads to detrimental interface reactions. We report the effect of atmospheric exposure on ultra-thin yttrium oxide, and details of silicon substrate reactions during post-deposition anneals. Infrared absorption analysis indicates significant absorption of water vapor during atmospheric exposure, even for very short times (<15 minutes). X-ray photoelectron spectroscopy demonstrates that after OH absorption, a thermally activated interface reaction proceeds with an activation energy of 0.33 eV, consistent with substrate reaction with OH present in the film. The OH absorption rate is reduced for annealed films or when capping layers
are deposited *in-situ*. Similar oxidation processes are expected to occur in other high-k materials of interest, where the rate of OH absorption will depend on the deposition process and material thermal history.
3.1 INTRODUCTION AND EXPERIMENTAL APPROACH

There are significant on-going efforts to develop alternative high dielectric constant (high-k) gate dielectrics for advanced electronic devices.\textsuperscript{1-4} Among many problems to be overcome with high-k’s, stability and control of the silicon/dielectric interface is one of the most important. Various groups have shown that interface reactions occur during deposition or post-deposition high temperature treatments resulting in silicon substrate consumption, leading to formation of metal silicates, silicides, or SiO\textsubscript{2} at the metal oxide/Si interface.\textsuperscript{5-9} In order to control and/or minimize the interface reactions, the mechanisms causing the substrate consumption must be better understood. In this article, we demonstrate that exposing dielectrics to atmosphere after deposition can lead to significant hydroxide absorption, and that the OH can promote reactions between silicon and gate dielectric. Films that undergo a post deposition anneal tend to show a reduced OH absorption rate, presumably due to dielectric structural densification.

For this study, thin Y\textsubscript{2}O\textsubscript{3} films were deposited in a low-pressure remote plasma enhanced chemical vapor deposition (CVD) reactor using tris(2,2,6,6-tetramethyl-3,5-heptanedionato)yttrium (Y(TMHD)\textsubscript{3}) as the Y precursor introduced downstream from an O\textsubscript{2} plasma.\textsuperscript{10} For some films, an amorphous silicon capping layer was deposited on the dielectric at 250°-500°C, using plasma excited helium and downstream silane, without exposing the film to ambient. Substrates of 0.1-0.3 Ω\cdot cm p-type Si(100) were cleaned with the JTB-100 baker clean solution and dipped in 10:1 buffered-oxide-etch solution before being immediately transferred to the loadlock chamber without final water rinse. During high-k deposition, the substrate temperature was fixed in the range of 350° to
450°C. Thin films (<100 Å) were analyzed using X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), electron energy loss spectroscopy (EELS), as well as current vs. voltage and capacitance vs. voltage measurements. Thicker films (~500 Å) were analyzed using transmission Fourier transform infrared spectroscopy (FTIR).

3.2 RESULTS

Figure 3.1(a) shows the XPS spectra of the Si 2p region for films deposited at 400°C for 3 minutes. The deposited films underwent a one-minute post-deposition thermal anneal treatment at temperatures between 400 and 900°C in N₂ ambient (O₂ background concentration > 10⁻⁵ torr), and XPS data was collected for each annealed sample. The binding energies of 99.3 and 103.3 eV are assigned to Si substrate and Si-O-Si bonding, while the binding energy for Si-O-Y is near 102-103 eV due to the lower electronegativity of yttrium (1.22) compared to that of silicon (1.90).¹¹,¹² The peak positions for the as-deposited and annealed films are consistent with film composition consisting of predominantly Y-O-Si bonds. The material is amorphous (from TEM), with local bonding similar to that found in a crystalline silicate, and hence is referred to as “silicate”. The FWHM values of the Si-O peaks in the XPS spectra near 102-103 eV range from 2.45 to 2.7 eV and are larger than that of pure SiO₂ (1.98 eV), indicating multiple silicon bonding environments in the Y-O-Si films. As annealing temperature increases, the intensity of the Si-O peak is observed to increase, and the feature related to the Si substrate decreases, consistent with oxidation of the silicon substrate near the silicon/dielectric interface. The areas under the Si-O and Si peaks were calculated by
performing a Gaussian fit, and the ratio of Si-O to Si peak area is plotted vs. the inverse of temperature in Figure 3.1(b). A least-squares fit indicates the post-deposition oxidation is a thermally activated process with an activation energy of 0.33 eV. It is interesting to point out that the activation energy is very close to that found for oxidation of Y metal deposited by physical vapor deposition on silicon. TEM and EELS results of a film deposited at 400°C for 3 minutes and annealed at 900°C for 1 minute show a homogeneous, amorphous yttrium silicate layer with thickness of ~65 Å, consistent with the XPS results, and clear evidence of yttrium near the top surface of the film with yttrium concentration decreasing towards the dielectric/Si interface.

Transmission FTIR spectra of thicker films (~500 Å) are shown in Figure 3.2. XPS analysis of thicker films generally showed a composition closer to Y₂O₃ as compared to the silicate structure observed for very thin films. The top group of curves in Figure 3.2(a) is from an as-deposited film with no capping layer, where the spectra were obtained after various exposure times to the ambient. The broad peak at 3100-3600 cm⁻¹ is due to OH bonding, and the films clearly show post-deposition OH absorption, even after only 15 minutes exposure to air. For significant H₂O incorporation, we would expect to see an OH bending mode at ~1600 cm⁻¹, and a feature at 1600 cm⁻¹ is observed in the spectra as a shoulder on the carboxyl (C=O) stretching mode at 1500-1600 cm⁻¹. The bottom curves are spectra for an as-deposited film with an a-Si capping layer deposited at 250°C. The films with capping layers show significantly less OH density, with some absorption observed after 5 days air exposure.

The effect of post-deposition annealing on OH absorption rate is shown in Figure 3.2(b), where the integrated area under the OH peak is plotted versus exposure time for
films annealed post-deposition at 600, 700, and 900°C. The films had been exposed to atmosphere for less than 1 hour before received the anneal treatments. Figure 3.2(b) shows that: i) post-deposition annealing significantly reduces the concentration of OH observed in the IR spectra; and ii) the rate of OH absorption in the annealed films is significantly reduced compared to that of the as-deposited film, which is attributed to film densification upon annealing. Significant water absorption has been reported for physical vapor deposition (PVD) Y₂O₃ films formed using e-beam evaporation of packed Y₂O₃ powder.¹⁴ IR spectra of thick PVD Y₂O₃ films obtained by sputtering thick yttrium metal oxidized at 900°C show minimal OH absorption even after exposure to atmosphere for 14 days, also consistent with film densification upon anneal. We therefore expect the post-deposition OH absorption rate to depends strongly on the deposition and anneal history of the film.

3.3 DISCUSSION AND CONCLUSION

The results described above indicate that during deposition and post-deposition anneals, the mixing reaction of Y, O and the Si substrate at the interface occurs. Silicon substrate consumption can be directly observed by annealing thick films deposited on silicon, where part of the substrate is masked to deposition. When the film is annealed then removed by etching, a large step is formed at the edge of the masked region, consistent with significant substrate consumption by the deposited film.¹⁰ It is likely that the oxidation of the substrate is significantly enhanced by the OH group in the films, as shown by the following equation:

\[ \text{Y-OH} + \text{Si} \rightarrow \text{Y-O-Si} + \frac{1}{2} \text{H}_2 \]
The above equation is just one possible reaction route, and other reactions schemes could contribute to the observed results. For example, \( \text{O}_2 \) in the \( \text{N}_2 \) ambient could also contribute to interface oxidation, and several groups have reported the oxygen partial pressure effects during anneals.\(^{6,7,14}\) Nevertheless, the significant OH density in our films suggests the importance of OH as a source of excess oxygen. Capping the dielectric with an \textit{in-situ} gate material (poly silicon or metal) can significantly minimize the OH absorption.

It is important to note that some OH generation is expected to occur on the deposition surface during CVD processes (depending on the precursor and precursor dissociation pathway) so that capping may not necessarily eliminate excess oxygen related interface oxidation. It is also important to note that this OH absorption process will also be expected to occur in other high-k materials of interest. The rate of OH absorption, relative to that shown here, is expected to depend upon the material, details of the deposition process, and material thermal history.

### 3.4 ACKNOWLEDGEMENTS

The authors acknowledge funding from SRC/SEMATECH Center for Front End Processes and NSF Grant CTS-0072784. The authors also thank Dr. S. Stemmer at Rice University for TEM/EELS analysis.
3.5 REFERENCES


Figure 3.1a  Si 2p XPS spectra after annealed at various temperatures for 1 minute. (1) as-deposited; (2) 600°C; (3) 700°C; (4) 800°C; (5) 900°C.
Figure 3.1b  Si-O/Si peak area ratio vs. 1000/T. An activation energy of 0.33 eV was obtained.
Figure 3.2a  FTIR OH peak growth over time. Capped films show slower OH absorption.
Figure 3.2b  FTIR OH peak growth over time. Annealed films without capping layers show slower OH absorption.

CHAPTER 4

ELECTRON ENERGY LOSS SPECTROSCOPY ANALYSIS OF INTERFACE STRUCTURE OF YTTRIUM OXIDE GATE DIELECTRICS ON SILICON

D. Niu, R. W. Ashcraft  
Department of Chem. Eng., North Carolina State University, Raleigh, NC 27695

Z. Chen, S. Stemmer  
Department of Mech. Eng. and Materials Science, Rice University, Houston, TX 70005

G. N. Parsons  
Department of Chem. Eng., North Carolina State University, Raleigh, NC 27695

ABSTRACT

Interface stability of high dielectric constant gate insulators on silicon is an important issue for advanced gate stack engineering. In this article we analyze the silicon/dielectric interface structure for thin Y$_2$O$_3$ and Y silicate films deposited by chemical vapor deposition on clean and pre-nitrided Si(100) using high resolution transmission electron microscopy, electron energy loss spectroscopy, and X-ray photoelectron spectroscopy. The analysis shows the films to be stoichiometric Y$_2$O$_3$ on top and Y-silicate/SiO$_2$ at the dielectric/Si interface. Pre-nitridation of the silicon surface
impedes the reaction between the depositing film and the substrate, promoting a Si-free Y$_2$O$_3$ structure. Possible mechanisms leading to the observed Y$_2$O$_3$ and Y silicate structures are discussed.
4.1 INTRODUCTION

The International Technology Roadmap for Semiconductors has called for the equivalent of a sub-1 nm silicon dioxide gate dielectric.\textsuperscript{1} The leakage current of pure SiO\textsubscript{2} at 1 nm would be unacceptably high, leading to problems in reliability and heat generation. High dielectric constant (high-k) materials enable larger film thicknesses for the same gate capacitance, and therefore lower leakage current. One of the important issues to be addressed with high-k dielectrics is the stability of the high-k/silicon interface. Several metal oxides that are potentially stable in contact with silicon are under investigation,\textsuperscript{2-6} including Al\textsubscript{2}O\textsubscript{3}, Y\textsubscript{2}O\textsubscript{3}, La\textsubscript{2}O\textsubscript{3}, HfO\textsubscript{2}, and ZrO\textsubscript{2}. Metal silicates, such as Zr, Hf, and Y, have also attracted attention.\textsuperscript{7,8} Many research groups have reported interface reactions with the silicon substrate during deposition or post-deposition anneals that lead to mixed metal/oxygen/silicon layers at the interface. The mixed layers have a smaller k than the deposited dielectric, reducing the net dielectric constant of the insulating layer. In this article, we analyze the interface structures of thin Y\textsubscript{2}O\textsubscript{3} and Y silicate on Si(100) deposited by chemical vapor deposition (CVD) using X-ray photoelectron spectroscopy (XPS), high resolution transmission electron microscopy (HRTEM), and electron energy loss spectroscopy (EELS), and use the sub-nanometer resolution to gain insight into mechanisms associated with dielectric/substrate reactions during deposition.

4.2 EXPERIMENTAL

Thin Y\textsubscript{2}O\textsubscript{3} films were deposited by oxygen plasma assisted CVD using tris(2,2,6,6-tetramethyl-3,5-heptanedionato)yttrium (Y(TMHD)\textsubscript{3}) introduced downstream.
from an O\textsubscript{2} plasma. The substrate temperature was fixed in the range of 350 to 450°C. Substrates of 0.1-0.3 Ω\cdot cm p-type Si(100) were cleaned with a JTB-100 baker clean solution and dipped in 10:1 buffered HF solution before being immediately transferred to the loadlock chamber. Details of the operation conditions and sample preparation are presented elsewhere.\textsuperscript{9} XPS was performed on a Riber LAS 3000 with a MAC2 analyzer using non-monochromatic Mg K\textsubscript{α} X-rays (1253.6 eV). Scanning transmission electron microscopy (STEM)/EELS data was collected using a JEOL JEM 2010F 200 kV transmission electron microscope equipped with a field emission gun, an annular dark-field (ADF) detector, and a Gatan GIF200 post-column imaging filter,\textsuperscript{10} capable of achieving of sub-0.2 nm probe sizes for microanalysis and incoherent Z-contrast lattice imaging.

4.3 RESULTS

Figure 4.1 shows the XPS Y 3d spectra for films deposited at 400°C for 3, 6.5, and 30 minutes with thicknesses of approximately 65 Å and 100 Å (determined from TEM), and ~500 Å (determined from step-height profilometry) respectively. Each film in Figure 4.1 was annealed \textit{ex-situ} at 900°C in N\textsubscript{2} ambient (with >10\textsuperscript{-5} Torr O\textsubscript{2}) for 1 minute. XPS analysis of the thickest film shows features consistent with Y\textsubscript{2}O\textsubscript{3} in the Y 3d spectrum at 156.8 and 158.8 eV (3d\textsubscript{5/2} and 3d\textsubscript{3/2}).\textsuperscript{11} For the thinner films, the Y 3d peaks are shifted to higher binding energies, consistent with an oxide structure that contains significant Y-O-Si (Y-silicate) bonding. For the 100 Å film the peak positions are between the peaks for the other samples, consistent with a multiple-layer structure. The Si 2p spectra for the 500 Å film shows no evidence for silicon in the top 50-75 Å of
the film (i.e. the thickness probed by XPS), but a Si-O peak at 102.5 eV is observed in the 65 Å film, consistent with Y silicate bonding.

Figure 4.2 shows (a) HRTEM and (b) EELS results of a film deposited under the same conditions as the 65 Å film shown in Figure 4.1. Annual dark field imaging was used to position a ~0.2 nm probe for EELS of the Si L-edge for compositional analysis through the film thickness. The Si L-edge data in the figure is offset for clarity. The inset of Figure 4.2(b) shows the ADF image. Region 1 is the silicon substrate with an edge onset at 99 eV and clear periodic fringes in the TEM. Region 2 is dark in the ADF with the edge onset shifted to a higher energy loss (105 eV). Also, the EELS near-edge fine structure shows peaks near 106, 108, and 115-116 eV, similar to SiO$_2$. The TEM image indicates the thickness of region 2 is about 2.0 nm, and the yttrium concentration in region 2 is below the detection limit of the method. However, EELS is less sensitive to Y than to Si, and we cannot rule out the possibility of some yttrium in region 2. Region 3 is lighter in ADF, consistent with an increased concentration of the heavier element (yttrium). Si L-edge onset in region 3 is approximately 104 eV, with another feature at ~116 eV, consistent with yttrium silicate. HRTEM analysis of a 100 Å film, deposited under the same conditions as the 100 Å film in Figure 4.1, shows a clear double-layer structure, with a crystalline layer on top and an amorphous layer at the interface, consistent with the XPS results.

The effects of substrate pretreatments were also investigated. Figure 4.3 shows the Y 3d spectra of thin films deposited for 1 minute on (1) clean Si and (2) nitrided Si, respectively. The nitridation was performed *in-situ* at 400°C by exposing the clean silicon surface to a N$_2$ plasma for 20 minutes prior to Y$_2$O$_3$ deposition. This plasma
pretreatment leads to approximately one monolayer of N at the Si/dielectric interface.\textsuperscript{12} After dielectric deposition the films were annealed \textit{ex-situ} at 900°C in N\textsubscript{2} for 10 minutes. For the film deposited on nitrided Si (spectrum 2), the Y 3d\textsubscript{5/2} peak appears at a slightly lower binding energy than that for the film deposited on clean Si. The peak positions in both films are shifted higher relative to Y\textsubscript{2}O\textsubscript{3} (156.8 eV), consistent with a Y-O-Si structure, with a larger Y/Si ratio (i.e. less interface reaction) in the films deposited on the nitrided silicon. The Si 2p and O 1s spectra also show consistent results.\textsuperscript{9}

Figure 4.4 shows results of TEM/EELS analysis for a 70 Å film deposited on nitrided silicon. The film was annealed in N\textsubscript{2} at 900°C for 1 minute before analysis. HRTEM results in Figure 4.4(a) suggest three regions in the film. The top layer (region 1) is partially crystallized, while the bottom layers (region 2 and 3) remain amorphous. The EELS data was acquired at ~1 nm (region 2), ~2.3 nm (region 3), and ~5.5 nm (region 4) from the substrate. The Si L-edge curves are again offset for clarity. For region 2, the EELS data shows an onset edge of 105 eV and peaks near 106, 108, and 115-116 eV, consistent with a SiO\textsubscript{2}-like layer. For region 3, Si peaks are still observed but with reduced intensity as compared to region 2, consistent with a Y-O-Si structure. In region 4, no silicon features are observed in the EELS data, consistent with an Y\textsubscript{2}O\textsubscript{3} structure.

\section*{4.4 DISCUSSION AND CONCLUSIONS}

Two distinct issues need to be addressed to more fully understand interface reactions during high-k deposition and post-deposition processing: 1) SiO\textsubscript{2} formation at the silicon/dielectric interface; and 2) reactions between the dielectric and the substrate.
that lead to mixed metal/oxygen/silicon (silicate) layers. The data presented above indicates that for the case of Y₂O₃ deposition on silicon, both SiO₂ and silicate layers can form near the interface.

Several possible routes exist for introduction of excess oxygen into the interface reaction zone. One possibility is diffusion of residual oxygen present during annealing through the high-k layer, and another possibility is hydroxides, produced during deposition or introduced by post-deposition absorption from the ambient.¹³ Recent results of Y-silicate films that were capped in-situ with poly-Si before annealing indicate that interfacial SiO₂ is significantly reduced (<0.5 nm) as compared to uncapped films (~2 nm observed here),¹⁴ consistent with significant oxidation resulting from O₂ diffusion or H₂O absorption.

Regarding the formation of the Y-O-Si layer, it is likely that diffusion of Si through the interface layer plays an important role, although metal diffusion may also occur. The importance of silicon diffusion is consistent with the result of the N₂ pretreatment studies. The presence of interface nitrogen leads to films with a larger Y/Si ratio, and promotes formation of Y₂O₃ films. This is consistent with interface N decreasing the rate of Si diffusion from the substrate into the deposited dielectric.

It is important to note that the ~2 nm interfacial SiO₂ is observed for uncapped films after exposure to atmosphere. Using in-situ polysilicon capping layers, interfacial layers less than 0.5 nm have been achieved, so we expect that the approaches to control interface composition reported here (in-situ capping and substrate pretreatment) will allow equivalent oxide thicknesses (EOTs) to scale to ≤1.0 nm. In the 1 nm EOT regime,
the surface pre-nitridation process presented will reduce the rate of interface silicate formation, but silicate formation mechanisms will still be active.

Ideally, one would like to know the mechanisms that govern silicon diffusion and how it can be controlled. With the data presented here, two limiting possibilities can be described. One possibility is that the extent of silicon intermixing is determined by the rate of silicon diffusion through the amorphous interface layer, and crystallization proceeds in the region where Si concentration is sufficiently low. A second possibility is that the extent of silicon diffusion is determined by the rate of Y$_2$O$_3$ crystallization, where silicon inter-diffusion and reaction with the crystalline Y$_2$O$_3$ layer is slow. Unfortunately, there is not yet sufficient data to distinguish these two processes and determine the rate-limiting step in the interface reaction process. Understanding these reactions in more detail will be important to tailor silicon gate stacks for advanced device structures.

4.5 ACKNOWLEDGEMENTS

The authors thank the funding from SRC/SEMATECH Center for Front End Processes and NSF Grant CTS-0072784. Susanne Stemmer gratefully acknowledges the use of the STEM facilities at the RRC at the University of Illinois at Chicago (NSF DMR-960172).


4.6 REFERENCES


Figure 4.1  XPS Y 3d spectra of CVD “Y₂O₃” films with various thicknesses.
Figure 4.2a  TEM of the film deposited at 400°C for 3 min and annealed at 900°C for 1 min. The thickness is about 65 Å.
Figure 4.2b  Si L-edges measured across the film. The locations correspond to those on the TEM image. The inset is the ADF image.
Figure 4.3  XPS Y 3d spectra of CVD “Y₂O₃” films on (1) bare Si; (2) nitrided Si.
**Figure 4.4a** TEM of Y$_2$O$_3$ on nitrided Si: (1) Si bulk; (2) 1 nm from Si interface; (3) 2.3 nm from Si interface; (4) 5.5 nm from Si interface.
Figure 4.4b  Si L-edges of the same film: (1) Si bulk; (2) 1 nm from Si interface; (3) 2.3 nm from Si interface; (4) 5.5 nm from Si interface.
Chapter 5 is a draft of a manuscript to be submitted to Applied Physics Letters.

CHAPTER 5

REACTION-RATE LIMITED SUBSTRATE OXIDATION DURING ANNEALING OF Y2O3 ON SILICON

D. Niu, R. W. Ashcraft and G. N. Parsons

Department of Chem. Eng., North Carolina State University, Raleigh, NC 27695

ABSTRACT

Thermal oxidation of silicon typically proceeds under mass transfer limited conditions, where the oxidation rate is determined by the rate of oxygen diffusion to the Si/SiO2 interface. In this article, we demonstrate using X-ray photoelectron spectroscopy and etching experiments, that interface reactions between chemical vapor deposited yttrium oxide and silicon results in significant macroscopic consumption of the silicon substrate during post-deposition anneal. The extent of silicon consumption increases as the thickness of the deposited dielectric increases, consistent with reaction-rate limited oxidation. Oxidation likely proceeds through absorption of water and OH groups within the dielectric layer before the anneal, followed by relatively fast diffusion of OH to the Si/dielectric interface during the anneal. Reaction rate limited oxidation is not consistent
with other proposed oxidation processes, such as metal catalyzed oxygen dissociation, which rely on oxygen diffusion through the dielectric layer.
5.1 INTRODUCTION

Understanding interface oxidation mechanisms is a critical issue in high dielectric constant materials research.\(^1\) Interface reactions leading to formation of SiO\(_2\) or metal silicate during deposition and post-deposition annealing have been reported on almost every metal oxide as potential high-k gate dielectrics, including Al\(_2\)O\(_3\), Y\(_2\)O\(_3\), La\(_2\)O\(_3\), HfO\(_2\), and ZrO\(_2\).\(^2\)-\(^7\) X-ray photoelectron spectroscopy (XPS) analysis of films with different thicknesses can provide valuable information on interface structures, but composition and thickness cannot be characterized independently. High-resolution transmission electron spectroscopy and electron energy loss spectroscopy (HRTEM/EELS) can be used to observe interface structures directly. For example, we have reported that a 65 Å “Y\(_2\)O\(_3\)” film is actually comprised of 20 Å SiO\(_2\) and 45 Å Y-O-Si.\(^8\) TEM images of a thicker film (100 Å) show clear evidence for ~40 Å crystalline Y\(_2\)O\(_3\) on amorphous mixed SiO\(_2\)/Y-silicate layer, but thickness of interface region is not observed to change significantly as film thickness increases from 65 to 100 Å, suggesting that the interface oxidation could be self-limiting. However, XPS analysis of annealed films shows thermally activated interface oxidation, consistent with a continuing reaction.\(^9\) Interface oxidation is generally observed to proceed more quickly than silicon oxidation under similar conditions. Processes including metal catalyzed O\(_2\) dissociation, charge enhanced O\(^+\) ion diffusion, and OH mediated oxidation are considered possible, but previous experiments have not distinguished between these mechanisms.

In this article, we show that when Y\(_2\)O\(_3\) on Si is annealed at 900°C in N\(_2\) (with some O\(_2\) present), the extent of silicon oxidation increases in proportion with the thickness of the deposited dielectric, consistent with a reaction-rate limited silicon
oxidation process where significant amounts of excess oxygen is available for reaction at the interface. This observation supports the hydroxyl-mediated oxidation mechanism, and is not consistent with metal catalyzed oxidation or charge enhanced diffusion mechanisms.

5.2 EXPERIMENTAL

A low-pressure remote plasma enhanced chemical vapor deposition (CVD) reactor was used to deposit thin Y2O3 films. Y precursor was tris(2,2,6,6-tetramethyl-3,5-heptanedionato)yttrium (Y(TMHD)3) introduced downstream from an O2 plasma. Substrates of 0.1-0.3 Ω⋅cm p-type Si(100) were cleaned with the JTB-100 baker clean solution and dipped in 10:1 buffered-oxide-etch solution before being immediately transferred to the loadlock chamber without final water rinse. During high-k deposition, the substrate temperature was fixed at 400°. Details of operation conditions are described elsewhere. For some samples, polycrystalline silicon capping layers were deposited on the dielectrics in the same reactor without breaking vacuum. Capping layers, typically 100-200Å thick, were formed by introducing silane (2% in He) downstream from a helium plasma. Thin insulating films (<100 Å) were analyzed using XPS, transmission electron microscopy (TEM), electron energy loss spectroscopy (EELS), ellipsometry, as well as current vs. voltage and capacitance vs. voltage measurements. Thick films were analyzed using transmission Fourier transform infrared spectroscopy. The step-height measurement was conducted on a Tencor Alpha-Step 500 Surface Profiler.
5.3 RESULTS

Figure 5.1 shows XPS spectra in Si 2p region for films deposited at 400°C for 3, 6.5, and 30 minutes with thicknesses of approximately 65 Å and 100 Å (determined from TEM), and ~500 Å (determined from step-height profilometry) respectively. No polysilicon capping layer was used for these films. After deposition, the films were annealed ex-situ at 900°C for 1 minute in N₂ (background O₂ concentration ~10⁻⁴ Torr).

The binding energies of 99.3 and 103.3 eV are assigned to Si substrate and Si-O-Si bonding structures, while the binding energy for Si-O-Y is near 102-103 eV due to the lower electronegativity of yttrium (1.22) compared to that of silicon (1.90).¹⁰,¹¹ For the 65 Å film, the Si-O peak is shifted to a lower binding energy (~102.4 eV) relative to that for pure SiO₂ bonding, consistent with a significant Y-contained oxide bonding structure (Y-silicate). The full-width-half-maximum (FWHM) value of the Si-O peak for the 65 Å film is 2.44 eV, which is larger than that of pure SiO₂ (1.98 eV), consistent with a Y-O-Si layer on top of SiO₂ layer. This two-layer structure has been confirmed by HRTEM/EELS analysis of deposited films exposed to air. Specifically, for the 65 Å film HRTEM/EELS results indicate 45 Å amorphous Y-O-Si on top of 20 Å SiO₂.⁸ For the 100 Å film, the substrate peak is not visible in XPS, and the Si-O peak is shifted to an even lower binding energy compared to that for the 65 Å film, consistent with a more Y-rich silicate structure on SiO₂. For the 500 Å film, XPS shows no evidence for Si substrate or Si-O peaks, consistent with Si-free Y₂O₃ in the top-most part of the thick film.

Figure 5.2 is a schematic of the substrate consumption experiment. First, a thick film (~500Å) was deposited, followed by 10% HF etching of part of the sample to create
a step, as shown in Figure 5.2(a). For deposition time of 30 minutes, the step-height is 500 Å. After the measurement, the film was annealed at 900°C for 3 minutes in N2. The step-height was re-measured, and a value of 240 Å was obtained, as shown in Figure 5.2(b). At last, part of the film was etched away using 10% HF solution. The measurement of step-height from the area where the film was just removed to the top of the film gave a value of ~ 425 Å, as shown in Figure 5.2(c), indicating that about 285 Å silicon substrate has been consumed during post-deposition annealing. Similar experiments were done for Y2O3 films with in-situ polysilicon capping layers. For similar film thicknesses and anneal conditions, the capped films showed less substrate consumption.

Figure 5.3 shows the oxidation of H-F last bare Si for various times in N2 at 900°C. The thickness was determined by ellipsometry. The oxidation rate is very fast for the first 1-3 minutes, and then increases slowly. Oxidation for 3 minutes results in 16.7 Å SiO2 compared to 285 Å Si consumed during annealing of Y2O3 shown in Figure 5.2.

Figure 5.4 shows the thickness of Si substrate consumed as a function as the total thickness of the dielectric after anneals. The round dots are calculated by converting the SiO2 thickness in Figure 5.3 into Si thickness using atomic density of 5.0×10^{22} atoms/cm^3 for Si and 2.2×10^{22} molecules/cm^3 for SiO2. The square points are estimated from HRTEM/EELS and MEIS data. HRTEM images show 20 Å SiO2 and 45 Å Y-O-Si for the 65 Å film. For the 100 Å film, SiO2 and Y-O-Si layers are 20 Å and 40 Å, respectively. EELS and MEIS data indicates the average concentration of Si is ~at. 15%, which requires an average composition of (Y2O3)(SiO2)_{1.36}. The atomic density of Y-O-
Si of this composition is roughly estimated to be $1.84 \times 10^{22}$ molecules/cm$^3$, using a weighted average of the SiO$_2$ and Y$_2$O$_3$ ($1.34 \times 10^{22}$ molecules/cm$^3$) densities. The triangle dot is obtained from Figure 5.2. Figure 5.4 shows that the silicon consumption is a strong function of the total Y$_2$O$_3$ thickness. When there is no Y$_2$O$_3$ (the round dots), the consumption is very slow, as evident in Figure 5.3. For very thin Y$_2$O$_3$ films with thicknesses from 65 to 100 Å (the square dots), the substrate oxidation does not change much, although it is apparently enhanced compared to no Y$_2$O$_3$ case. However, the Si consumed is significantly increased for the thick Y$_2$O$_3$ film (the triangle dot), indicating the diffusion is not the limiting step.

5.4 DISCUSSION AND CONCLUSIONS

Data in Figure 5.1 indicates a structure of Y$_2$O$_3$/Y-O-Si/SiO$_2$ on Si for a thick yttrium oxide film. For the 65 Å film HRTEM/EELS results indicate 45 Å amorphous Y-O-Si on top of 20 Å SiO$_2$. However, Figure 5.2 shows that for a ~500 Å, silicon consumption is over 250 Å. There are several possible mechanisms that might explain this substantial substrate consumption. Since we started macroscopic analysis with etching of part of the as-deposited film, the interface reactions during deposition are not considered in the following analysis assuming there are no reaction intermediates (such as Y-OH) from the dissociation of the yttrium precursor left in the film. A reaction scheme can be described as follows:

\[
O_2 + Si \rightarrow SiO_2 \quad (1)
\]

\[
O_2 + Y^{3+} \rightarrow 2O + Y^{3+} \quad (2)
\]

\[
2O + Si \rightarrow SiO_2 \quad (3)
\]
\[
\text{Y-OH} + \text{Si} \rightarrow \text{SiO}_2 \quad (4)
\]

\[
\text{Y-OH} + \text{Si} \rightarrow \text{Y-O-Si} \quad (5)
\]

Reaction (1) is oxidation of the substrate due to the residual O\textsubscript{2} in the annealing N\textsubscript{2} ambient, and several groups have studied the effects of residual O\textsubscript{2} during high temperature annealing for several high-k materials\textsuperscript{3,7,12}. Figure 5.3 shows the oxidation study of blank Si with residual O\textsubscript{2} (with partial pressure in order of ~10^{-4} torr) in N\textsubscript{2} at 900°C. Oxidation for 3 minutes shows the thickness of SiO\textsubscript{2} is ~16.7 Å, indicating that residual O\textsubscript{2} alone cannot explain the consumption of 285 Å silicon and other reaction routes must be considered. One possible route, shown in reaction (2), is catalytic dissociation of O\textsubscript{2} assisted by yttrium ions, followed by oxidation of the substrate due to atomic oxygen produced, shown in reaction (3). If this is the dominating mechanism, one would expect the substrate oxidation decreases with increasing film thickness. However, HRTEM of thin films and the etching experiment of thick films show the opposite trend. Therefore, catalytic dissociation of O\textsubscript{2} assisted by yttrium ions is not the main cause. Reaction (4) is formation of SiO\textsubscript{2} through diffusion of excess OH group in the film down to the substrate. Water absorption during sample transfer has been shown to be fast and dramatic\textsuperscript{9}, which can lead to a large amount of Y-OH formation. Significant reduction of SiO\textsubscript{2} formation with \textit{in-situ} capping layers has been reported\textsuperscript{13}, implies that water pickup during post-deposition and/or residual O\textsubscript{2} in the annealing ambient is the main cause for SiO\textsubscript{2} formation. Reaction (5) is formation of yttrium silicate via diffusion of silicon atoms through the amorphous silicate/SiO\textsubscript{2} layers. Results of the same Y-silicate films that were capped \textit{in-situ} with poly-Si before annealing
indicate that significant silicate is formed, also implying silicon diffusion during deposition occurs.\textsuperscript{8}

Etching studies clearly show that the substrate consumption is not self-limiting during post-deposition annealing. The data suggests that the extent of oxidation is enhanced by increasing the thickness of the dielectric deposited on the silicon, consistent with an oxidation process that proceeds through reaction with adsorbed oxygen (likely as OH) that diffuses quickly in the film. The data is not consistent with a process that relies on diffusion of O\textsubscript{2} (or other species) from the ambient through the dielectric layer. Different oxidation kinetics could be expected in other high-k dielectrics, such as ZrO\textsubscript{2} and HfO\textsubscript{2} that do not absorb water as quickly as Y\textsubscript{2}O\textsubscript{3}.

\section*{5.5 ACKNOWLEDGEMENTS}

The authors acknowledge funding from SRC/SEMATECH Center for Front End Processes and NSF Grant CTS-0072784. They also thank Dr. S. Stemmer at Rice University for TEM/EELS analysis.
5.6 REFERENCES


Figure 5.1  XPS Si 2p spectra of films with different thicknesses.
Figure 5.2  Illustration of the substrate consumption. (a) Film was deposited at 400°C. Part of the film was etched by HF; (b) Film was annealed at 900°C in N₂; (2) part of the annealed film HF was etched by HF.
Figure 5.3  Oxidation of HF-last bare Si at 900°C in N₂.
Figure 5.4  Thickness of Si substrate consumed as a function as the total thickness of the dielectric after anneals.
CHAPTER 6

CHEMICAL, PHYSICAL, AND ELECTRICAL
CHARACTERIZATIONS OF OXYGEN PLASMA ASSISTED
CHEMICAL VAPOR DEPOSITED YTTRIUM OXIDE ON SILICON

D. Niu, R. W. Ashcraft, Z. Chen#, S. Stemmer#, G. N. Parsons

Department of Chemical Engineering, North Carolina State University,
Raleigh, NC 27695

#Department of Mechanical Engineering and Materials Science, Rice University,
Houston, TX 70005

ABSTRACT

Understanding and controlling interface and bulk chemical stability of CVD high-k dielectrics is an important research issue. In this paper, we report thin Y₂O₃ films deposited by oxygen plasma assisted chemical vapor deposition using two yttrium diketonate precursors. Unacceptable large hysteresis in C-V data, presumably due to the incorporation of fluorine, is observed for the films from the F-contained precursor. For films deposited with the hydrogenated precursor and exposed to air after deposition, transmission electron microscopy shows a triple layer structure after annealing, and
electron energy loss spectroscopy and X-ray photoelectron spectroscopy show the film to be stoichiometric Y$_2$O$_3$ on top and yttrium silicate at dielectric/Si interface, which is also confirmed by Fourier transform inferred spectroscopy, X-ray diffraction, and atomic force microscope. Pre-nitridation of the silicon surface impedes the reaction with the substrate, promoting the Y$_2$O$_3$ structure. A substantial consumption of silicon substrate is directly demonstrated by a carefully designed etching experiment. Several possible mechanisms consistent with the observed results, including Si diffusion, crystallization of Y$_2$O$_3$, and reaction with absorbed OH, are discussed.
6.1 INTRODUCTION

The continuous scaling of complementary metal-oxide-semiconductor (CMOS) devices requires an equivalent of a sub-1 nm silicon dioxide for gate dielectrics.\(^1\) Several metal oxides, including \(\text{Al}_2\text{O}_3\), \(\text{Y}_2\text{O}_3\), \(\text{La}_2\text{O}_3\), \(\text{HfO}_2\), and \(\text{ZrO}_2\) which are potentially stable in contact with silicon, have been under investigation to replace \(\text{SiO}_2\).\(^2\)\(^-\)\(^7\) Several research groups have reported results that demonstrate oxidation of the silicon substrate during deposition or during post-deposition anneals. Such silicon consumption reactions are particularly detrimental, in part, because they typically result in a thin interface layer with a relatively small dielectric constant that reduces the overall capacitance of the gate stack.

Metal silicates, with predominant metal-oxygen-silicon bonds, have also attracted extensive attention.\(^8\)\(^-\)\(^10\) \(\text{Zr}\) and \(\text{Hf}\) silicates with low \(\text{Zr}\) and \(\text{Hf}\) concentrations have been demonstrated \(k\sim11\) and an amorphous microstructure after annealing at 1050°\(\text{C}\) for 20 seconds.\(^8\) However, phase separation phenomena have been observed when \(\text{Zr}\) silicate with a composition of 50% \(\text{ZrO}_2\) and 50% \(\text{SiO}_2\) undergoes 900°\(\text{C}\) rapid thermal anneal treatments in argon.\(^10\) On the other hand, yttrium silicate with a composition of up to 72% \(\text{Y}_2\text{O}_3\) has been formed on silicon(100) with no \(\text{SiO}_2\) interfacial layer by oxidizing yttrium metal or silicide at 900°\(\text{C}\), indicating its good thermostability.\(^11\) In this article, we report oxygen plasma assisted chemical vapor deposition (CVD) of \(\text{Y}_2\text{O}_3\) and \(\text{Y}\) silicate on silicon (100) using two yttrium precursors, and the relation between the precursor structure and the film properties is discussed. Interface and bulk structures are analyzed using various techniques, and possible interface reactions during deposition and during post deposition annealing are discussed.
6.2 EXPERIMENTAL

Figure 6.1 is the schematic of the deposition system used in this study for Y$_2$O$_3$ film deposition. The reactor system allows gas flow (O$_2$ in this study) into a top plasma excitation region, and metal-organic precursor inlet downstream through a tube, with the tube outlet positioned close to the silicon substrate. For metal organic precursors, two different solid materials were utilized: yttrium hexafluoroacetylacetonate (Y(HFAA)$_3$), and tris(2,2,6,6-tetramethyl-3,5-heptanedionato)yttrium (Y(TMHD)$_3$). An important distinction between these is that the first contains fluorine in the ligands, whereas the second contains hydrogen. The precursor was introduced downstream from the O$_2$ plasma by flowing 5 standard cubic centimeters per minute (sccm) of argon carrier gas through a double-ended cylinder that was constantly kept at a fixed temperature in the range of 130 to 180°C. O$_2$ or N$_2$O flowed at 100 sccm into the radio-frequency (RF, 13.56 MHz) plasma generation zone 1~2 cm above the substrate, and 5 to 50 watts of RF power was applied. The substrate temperature was fixed in the range of 350 to 450°C, and the process pressure was maintained at 0.2 torr. The substrates were 0.1-0.3 Ω⋅cm p-type Si(100) cut into 1 inch by 1 inch samples prior to deposition. The substrates were cleaned with a JTB-100 baker clean solution for 5 minutes, followed by 5-minute deionized (DI) water rinse and 30-second dip in 10:1 buffered HF solution before being immediately transferred to the loadlock chamber without final DI water rinse. Thin films (<100 Å) were analyzed using X-ray photoelectron spectroscopy (XPS), high resolution transmission electron microscopy (HRTEM), and electron energy loss spectroscopy (EELS).$^{12,13}$ Relatively thick films (~500 Å) were analyzed using Fourier Transform
Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), and Atomic Force Microscope (AFM).

XPS was conducted on a Riber LAS 3000 with a MAC2 analyzer. Non-monochromatic Mg K$_\alpha$ x-rays (1253.6 eV) were used for all the measurements. Survey and detailed spectra were obtained with 1.0 and 0.1 eV step sizes respectively. Most of the XPS data was collected from thin films, enabling the silicon substrate signal at 99.3 eV to be used as a reference peak position. For all films, the adventitious carbon peak near 285 eV was also used as a reference to adjust the spectra to compensate for charging. Using two peaks for simultaneous reference confirmed the linearity of the analyzer response. STEM/EELS data was collected using a JEOL JEM 2010F 200 kV transmission electron microscope capable of achieving of sub-0.2 nm probe sizes for microanalysis and incoherent Z-contrast lattice imaging. The composition across the gate stacks was analyzed by positioning the 0.2 nm probe at different positions in the annular dark-field (ADF) image and recording an EELS spectrum. FTIR was performed on a Nicolet Magna 750. Mid-IR (a wavenumber range of 4000-400 cm$^{-1}$) and far-IR (<600 cm$^{-1}$) spectra were collected on substrates with one side polished and the other side etched to “orange-peel” roughness. The resolution and number of scans were set at 8 and 256, respectively. AFM was measured using Digital Instruments Dimension 3000 in an intermittent-contact mode. The cantilever probes were c-Si with nominal tip radius of 5-10 nm. Capacitance-voltage (C-V) and current-voltage (I-V) measurements were conducted on an HP 4283A LCR meter and an HP 4145 meter, respectively. The devices were MOS capacitors formed by evaporating 2000 Å aluminum on the films through
6.3 RESULTS

6.3.1 \( \text{Y}_2\text{O}_3 \) Deposition Using \( \text{Y(HFAA)}_3 \)

\( \text{Y(HFAA)}_3 \) is a solid powder with a vapor pressure of \(-0.2 \text{ Torr at } 100^\circ C\), and it remains stable in contact with air. For our experiments, we used it as purchased, and we loaded it directly in laboratory air into a stainless steel cylinder mounted in an argon flow line. The cylinder was evacuated at room temperature, and then heated to \( 130^\circ \text{ to } 180^\circ C \) to achieve deposition. Figure 6.2(a)-(c) are the O 1s, Y 3d, and Si 2p XPS spectra of four samples obtained using \( \text{Y(HFAA)}_3 \) as Y precursor and \( \text{N}_2\text{O} \) as O precursor, respectively. Sample (1) was a \(-50 \text{ Å thin film deposited at } 400^\circ C \) with a RF power of 5 W, while samples (2)-(4) were thick films (\(-1000 \text{ Å} \) deposited at \( 400^\circ C \) with RF powers of 5, 10, and 25 W, respectively. In O 1s region, binding energies of 533.0 and 529.5 eV are assigned to pure \( \text{SiO}_2 \) and \( \text{Y}_2\text{O}_3 \), respectively. In Y 3d region, binding energy of 156.8 eV (3d\(_{5/2}\)) is assigned to \( \text{Y}_2\text{O}_3 \). In Si 2p region, binding energies of 103.3 and 99.3 are assigned to pure \( \text{SiO}_2 \) and Si substrate, respectively. Figures 6.2(a) and 6.2(b) show that the spectra for samples (2)-(4) are very similar, indicating little effect of the plasma power on chemical structure of the films. Even though the peaks at \(-529.5 \text{ eV in the O 1s spectra appear to be pure } \text{Y}_2\text{O}_3 \), the peaks are shifted about 5 eV to higher binding energy relative to the pure \( \text{Y}_2\text{O}_3 \) position in Y 3d spectra. No features were observed in Si 2p region for these thick films. The shift of the Y features to higher binding energy is consistent with the effect expected from fluorine in the films. The high electronegativity
of F (3.98 on the Pauling scale, compared to 3.44 for O) results in F pulling charge from the Y, leading to a higher binding energy of the remaining charge.\textsuperscript{16} The incorporation of Si (electronegativity of 1.9, compared to 1.22 for Y) into the Y\textsubscript{2}O\textsubscript{3} structure will also cause Y features to shift to higher binding energy, but the magnitude will not be as large as for that of F. Likewise, the O 1s peak is expected to shift to higher binding energy upon incorporation of Si or F into the film. For a thin film (sample 1 in Figure 6.2a), the O 1s peak is observed to shift to higher binding energy, consistent with O and/or F in the film. The Y 3d spectrum for the thin film in Figure 6.2(b) also shows a 2 eV shift to higher binding energy, but it is not as pronounced as that for thicker films (samples 2, 3, and 4). The spectra for the thin film in Figures 6.2a, 6.2b, and 6.2c are consistent with mixing of silicon into the Y\textsubscript{2}O\textsubscript{3} structure, with less F incorporation than observed in thicker films. A large shift to higher binding energy in the O 1s spectra in Figure 6.2a is not observed for the thicker films. This is not completely understood, but it suggests a lack of O-F bonds in these materials, suggesting stable fluorinated bonding structures present on the deposition surface before oxidation.

Figure 6.3 is a typical C-V curve of a thin film deposited for 5 minutes and then annealed \textit{ex-situ} at 700°C in N\textsubscript{2} at 1 atm for 10 minutes. The deposition time is the same as for sample 1 in Figure 6.2, but the samples in Figure 6.2 did not undergo a post-deposition anneal. Gate electrodes were Al, evaporated through a shadow mask forming electrodes with area 7.07\times10^{-4} cm\textsuperscript{2}. The CV shows a large hysteresis (~0.9 V) consistent with active charge traps in the bulk of the film. C-V analysis before and after prolonged anneals showed similar hysteretic results, suggesting that the trap states are intrinsic to the material structure. Improved results are obtained using non-fluorinated precursors.
6.3.2 \( Y_2O_3 \) Deposition Using \( Y(TMHD)_3 \)

\( Y(TMHD)_3 \) is a solid with a vapor pressure of 0.05 torr at 95°C, which is somewhat smaller than that of \( Y(HFAA)_3 \). This precursor is also commercially available, and it was handled and introduced as purchased in a similar manner as described for \( Y(HFAA)_3 \). We examined deposition using this precursor on clean silicon, and on silicon pretreated with \textit{in-situ} plasma oxidation and nitridation steps. The pretreatment steps were used to modify the interface formation process during the initial deposition.

6.3.2.1 Deposition On Clean Silicon (100)

Figure 6.4 shows the XPS spectra of the Y 3d, Si 2p and O1s regions for films deposited at 400°C for 3, 6.5, and 30 minutes with thicknesses of approximately 65 Å and 100 Å (determined from TEM), and ~500 Å (determined from step-height profilometry) respectively. After deposition, films were annealed \textit{ex-situ} at 900°C in N\(_2\) (with >10\(^{-5}\) Torr O\(_2\)) for 1 minute. The thickest film shows features consistent with \( Y_2O_3 \) structure in the Y 3d and O 1s spectra at 156.8 and 158.8 eV (3d\(_{5/2}\) and 3d\(_{3/2}\)) and 529.5 eV respectively, and there is no evidence for a Si 2p feature, consistent with a thick \( Y_2O_3 \) film.\(^{15}\) The peak at 532.5 eV in the O 1s spectrum is likely due to a slight amount of water absorbed on the sample surface. The spectra for the thinner films show significant shifts in Y 3d and O 1s binding energy, consistent with an oxide structure that contains significant Y-O-Si (Y-silicate) bonding. For the 100 Å film the peak positions are between the peaks for the other samples, consistent with a multiple-layer structure. The peak at 102.5 eV of the Si 2p Si-O spectrum is also consistent with the thinnest films consisting of significant yttrium silicate bonding structure.
Figure 6.5 shows STEM/EELS results of a film deposited under the same conditions as the 3-minute deposition film shown in Figure 6.4. The TEM image in 6.5(a) shows the fine structure of the silicate film with thickness of 65 Å. Annual dark field imaging, shown in Figure 6.5(b), was used to position a ~0.2 nm probe for EELS of the Si L-edge for compositional analysis through the film thickness. Figure 6.5(c) shows the Si L-edge electron energy loss spectra measured at different locations across the film. The spectra are offset for clarity. Region (i) is the silicon substrate with an edge onset energy of 99 eV and clear periodic fringes shown by TEM. In region (ii), the edge onset is shifted to a higher energy loss (105 eV) with peaks at 102, 106, and 115-116 eV, consistent with SiO$_2$. The yttrium concentration is below the detection limit of the method, with possibly some Y incorporation. The thickness of region (ii) is about 15-20 Å. Region (iii) shows a lighter contrast in the ADF image as compared to region (ii), and the Si L-edge peak shifts slightly from 109 eV to a lower energy loss of 108.7 eV. These spectral signatures clearly indicate a more yttrium-rich structure mixed with Si-O in region (iii) of this film. HRTEM analysis of a 100 Å film, deposited under the same conditions as the 100 Å film in Figure 6.4, shows a clear double-layer structure, with a crystalline layer on top and an amorphous layer at the interface, consistent with the XPS results. The interface layer is about 20 Å thick. It is interesting to note that the thickness of the interfacial oxide is independent of the total film thickness.

C-V results are shown in Figure 6.6. The films were deposited under the same conditions as the 65 and 100 Å films in Figure 6.4, and received a post-metallization anneal in N$_2$/H$_2$ at 400°C for 30 minutes. Fitting the C-V data for the 65 Å film results in EOT of ~29 Å. Assuming interfacial oxide layer to be 15-20 Å thick with a dielectric
constant of 3.9, the dielectric constant of the silicate is calculated to be 12-18, consistent with literature values. Some hysteresis (< 20 mV) has been observed for both films. The flatband voltage is shifted in the negative direction (~0.9 V), indicating the presence of positive fixed charge, similar to Y silicate films formed by PVD. The flatband voltage does not change with film thickness.

FTIR measurements were conducted on thick films (~1500 Å), as shown in Figure 6.7. For the as-deposited film, the broad peak from 3100 to 3600 cm\(^{-1}\) is assigned to OH bonding, indicating significant water absorption from the atmosphere. The doublet peak at 1400-1600 cm\(^{-1}\) is due to the stretching mode of carboxyl, presumably from the incomplete oxidation of the precursor. The small shoulder near 1600 cm\(^{-1}\) is the bending mode of water. The broad feature around 350 cm\(^{-1}\) is Y-O-Y stretching mode. After a 900°C anneal in N\(_2\) for 10 minutes after deposition, the spectrum (top curve) clearly shows the disappearance of OH peak, and the C peak is also significantly reduced. The sharp triplet features at 302, 335, and 372 cm\(^{-1}\) is consistent with the film bulk being crystalline Y\(_2\)O\(_3\), which is also consistent with the structure derived from XPS data, as shown in figure 6.4. The crystallization is further justified by XRD data, as shown in figure 6.8. Curve 1 is for the sample after 900°C annealing in N\(_2\) for 10 minutes, while curve 2 is for the as-deposited film. Curve 2 shows no clear features in the scanned 2\(\theta\) range, indicating an amorphous structure. On the other hand, curve 1 shows clear peaks of crystalline Y\(_2\)O\(_3\) which are assigned to Y\(_2\)O\(_3\) (222), (400), and (211). AFM data in Figure 6.9 also shows the effect of crystallization on film roughness. The as-deposited film in Figure 6.9(a) has a roughness of 3.9 Å, whereas the film annealed at 900°C in N\(_2\) has a roughness of 7.6 Å.
6.3.2.2 Deposition On In-Situ Pretreated Silicon

The effects of substrate pretreatments were also investigated. Figure 6.10 shows the XPS spectra of thin Y$_2$O$_3$ films deposited for 1 minute on (1) clean Si, (2) nitrided Si, (3) oxidized Si, respectively. The nitridation was performed \textit{in-situ} at 400°C with the plasma power of 20 W and N$_2$ flow rate of 200 sccm for 20 minutes. The pre-oxidation was performed \textit{in-situ} at 300°C with the plasma power of 10 W for 10 minutes. Helium and O$_2$ flow rates were 100 sccm and 20 sccm, respectively. XPS analysis of similarly prepared surfaces indicates that for the pre-oxidation step, ~1 nm is produced. For the pre-nitridation step, approximately 1 monolayer of nitrogen is introduced, with some oxygen also present on the surface.\textsuperscript{11} After deposition on the pre-treated surfaces, the films were annealed \textit{ex-situ} at 900°C in N$_2$ for 10 minutes. The O 1s and Y 3d peaks for all three films are shifted to higher binding energies relative to Y$_2$O$_3$ (329.5 eV in O 1s and 156.8 eV in Y 3d), consistent with a Y-O-Si structure. The Si 2p peaks between 102 and 103 eV for the three films also indicate the Y-O-Si structure. For the film deposited on nitrided Si (spectrum 2), the O 1s and Y 3d$_{5/2}$ peaks appear at slightly lower binding energies than those for the films deposited on clean Si (spectrum 1) and pre-oxidized Si (spectrum 3). The Y/Si ratios (estimated by taking the ratio of Y 3d$_{5/2}$ peak intensity to Si-O peak intensity) for the films deposited on the nitrided silicon and oxidized Si are larger than for the film deposited on clean Si, indicating less interface reactions with the substrate on pretreated Si.

EELS analysis was conducted on a film deposited for 3-minutes on nitrided Si and annealed for 1 minute, and the results are shown in Figure 6.11. The TEM image in Figure 6.11(a) indicates a multi-layered structure with thickness of about 70 Å. The top
layer (region ii) shows clear crystallites, consistent with Y$_2$O$_3$, while the layers (region ii and iii) close to the silicon substrate remain amorphous. This is further confirmed by the EELS spectra as shown in Fig. 6.11 (b) and the Si concentration profile extracted from Si L-edges data as shown in Fig. 6.11(c). The spectra are again offset for clarity. The EELS spectra were taken at various distances from the substrate: (i) the bulk of the substrate; (ii) 1.0 nm from the substrate; (iii) 2.3 nm from the substrate; (iv) 5.5 nm from the substrate. For region (ii), the EELS data shows an onset edge of 105 eV and peaks near 106, 108, and 115-116 eV, consistent with a SiO$_2$-like layer. For region (iii), Si peaks are still observed but with reduced intensity as compared to region (ii), consistent with a Y-O-Si structure. In region (iv), no silicon features are observed in the EELS data, consistent with a Y$_2$O$_3$ structure. The lack of Si in the top layer can be explained by the impedance of Si diffusion due to an oxynitride layer at the interface. The samples analyzed by XPS were annealed for longer anneal times (10 minutes) than those analyzed by EELS (1 minute), but consistent results are obtained from both analyses. Furthermore, the XPS data obtained at longer anneal times is consistent with more extended silicon diffusion though the oxynitride layer leading to a thicker Y-silicate layer.

6.3.2.3 Macroscopic Silicon Substrate Consumption

The data presented above shows clear mixing of the silicon substrate with the deposited dielectric during deposition and during post-deposition annealing. The extent of the silicon consumption is not limited to the ultra-thin layers shown in the TEM images. Rather, the silicon consumption can be observed on a macroscopic scale as shown schematically in Figure 6.12. For this demonstration, we first deposited an
yttrium oxide dielectric layer on silicon where part of the Si substrate was masked with a glass slide. The film thickness was sufficiently large (~500 Å) so that it could easily be measured by step-height profilometry. After thickness measurement, the film was subjected to an anneal at 900°C for 3 minutes, and the thickness was re-measured. The measured thickness was significantly reduced (from 500 to ~240Å) upon anneal suggesting radical densification. However, when part of the film was then removed by wet etching in HF, which removes the yttrium silicate at the interface, a marked effect was observed when the step edge was again profiled. A step downward of ~285 Å was observed in the silicon where the edge of the dielectric had previously been, and a step up of ~525 Å was observed at the edge of the remaining dielectric. In this experiment, it is presumed that most of the silicon substrate consumption occurs during post-deposition annealing, but similar reactions will occur during deposition (as shown by the XPS data above). Furthermore, the IR results of the as-deposited film showed significant evidence for OH incorporation, suggesting a possible route for enhanced reactivity between the deposited dielectric and the silicon substrate.

6.4 DISCUSSION

The data presented above shows that during plasma assisted chemical vapor deposition of yttrium oxide based dielectrics, the initial deposited layers will mix and react with the substrate silicon to form a thin metal silicate or silicon oxide interface structure. Further deposition results in a film with composition closer to Y₂O₃. The data presented above indicates that for the case of Y₂O₃ deposition on silicon, both SiO₂ and silicate layers can form near the interface. The top Y₂O₃ layer tends to crystallize readily
during 900°C anneals, while the bottom layers remain amorphous. When thin layers (~65 Å) are deposited on clean silicon, the EELS and XPS data shows that the substrate silicon has moved throughout the film layers, whereas when the substrate is pre-nitrided, the silicon mixing is reduced enabling the top portion of the thin layer to crystallize upon anneal. Two distinct issues need to be addressed to more fully understand interface reactions during high-k deposition and post-deposition processing: 1) SiO$_2$ formation at the silicon/dielectric interface during deposition and high-temperature anneal; and 2) reactions between the dielectric and the substrate that lead to mixed metal/oxygen/silicon (silicate) layers. A possible reaction scheme of the elementary reactions based on the results in section 6.3 can be described as follows:

**During Deposition**

\[
\begin{align*}
    \text{Si} + \text{O}^* & \rightarrow \text{SiO}_2 \\
    \text{Y-O-R} + \text{Si} & \rightarrow \text{Y-O-Si} + \text{R} \\
    \text{Si} + \text{Y-O-Si} & \rightarrow \text{Y-O-Si} + \text{Si}^* \\
    \text{Y-O-R} + \text{O}^* & \rightarrow \text{Y}_2\text{O}_3
\end{align*}
\]

**During Post-deposition**

\[
\text{Y}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow \text{Y-O-H}
\]

**During Annealing**

\[
\begin{align*}
    \text{Y-O-H} + \text{Si} & \rightarrow \text{Y-O-Si} \\
    \text{Y-OH} + \text{Si} & \rightarrow \text{SiO}_2 \\
    \text{O}_2 + \text{Si} & \rightarrow \text{SiO}_2
\end{align*}
\]
Note that the reactions are written schematically, and are not fully balanced. Reaction (1) is formation of SiO$_2$ by the reaction of Si substrate with O radical from O$_2$ plasma. In reaction (2), the organic ligand (R) leaves the precursor, and the resulted Y-O radical reacts with Si to form Y-O-Si. Reaction 3 is diffusion of Si atom through the newly formed silicate. Then reaction (2) and (3) will be repeated until Si diffusion is kinetically limited. Beyond that point, formation of Y$_2$O$_3$ starts occurring, as shown in reaction (4). Reaction (5) is formation of yttrium hydride due to water pickup during sample transfer. During annealing, more Si diffuses through silicate and reacts with yttrium hydride to form silicate, as shown in reaction (6). Reaction (7) is formation of SiO$_2$ by OH diffusing down to the substrate and oxidizing it. Reaction (8) is oxidation of the substrate by residual O$_2$ in N$_2$ ambient.

Several sources are possible for introduction of excess oxygen into the interface reaction zone to oxidize the substrate and form SiO$_2$, summarized in reaction (1), (7) and (8). During deposition, O radicals from O$_2$ plasma could insert into the substrate matrix, leading to SiO$_2$ formation, as shown reaction (1). During annealing, a possibility is diffusion of residual oxygen present through the high-k layer shown in equation (8), and several groups have reported the oxygen partial pressure effects during anneals.$^{3,7,19}$ Another possibility is hydroxides, produced during deposition (not shown in equations above, but discussed elsewhere)$^{20}$ or introduced by post-deposition absorption from the ambient$^{17}$ shown in equation (7). Recent results of Y-silicate films that were capped in-situ with poly-Si before annealing, which can effectively eliminate reaction (5)-(8), and significantly reduce interfacial SiO$_2$ (<0.5 nm) as compared to uncapped films (~2 nm
observed here). Oxidation in uncapped films is consistent with significant oxidation resulting from H₂O absorption or residual O₂ diffusion.

Regarding formation of yttrium silicate, there are also several possible routes. During deposition, a likely mechanism for initial substrate oxidation is that reaction intermediates from the dissociation of the yttrium precursor react with the substrate to form suboxides that could further incorporate metal, leading to the silicate structure, as shown in reaction (2). Reaction intermediates need not react directly with silicon to explain the observed results. It is also possible that intermediates or the metal oxide itself enhances the rate of silicon oxidation, by assisting in the dissociation and/or diffusion of oxygen by charge enhanced processes. However, if such charge enhanced diffusion processes exist, it is not clear if the interface structure would depend strongly on substrate doping type and density. To date, no clear trend has been observed.

Diffusion of Si through the interface layer could also play an important role in interface silicate formation, as shown in reaction (3), although metal diffusion may also occur. The EELS data indicates the gradient of the yttrium concentration increases and the silicon concentration decreases as the distance from the interface increases, consistent with Si diffusion and reaction. To account for the observed profiles, the silicon diffusion would have to be fast through initial silicate layer during deposition, and some diffusion of the metal would also be required. Silicon atoms could diffuse through the yttrium silicate layer and react with excess oxygen (e.g. OH) in the film or in the N₂ ambient. The importance of silicon diffusion is consistent with the results of the N₂ and O₂ pretreatment studies discussed above. The pretreatments lead to films with a larger Y/Si ratio, and promote formation of Y₂O₃ films. This is consistent with interface N
decreasing the rate of Si diffusion from the substrate into the deposited dielectric. For the 
O$_2$ pretreatment case, the dense thin SiO$_2$ preformed could also reduce the Si diffusion 
rate. Results of the same Y-silicate films that were capped in-situ with poly-Si before 
annealing indicate that significant silicate is formed, also implying silicon diffusion 
during deposition occurs.$^{22}$

With the data presented here, two mechanisms that govern silicon diffusion can 
be described. One possibility is that the extent of silicon intermixing is determined by the 
rate of silicon diffusion through the amorphous interface layer, and crystallization 
proceeds in the region where Si concentration is sufficiently low. A second possibility is 
that the extent of silicon diffusion is determined by the rate of Y$_2$O$_3$ crystallization, where 
silicon inter-diffusion and reaction with the crystalline Y$_2$O$_3$ layer is slow. Recent EELS 
analysis of Y silicate films with various thicknesses indicates that the first possibility is 
more likely than the second.

6.5 SUMMARY AND CONCLUSIONS

Remote oxygen plasma assisted CVD of thin Y$_2$O$_3$ films by using two yttrium 
diketonate precursors are described. The F-containing precursor produces films with 
fluorine that leads to unacceptable electrical properties. The hydrogenated precursor, on 
the other hand, avoids the problems with the F-contained precursor. After anneal a triple 
layer structure with stoichiometric Y$_2$O$_3$ on top and yttrium silicate and SiO$_2$ at 
dielectric/Si interface has been observed by XPS, HRTEM/EELS, FTIR, XRD, and 
AFM. A substantial consumption of silicon substrate is directly observed, likely 
involving both SiO$_2$ and yttrium silicate formation. Formation of SiO$_2$ mainly occurs
during post-deposition annealing resulting from H$_2$O absorption or residual O$_2$ diffusion. Reactions of reactive intermediates formed on the deposition surface during precursor dissociation with diffused Si likely result in yttrium silicate formation. Further experiments involved distinguishing excess O sources are needed to fully understand the process.

6.6 ACKNOWLEDGEMENT

The authors thank Dr. Jon-Paul Maria at NC State for XRD analysis and Dr. Gerry Lucovsky and Bruce Rayner for far-IR analysis. The funding is from SRC/SEMATech Center for Front End Processes and NSF Grant CTS-0072784.
6.7 REFERENCES


21. S. Campbell, *(private communication).*

**Figure 6.1** Schematic of remote plasma enhanced CVD system.
Figure 6.2a  XPS O 1s spectra for films from fluorinated precursor:

(1) “thin sample” (~50 Å) deposited with plasma power 5 W;  (2) “thick sample” (~1000 Å) with plasma power of 5 W; (3) “thick sample” (~1000 Å) with plasma power of 10 W; (4) “thick sample” (~1000 Å) with plasma power of 25 W.
Figure 6.2b  XPS Y 3d spectra for films from fluorinated precursor.
Figure 6.2c  XPS Si 2p spectra for films from fluorinated precursor.
Figure 6.3  C-V result of a film from fluorinated precursor Y(HFAA)$_3$. Large hysteresis (~0.9 eV) indicates the presence of oxide-trapped charges.
Figure 6.4a  XPS O 1s spectra for films with different thicknesses from hydrogenated precursor.
Figure 6.4b  XPS Y 3d spectra for films with different thicknesses from hydrogenated precursor.
Figure 6.4c  XPS Si 2p spectra for films with different thicknesses from hydrogenated precursor.
Figure 6.5a TEM image of the film deposited at 400°C for 3 min and annealed at 900°C for 1 min. The thickness is about 65 Å.
Figure 6.5b  ADF image of the film deposited at 400°C for 3 min and annealed at 900°C for 1 min. The thickness is about 65 Å.
Figure 6.5c  EELS shows Si L-edges measured across the film. The locations correspond to those on the TEM image.
Figure 6.6  C-V results of a film from hydrogenated precursor Y(TMHD)$_3$. Negative flatband shifts indicate the presence of positive fixed charges. Flatband voltage $V_{fb}$ does not change with film thickness.
Figure 6.7  Mid and Far IR spectra of as-deposited and annealed films. As-deposited film shows significant OH and C and broad feature of Y-O. The OH and C peaks are almost completely removed after anneal. Y-O triplet peaks become very sharp, indicating crystallization of the film.
Figure 6.8  XRD results of films from hydrogenated precursor. (1) after anneal at 900°C in N₂, clear features of crystallized Y₂O₃ observed; (2) as-deposited, no clear features.
Figure 6.9a  AFM image of the as-deposited sample with roughness $\sim$3.9 Å.
Figure 6.9b  AFM image of the annealed sample with roughness ~7.6 Å.
Figure 6.10a XPS O 1s spectra for films deposited using hydrogenated precursor on: (1) bare Si; (2) nitrided Si; (3) oxidized Si.
Figure 6.10b XPS Y 3d spectra for films deposited using hydrogenated precursor on: (1) bare Si; (2) nitrided Si; (3) oxidized Si.
Figure 6.10c  XPS Si 2p spectra for films deposited using hydrogenated precursor on: (1) bare Si; (2) nitried Si; (3) oxidized Si.
Figure 6.11a TEM of Y₂O₃ on nitrided Si. The thickness is about 70 Å.
Figure 6.11b  EELS spectra of Y$_2$O$_3$ on nitrided Si taken at various distances from the substrate: (i) the bulk of the substrate; (ii) 1.0 nm from the substrate; (iii) 2.3 nm from the substrate; (iv) 5.5 nm from the substrate.
Figure 6.11c  Si concentration depth profile of Y$_2$O$_3$ on nitrided Si.
Figure 6.12  Illustration of the substrate consumption. (a) as-deposited.

The step from Si to $Y_2O_3$ is $\sim$500 Å; (b) annealed at 900°C in N$_2$. The step from Si to $Y_2O_3$ is $\sim$240 Å; (c) HF etching of part of the film deposited. The second step from Si to $Y_2O_3$ is $\sim$525 Å, indicating $\sim$285 Å Si is consumed.
We use electron energy-loss spectroscopy (EELS) in scanning transmission electron microscopy to investigate interfacial reactions of chemical vapor deposited (CVD) \( \text{Y}_2\text{O}_3 \) films with the Si substrate and with \textit{in-situ} polycrystalline Si (“poly-Si”) capping layers after post-deposition annealing. We find that \textit{in-situ} capping layers significantly reduce the formation of SiO\(_2\) at the interface with the substrate, but silicates form at the substrate and the capping layer interfaces. Pre-deposition nitridation of the Si surface can impede
the reaction at the substrate interface, resulting in crystallization of Y$_2$O$_3$ in the film interior. Possible mechanisms of the silicate formation are discussed.
7.1 INTRODUCTION AND APPROACH

Rare earth oxides and silicates are attractive candidates to replace SiO₂ as gate dielectric in aggressively scaled complementary metal-oxide-semiconductor (CMOS) devices. For example, Y₂O₃ has a dielectric constant (k) of ~ 16-18, which is greater than that of SiO₂ (k = 3.9), is potentially thermodynamically stable in contact with silicon (see ref.¹ and references cited therein), and the offsets of its valence and conduction bands with respect to silicon are high.² Many research groups have reported SiO₂ formation at the interface between silicon and high-k oxides during high temperature anneals in oxygen containing atmospheres.³⁻⁷ Thick interfacial SiO₂ layers limit the achievable capacitance densities. Oxygen diffusion through the high-k oxides as well as reactions with OH or related species in films exposed to atmospheric conditions⁸ are thought to promote this reaction. Y₂O₃ strongly adsorbs and reacts with water.⁹ Capping layers, such as silicon, that are deposited in-situ, immediately following the gate dielectric deposition, can minimize SiO₂ formation, by preventing oxygen diffusion during annealing and/or reducing the uptake of OH species.¹⁰ In addition to interfacial SiO₂ formation, reactions of rare-earth oxides, such as Y₂O₃, with silicon to form silicates have been reported.⁵,¹¹ Nitridation of the Si surface prior to deposition can impede this reaction.¹² Controlling and understanding these interfacial reactions is of great scientific and technological interest. For example, poly-Si gate electrodes are likely to be employed in next-generation CMOS using high-k oxides. In this letter we report on reactions of Y₂O₃ with the silicon substrate and silicon capping layers after post-deposition, high-temperature anneals using electron energy-loss spectroscopy (EELS)
with sub-nanometer spatial resolution in scanning transmission electron microscopy (STEM).

P-type Si (100) substrates were cleaned with a JTB-100 Baker solution and dipped in 10:1 buffered HF solution. Films were either deposited directly on clean Si, or after a nitridation step, respectively. Nitridation was performed in-situ at 400 °C by exposing the Si surface to a N₂ plasma for 20 minutes prior to Y₂O₃ deposition. Y₂O₃ was deposited by oxygen plasma assisted CVD using tris(2,2,6,6-tetramethyl-3,5-heptanedionato)yttrium (Y(TMHD)₃) introduced downstream from an O₂ plasma. The substrate temperature was between 350 and 450°C and the pressure was 0.2 torr during deposition. A Si capping layer was deposited on the dielectric at 500°C, using plasma excited helium and downstream silane, without exposing the film to air. After deposition, the samples were annealed ex-situ at 900 °C in N₂ (with > 10⁻⁵ torr O₂) for 1 min. The Si capping layer crystallized during deposition and/or anneal. High-resolution transmission electron microscopy (HRTEM) was performed using a JEOL 2010F field-emission transmission electron microscope (TEM) equipped with annular dark field detectors and a Gatan imaging filter for EELS. For EELS and atomic resolution high-angle annular dark field (ADF) imaging, the microscope was operated in STEM mode, using a probe size of approximately 0.2 nm. The ADF image was used to precisely position the probe at different locations across the Si/dielectric/poly-Si stack, to record the EELS spectra.

7.2 RESULTS

Figure 7.1 (a) shows a HRTEM image of a ~14 nm thick film on bare silicon. The film is mostly amorphous. The small crystallite in the middle of the film shown in
Fig. 7.1 (a) was one of two observed in this TEM sample. Figure 7.1 (b) shows an ADF image of the gate dielectric stack. A less than 0.5 nm wide dark layer at the film/substrate interface can be observed and is due to an extremely thin interfacial SiO$_2$ that is not visible in HRTEM. The layer appears darker in ADF than the rest of the film, which contains Y, because the contrast in ADF is roughly proportional to the square of the atomic number. A thin dark (~0.5 nm) layer was also observed at the film/poly-Si interface. Figure 7.1 (c) shows an EELS line profile of the Si L-edge across the dielectric. The profile was obtained by integration over a suitable energy window after background subtraction and normalizing to the counts in the Si substrate. The concentration of Si in the film decreases away from the Si substrate surface and then increases again near the interface with the poly-Si capping layer, indicating significant reaction of the Y$_2$O$_3$ film with both Si interfaces to form an amorphous silicate during the anneal. Except for one location, significant amounts of Si (Si counts $>$10% of bulk Si counts) can be detected in the film interior. The amount of Si in the film was sufficient for the film to have a mostly amorphous structure, as pure Y$_2$O$_3$ would crystallize below 900 °C. Figure 7.1 (d) shows a HRTEM micrograph of the film grown on nitrided Si under identical deposition conditions and time as the film on bare Si. The entire thickness of the dielectric is about 11 nm, which is ~3 nm less than the film on bare Si. The interior of this film is crystallized, suggesting little Si in Y$_2$O$_3$, whereas the interfacial regions with Si and poly-Si are amorphous, and about 1.8 nm and 2.6 nm wide, respectively. The dark layer at the Si interface in the ADF image in Fig 7.1 (e), related to SiO$_2$, is about 0.5 nm. The concentration profile of Si across the dielectric is also shown in Fig. 7.1 (c). In the film interior (crystallized region) the Si concentration is
below the detection limit of the method, consistent with the observation that the film crystallizes if the Si concentration is low. Furthermore, the Si concentration away from the Si substrate interface decreases more quickly than at the poly-Si interface. Taking the position where the Si counts are above 10% of the bulk Si value as a measure, the interfacial reaction layer is about 2 nm wide at the Si interface, and about 2.5 nm wide at the poly-Si interface, consistent with the widths of the crystallized parts of the film.

7.3 DISCUSSION AND CONCLUSIONS

The results show that in-situ capping layers can successfully prevent extensive SiO$_2$ formation at the interface with Si. The extremely thin (<0.5 nm) SiO$_2$ layer observed here might have formed after substrate cleaning, or due to a reaction with small amounts of excess O in the films or the deposition process. During annealing, and possibly already during deposition, Y$_2$O$_3$ reacts with both the Si substrate and the poly-Si electrode to form a silicate. The Si profiles and crystallization behavior show that this reaction can be impeded at the substrate interface by a pre-deposition nitridation step that likely slows the Si diffusion from the substrate. Furthermore, the reduced overall film thickness of the dielectric on nitrided Si compared to the film on bare Si is a further indication of the impeded reaction of the pre-nitrided samples, as less silicate is formed for this film. The silicate formation reaction is interesting because it should require excess oxygen. Other authors have observed silicate formation at the upper (capping layer) interface in Y$_2$O$_3$ deposited in ultra-high vacuum by physical vapor deposition, but not at the Si substrate. $^{10}$ The difference to our observation could be due to excess O or OH species present in the low-temperature CVD environment (and incorporated in the
film). Alternatively, the observed silicate and yttria phases could be nonstoichiometric. If excess oxygen introduced during the CVD deposition process is responsible for the silicate formation, it is not sufficient to cause extensive SiO$_2$ formation. Films deposited in the same reactor, but capped with Al after air exposure, show much thicker (~ 2nm) interfacial SiO$_2$ (or Si-O-H) layers.$^{14}$ Recent thermodynamic data shows that the reaction to form Y-silicates from the binary oxides is exothermic.$^{15}$ Therefore, interfacial SiO$_2$ in uncapped or *ex-situ* capped CVD samples probably forms once the silicate reaction is completed and enough excess oxygen is available, or if silicate formation is kinetically limited, for example by the rate of Si diffusion from the substrate. Further measurements, in particular of the as-deposited film stoichiometry, are necessary to clarify the silicate reaction mechanism.

### 7.4 ACKNOWLEDGEMENTS

The authors thank the SRC/SEMatECH Front End Process Center for support. Susanne Stemmer gratefully acknowledges the use of the STEM facilities at the RRC at the University of Illinois at Chicago (NSF DMR-960172) and Greg Parsons acknowledges support from NSF (CTS-0072784).
7.5 REFERENCES


Figure 7.1 (a) HRTEM micrograph of the film grown on bare Si. (b) Annular dark-field image (filtered) of the film on bare Si. (c) EELS line profiles of across (b) and (e) for the Si L edge as a function of distance from the Si substrate interface. Open squares are from the film on bare Si, circles from the film on nitrided Si. Note that the films have different thickness (the position of the interfaces and layers are indicated as a guide). (d) HRTEM of the film on nitrided Si. (e) Annular dark-field image of the film on nitrided Si.
ABSTRACT

In this article, we report nitridation of chemical vapor deposited yttrium oxide using N₂ plasma during deposition and post-deposition treatments, in efforts to create yttrium oxynitride that would display better thermal stability and electrical properties than those of yttrium oxide. Chemical bonding, concentration, and distribution of N in Y₂O₃ films after deposition and after high-temperature anneal were characterized using X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy, and Auger
electron spectroscopy. Analysis of the interfacial structures indicates that the use of N\textsubscript{2} instead of O\textsubscript{2} in the plasma source reduces the oxygen concentration in the deposition ambient and minimizes the substrate oxidation. C-N is likely the main form of nitrogen bonding in the as-deposited films, and IR results indicate exchange of N with O to form C-O bonds occurs during prolonged exposure to the air. Y\textsubscript{2}O\textsubscript{3} films deposited using diluted N\textsubscript{2} plasma show increased N incorporation, primarily as C-N. High-temperature annealing results in the release of N from the surface of as-deposited Y\textsubscript{2}O\textsubscript{3} films and results in a film structure that is resistant to N incorporation. Yttrium oxynitride may be inherently unstable, especially in contact with moisture.
8.1 INTRODUCTION

The continuous shrinkage of complimentary-metal-oxide-semiconductor (CMOS) devices requires aggressive scaling of gate dielectrics. According to the updated International Technology Roadmap for Semiconductors, gate dielectrics with a thickness equivalent to 1 nm SiO$_2$ will be needed within 3-5 years. For SiO$_2$ with this thickness, direct tunneling currents due to quantum mechanical effects through the oxide would be too high, leading to power dissipation and reliability problems. Intense research has been focused on high dielectric constant (high-k) materials as replacements for SiO$_2$. Metal oxides, including Al$_2$O$_3$, Y$_2$O$_3$, HfO$_2$, ZrO$_2$, and La$_2$O$_3$, which are thermodynamically stable with silicon, have been investigated. However, formation of interfacial layers is commonly observed during deposition or post-deposition anneals of these metal oxides. The oxidizing agent such as O$_2$, N$_2$O, or H$_2$O used during deposition, or present in the annealing ambient, is believed to be the cause of substrate oxidation forming SiO$_2$ or metal silicate. Dopant penetration is an important issue when using polycrystalline silicon (poly-Si) as the gate electrode. Park et al. have shown that boron can diffuse through 50-80 Å Al$_2$O$_3$ to the channel causing large flatband shifts (~1.54 V). Boron diffusion in HfO$_2$ has also been observed. The need to control boron penetration has recently inspired study of nitridation of gate dielectrics. Nitridation of the top layer of HfO$_2$ can effectively block boron diffusion. N incorporation in Hf silicate not only blocks boron diffusion, but also prevents the silicate from phase separating even after an 1100°C anneal for 60 seconds, while Hf silicate is phase-separated after annealed at 1000°C. Nitrided ZrO$_2$ remains amorphous after annealed at 800°C for 5 minutes.
High-k dielectric/silicon interface quality is crucial to electrical performance of MOS field-effect-transistors (MOSFETs). To date, most high-k’s have shown positive or negative flatband shifts which are presumably caused by fixed charges. Large fixed charge densities can cause severe degradation of channel mobility and reduction of drive current. N incorporation into high-k metal oxides may provide a way to control the flatband shifts by modifying the defect structures in the bulk and/or at the interface.

For SiO$_2$, in order to block dopant penetration and improve the reliability simultaneously, a concentration distribution with a large amount of nitrogen at the dielectric/poly Si interface and a small amount of nitrogen (less than 1 at.%) close to the substrate/SiO$_2$ interface is commonly employed.$^{14}$ It is reasonable to believe that the N concentration distribution is also important for metal oxynitrides to achieve optimal electrical performance. Another issue is the bonding environment of incorporated N atoms in metal oxynitrides.

In this article, we report chemical vapor deposition of Y$_2$O$_3$ using a Y-diketonate downstream from plasma excited N$_2$ with a goal of producing yttrium oxynitride. We find that the use of N$_2$ instead of O$_2$ reduces the oxygen concentration in the deposition ambient and minimizes the substrate oxidation. Chemical bonding, concentration, and distribution of N in Y$_2$O$_3$ films after deposition and after high-temperature anneal were studied using X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), and Auger electron spectroscopy (AES). Methods to increase N incorporation, including diluting N$_2$ plasma with helium and post-deposition N$_2$ plasma nitridation, were also investigated.
8.2 EXPERIMENTAL

$Y_2O_3$ films with 60-500 Å thicknesses were deposited in a remote plasma chemical vapor deposition (CVD) system. A $\beta$-diketonate precursor, tris(2,2,6,6-tetramethyl-3,5-heptanalidionate)yttrium ($Y(TMHD)_3$), was used as the Y precursor, which was introduced into the reactor downstream to a $N_2$ plasma. For comparison, some films were deposited using $O_2$ plasma. To change the N incorporation rate, $N_2$ plasma diluted with helium (He) was also used. The flow rate of $N_2, N_2 + He$, or $O_2$ was always maintained at 100 sccm during deposition. The substrate temperature was fixed at 400°C during deposition. The substrates were cleaned with a JTB-100 baker clean solution for 5 minutes, followed by 5-minute deionized (DI) water rinse and 30-second dip in 10:1 buffered HF solution before being immediately transferred to the loadlock chamber without final DI water rinse. After deposition, the films were annealed ex-situ in $N_2$ ambient in a quartz tube.

Thin (<150 Å) films were analyzed using X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). Relative thick films (~500 Å) were analyzed using Fourier transform infrared spectroscopy (FTIR).

XPS was conducted on a Riber LAS 3000 with a MAC2 analyzer. Non-monochromatic Mg K$_\alpha$ X-rays (1253.6 eV) were used for all measurements. Survey and detailed spectra were obtained with 1.0 and 0.1 eV step sizes respectively. AES surface scans were conducted using a Scanning Auger Microprobe (Physical Electronics 11-010) with the incident electron energy set at 3 keV. AES depth profile was measured using a Scanning Auger Microprobe (Physical Electronics 660) at Evans East. The energy of incident electron beam was 5 keV. A 3 keV Ar$^+$ ion beam was used to sputter the film
for the depth profile measurement. FTIR was performed on a Nicolet Magna 750 equipped with a KBr detector capable of reading from 4000 to 400 cm\(^{-1}\). Mid-IR (a wavenumber range of 4000-400 cm\(^{-1}\)) spectra were collected on double-side polished substrates with resistivities > 15 Ω·cm. The resolution and number of scans were set at 4 cm\(^{-1}\) and 256, respectively.

8.3 RESULTS

8.3.1 Comparison of Yttrium Oxide Deposited with O\(_2\) and N\(_2\) Plasma

Figure 8.1 shows the infrared (IR) spectra in the 4000-2500 cm\(^{-1}\) range for CVD Y\(_2\)O\(_3\) films deposited downstream from (1) an O\(_2\) plasma or (2) a N\(_2\) plasma. After deposition, films were exposed to the atmosphere for various times. Considering first the region between 4000 and 2500 cm\(^{-1}\), the spectra for the O\(_2\) and N\(_2\) plasma films show several similarities, including: the broad O-H stretching mode (3700-2700 cm\(^{-1}\)) and the methyl group C-H stretching modes at 2966 and 2877 cm\(^{-1}\). The film deposited with N\(_2\) plasma also shows additional features at ~3450 and ~3340 cm\(^{-1}\), which can be assigned to primary amine N-H asymmetric and symmetric stretching modes. In both sets of spectra, the O-H stretching mode peak increases as the film is exposed to ambient for longer times. This suggests that water vapor present in the ambient is being absorbed into the films, regardless of whether N\(_2\) or O\(_2\) is used as the deposition plasma.

Figure 8.2 shows the O-H peak area between 3750-2700 cm\(^{-1}\) from the IR spectra in Figure 8.1 plotted versus exposure time in ambient for films deposited with O\(_2\) and N\(_2\) plasma. The integrated area of the peaks between 3750 and 2700 cm\(^{-1}\) includes the peaks associated with C-H (in both films) and N-H stretching modes (observed in the N\(_2\) plasma
These additional overlapping peaks may have a small effect on the total peak area, and this influence will be discussed below. The rates of increase in OH concentration for films deposited with N$_2$ and O$_2$ plasma are quite similar, with a slightly smaller rate of increase for the N$_2$ plasma film.

Figure 8.3 shows XPS Si 2$p$ spectra for Y$_2$O$_3$ thin films deposited using O$_2$ and N$_2$ plasma. The film thicknesses are ~60 Å for both O$_2$ and N$_2$ plasma films. The spectra shown are for as-deposited films and films annealed at 600, 700, 800, and 900°C in N$_2$ for 1 minute. In both sets of spectra, two distinct features are observed at 102.4-102.6 and 99.3 eV, which correspond to Si-O (in Y-O-Si) and silicon substrate signals, respectively. For the as-deposited film, the Si-O peak intensity for the O$_2$ plasma film is significantly greater than the same peak for the N$_2$ plasma film, consistent with much less substrate oxidation when using N$_2$ plasma deposition. For the annealed films, the Si-O peak intensity increases and the silicon substrate peak intensity decreases as the anneal temperature increases.

The XPS spectra from Figure 8.3 were used in the creation of the Arrhenius plot shown in Figure 8.4. This figure plots the ratio of the change in intensity of the Si-O peak (~102.5 eV) to that of the substrate peak (99.3 eV) versus the inverse of anneal temperature. The slope of the line fit to the data allows for the extraction of an apparent activation energy for the Si-O bond formation process. The apparent activation energy was found to be 0.33 eV for films deposited with O$_2$ plasma and 0.37 eV for films deposited with N$_2$ plasma.
8.3.2 Chemical Structure and Properties of $Y_2O_3$ Films Deposited with $N_2$ Plasma

Figure 8.5 shows the infrared absorbance spectra for yttrium oxide films (~500 Å thick) deposited at 400°C with $N_2$ plasma. Spectra for an as-deposited film, a film annealed at 900°C in $N_2$ for 1 minute, and an as-deposited film with an in-situ amorphous silicon ($a$-Si) capping layer are shown. Spectrum (1), for an as-deposited film that had been exposed to ambient for 4 hours before the measurement, shows a large group of peaks in the 3700-2700 cm$^{-1}$ range. These peaks are similar to the $N_2$ plasma film in Figure 8.1, including the O-H stretching and the symmetric and asymmetric C-H and N-H stretching modes. Additionally, three peaks are observed at 2187, 2130, and 2035 cm$^{-1}$ which correspond to the nitrile C≡N stretching mode and isocyanate N=C=O stretching modes.$^{17}$ Another broad set of peaks is observed in the range of 1700-1200 cm$^{-1}$, with individual peaks occurring at 1660, 1545, 1490, 1420, 1380, and 1230 cm$^{-1}$. These peaks are associated with overlapping peaks from the H$_2$O bending modes, asymmetric and symmetric C(=O)$_2$ stretching modes in carboxylate groups, C-H bending modes in methyl groups, and the carbonyl C=O stretching mode. Another peak(s) in the range from 1650-1600 cm$^{-1}$ appears as a shoulder and is associated with the N-H bending of an amine. These peak assignments account for all readily visible peaks and shoulders in this range, although the complexity of the grouping could allow for the presence of other peaks that are not easily discernable. Curve fitting and deconvolution attempts failed to produce reliable results of peak positions and intensities. The large negative feature at 1107 cm$^{-1}$ is a result of the subtraction of the substrate spectrum from the sample spectrum. Spectrum (2) shows the IR data from a film deposited under the same conditions as (1), but which was also annealed ex-situ in $N_2$ at 900°C for 1 minute. The
spectrum was taken after the film had been exposed to ambient for 21 days. In contrast to the as-deposited film, the annealed film shows no distinct features in the 4000-1650 cm\(^{-1}\) range. A grouping of peaks of weak intensity is observed in the 1700-1200 cm\(^{-1}\) range. Similar to the as-deposited film, these peaks can be correlated to the stretching modes of carboxylate and carbonyl groups. The broad feature that is observed in the 1050-775 cm\(^{-1}\) range can be attributed to the Si-O stretching mode in yttrium silicate (Si-O-Y) and SiO\(_2\). This peak is due mainly to silicate bonding because the Si-O stretching mode in silicon dioxide exhibits a strong peak at 1077 cm\(^{-1}\), which is not seen in this spectrum. Spectrum (3) is data taken from an yttrium oxide film deposited under the same conditions as (1), but the film also underwent an in-situ a-Si capping process before exposure to the air which resulted in an yttrium oxide film with ~500 Å of a-Si on top. The a-Si deposition was conducted for one hour at 500°C using 2% silane diluted with helium. The capped film shows no distinct features above 2200 cm\(^{-1}\). The large peak that occurs at ~2017 cm\(^{-1}\) is the Si-H stretching mode that arises from the a-Si capping layer. A small shoulder is present on the Si-H peak at ~2200 cm\(^{-1}\), consistent with a C≡N stretching mode. It is presumed that small peaks are also present at ~2130 cm\(^{-1}\) and ~2035 cm\(^{-1}\), due to C-N bonding at a smaller concentration than that observed in the as-deposited film, spectrum (1). The large Si-H peak masks the less intense C-N peaks in the same range. Another set of peaks between 1700 and 1200 cm\(^{-1}\) creates a complex feature that is similar to the annealed film. This is again correlated to various C-O bonds of the carbonyl and carboxylate groups. Similar to the annealed film, the capped film shows a large, broad feature between 1050 and 775 cm\(^{-1}\) that can be attributed to Si-O stretching
in yttrium silicate. The yttrium silicate is formed at the $Y_2O_3/Si$ and $Y_2O_3/\alpha$-Si interfaces.$^{19}$

The most notable aspect of the spectra of the two films deposited using $O_2$ and $N_2$ plasma is the behavior of the array of peaks at 1700-1200 cm$^{-1}$ and the C-N peaks (2250-1950 cm$^{-1}$), as shown in Figure 8.1. The C-O peaks for the film deposited with $O_2$ plasma do not change with exposure time in ambient. For the film deposited with $N_2$ plasma, as exposure time in ambient increases, the C-N peaks decrease with time and the C-O peaks (1700-1200 cm$^{-1}$) increase. This suggests that the C-N bonds within the N$_2$ plasma film are unstable when exposed to H$_2$O or O$_2$ present in ambient at room temperature.

Figure 8.6 shows a plot of the areas of several peaks, or groups of peaks, as taken from the IR spectra of the $N_2$-plasma film in Figure 8.1, plotted as a function of exposure time to the ambient. The wavenumber ranges over which the peak areas were measured were 2275-1925 cm$^{-1}$ for the C-N peaks and 1730-1250 cm$^{-1}$ for the C-O peaks. It should be noted that the C-O peak area also includes the peak areas of the amine N-H bending and the methyl group C-H bending modes. The slopes corresponding to the peak area increase/decrease of the C-O and C-N peaks for the N$_2$ plasma film are approximately equal with opposite signs.

Figure 8.7 shows the XPS O 1$s$ (a), N 1$s$/Y 3$s$ (b), and Y 3$d$ (c) spectra for films deposited with $N_2$ plasma. The film thicknesses are ~500 Å. Spectrum (1) corresponds to an as-deposited film and spectrum (2) corresponds to a film annealed ex-situ for 1 minute at 900°C in a $N_2$. The annealed film shows structure consistent with $Y_2O_3$. There is a peak at 529.8 eV in the O 1$s$ spectrum, a peak at 394.8 eV in the Y 3$s$ spectra, and a
doublet corresponding to the $3d_{5/2}$ and $3d_{3/2}$ features of Y$_2$O$_3$ at 156.9 and 158.8 eV in the Y 3d spectrum. The as deposited film, however, shows very different structure. The data shows two features at 532.6 and 530.2 eV the O 1s spectrum, peaks at ~399.6 and ~395.2 eV in the N 1s and Y 3s spectra, and peaks at 158.1 and 160.1 eV in the Y 3d spectrum. For the as deposited film the observed O 1s and Y 3d spectra are consistent with OH groups present in the film, and the N 1s is consistent with C-N (and/or N-O) bonding. The shift of the Y 3d may also result from a small amount of fluorine (~2-3 at.%) observed in the XPS survey scan, which is residual in the deposition chamber from previous experiments with fluorinated precursors. Upon annealing, the XPS results are consistent with release of OH, N and F from the film.

Figure 8.8 shows the AES spectra for a thin film (~100 Å) deposited with N$_2$ plasma for 6.5 minutes. After deposition, the film was transferred in air, and the AES spectrum was taken, as shown by the bottom curve. This film was then transferred in vacuum to a nitridation chamber, and underwent a post-deposition nitridation process at 300ºC for 60 minutes in N$_2$ plasma. The resulting spectrum is the middle curve in Figure 8.8. Finally, the film was annealed in-situ at 900ºC in N$_2$ for 1 minute and the spectrum is shown by the top curve. All three spectra in Figure 8.8 show the characteristic oxygen (509 eV) and yttrium (122 eV) with small overlapped signals of Y and Si in the range of 70-110 eV. The bottom and middle spectra show small features at 272 and 379 eV, which correspond to carbon and nitrogen signals, respectively. The nitrogen signal after post-deposition nitridation is slightly larger (~8%) than after deposition (~6%), indicating a small increase in the nitrogen content for the post-deposition nitrided film. The N concentrations were estimated using the following equation$^{20}$:
Where $I_i$ and $S_i$ are the peak-to-peak intensity and sensitivity factor for species $i$. Upon annealing the films in $N_2$ at 900°C for 1 minute, the nitrogen signal decreases below the detection limit (0.1-1%). The small carbon peak may be due to adventitious hydrocarbon from the atmosphere.

Figure 8.9 shows the concentration profiles obtained from sputter depth profiling for yttrium, oxygen, nitrogen, and silicon for a film deposited for 6.5 minutes (~ 100 Å thick) using $N_2$ plasma and annealed at 900°C for 1 minute in $N_2$. The numerical values for the sputter depth are calculated using the sputtering rate of $SiO_2$ ($Y_2O_3$ standards not available). This figure shows that the annealed films are devoid of nitrogen at the surface, which is consistent with the AES surface survey, but still contain a small amount of nitrogen near the silicon/dielectric interface. The concentrations for yttrium and oxygen indicate an oxygen rich structure, but the values were obtained using the sensitivity factors for elemental species, and not species present in $Y_2O_3$.

Figure 8.10 shows capacitance-voltage measurements taken on films deposited with $N_2$ and $O_2$ plasma. Before measurement, both films underwent annealing at 900°C for 1 minute in $N_2$ (with some background $O_2$ ~10⁻⁴ torr) but neither film underwent a post-metallization forming gas anneal. The flatband voltages for both films determined by fitting the C-V curves using a program that includes the quantum mechanical effect are shifted to the negative direction with a slightly more negative shift (40 mV) for the film deposited with $N_2$ plasma. The negative flatband shifts indicate the presence of positive fixed charges. A hysteresis of ~0.1 V is also observed for both films. These

$$[N] = \frac{I_N/S_N}{I_N/S_N + I_O/S_O + I_Y/S_Y + I_C/S_C}$$  \hspace{1cm} (1)
results show that the small percentage of nitrogen found at the interface (as shown by AES depth profile in Figure 8.9) of annealed films deposited with N₂ plasma does not significantly affect the C-V characteristics of the Y₂O₃ films.

### 8.3.3 Effects of Diluted N₂ Plasma

Based on previous work on plasma CVD of silicon oxynitride,¹⁶ He-diluted N₂ plasma was used to increase N incorporation in Y₂O₃ films. Figure 8.11 shows the IR spectra for (1) a film deposited in a helium-diluted N₂ plasma (He/N₂= 3/1) and (2) a film deposited with 100% N₂ plasma. Both films were deposited at 400°C for 30 minutes and then exposed to ambient for ~15 minutes prior to analysis. The deposition rate for the diluted N₂ plasma was less than that for 100% N₂ plasma, and the resulting sample thicknesses were ~300 Å and 500 Å for the 3:1 He:N₂ and the 100% N sample, respectively. Both films show similar groups of peaks including OH, C-H, and N-H stretching modes between 3700-2700 cm⁻¹, C-N bonding in the range of 2300-1900 cm⁻¹, and another set of peaks (mainly C-O bonding) between 1700-1200 cm⁻¹. The spectra indicate that both films show predominant C-N bonding environments for nitrogen. However, there are several distinct differences between the two spectra. The O-H peak and the C-O peaks for the film deposited with diluted N₂ plasma are slightly smaller than the same peaks for the film deposited with N₂ plasma, consistent with the sample thickness difference. However, the C-N peaks are larger for the thinner film deposited with diluted N₂ plasma, suggesting that the helium-diluted N₂ plasma results in greater nitrogen incorporation into the film. Another interesting feature is that peak ratios in the 2300-2000 cm⁻¹ range are different for the two films. The isocyanate N=C=O stretching
modes (2130 and 2035 cm\(^{-1}\)) are stronger than the nitrile C≡N stretching mode (2187 cm\(^{-1}\)) for the film deposited using diluted N\(_2\) plasma, while the opposite trend is seen for pure N\(_2\) plasma film.

Figure 8.12 shows the AES spectra for films deposited with helium-diluted N\(_2\) plasma. The spectra are for a film annealed at 900\(^\circ\)C for 1 minute in N\(_2\) (bottom) and for an annealed film that underwent a post-anneal nitridation process at 400\(^\circ\)C in N\(_2\) plasma for 30 minutes (top). Both films exhibit only the characteristic C, Y, Si, and O signals. Annealing of the film deposited using diluted N\(_2\) plasma removed the nitrogen from the surface region of the film and left a small carbon signal, similar to the observations for the films deposited with N\(_2\) plasma. No change is observed in the annealed film after the post-anneal nitridation process, which indicates that the annealed films are very stable with respect nitrogen incorporation via N\(_2\) plasma.

8.4 DISCUSSION

8.4.1 Effects of O\(_2\) and N\(_2\) Plasma on Water Absorption and Substrate Oxidation

Control of silicon dioxide and metal silicate formation at the silicon/dielectric interface is an increasingly important issue as the equivalent oxide thickness of the gate stack continues to decrease. It has been shown that yttrium oxide films deposited by CVD using O\(_2\) plasma absorbs moisture very quickly when exposed to the air, and \textit{in-situ} Si capping layers can reduce substrate oxidation at the silicon/dielectric interface by preventing water absorption and slowing O\(_2\) diffusion.\(^{19,22}\) Figures 8.1 and 8.2 show that films deposited using N\(_2\) or O\(_2\)-plasma exposure exhibit a similar increase in the O-H peak area upon exposure to the ambient, with possibly a slightly slower rate of O-H bond
formation in the film deposited from N2-plasma. This suggests that a few atomic percent of nitrogen in the film does not have a significant effect on the water absorption properties.

It is important to compare the rate of substrate oxidation during post-deposition anneals at the silicon/dielectric interface for films deposited with N2 and O2 plasma. As shown in Figures 8.3 and 8.4, the rate of substrate oxidation is thermally activated, with apparent activation energies of Si-O bond formation of 0.33 eV for films deposited with O2 plasma and 0.37 eV for films deposited with N2 plasma. Note that these values are apparent activation energies that likely result from a set of reaction steps and not from one elementary step in the oxidation process. The apparent activation energy for oxidation of the N2-plasma film is slightly larger, which suggests that nitridation of the substrate or dielectric during deposition slows the rate of substrate oxidation.

The silicon substrate can be oxidized during deposition, and/or during post-deposition anneal. The XPS Si 2p results, presented above in Figure 8.3, indicate that during deposition, substrate oxidation can be reduced if the deposition plasma does not contain an oxidizing species. Figure 8.3 shows that the Si-O peak (~102.5 eV) for the as-deposited N2 plasma film is significantly smaller than that for the as-deposited O2-plasma film. For the N2 plasma deposition, the precursor (Y(TMHD)3) serves as the oxygen source during deposition, and without plasma excited oxygen, the precursor dissociation results in available oxidizing species to form SiO2 and silicate.
Nitridation of metal oxide dielectrics has been shown as a way to reduce leakage currents and preserve the amorphous nature of the film during high-temperature processes.\textsuperscript{13} Therefore, nitridation of yttrium oxide could be a way to improve the thermal stability and electrical properties, including flatband and threshold voltage. It should be noted that pure yttrium nitride is unstable in ambient and will react with water vapor to produce ammonia and yttrium oxide;\textsuperscript{23} zirconium nitride undergoes a similar reaction with water, but zirconium oxynitride films created by annealing ZrO\textsubscript{2} in NH\textsubscript{3} have been shown to be stable.\textsuperscript{24}

The IR spectra in Figure 8.1 as well as the XPS and AES spectra in Figure 8.7 and 8.8 all show the presence of nitrogen in the yttrium oxide films deposited using N\textsubscript{2} plasma. It is important to understand the chemical structure and bonding of the films, since the chemical structure and bonding determines the thermal stability, defects structure, and electrical properties. The IR spectra show the presence of C-N bonding of various types by the features between 2300 and 1900 wavenumbers. The XPS spectra show a feature at \textasciitilde399 eV, which is located in the range characteristic of C-N bonding, although N-O bonding is also possible. The AES data further confirms the nitrogen presence with a feature at \textasciitilde375 eV. From the analysis of the films, it is apparent that nitrogen in the film is present in the form of carbon-nitrogen bonds, although other N forms may also exist. The presence of Y-N bonds, which occur below the range characteristic of Y-O bonding (400-300 cm\textsuperscript{-1}), cannot be confirmed by the XPS or mid-IR data. The elimination of nitrogen during anneal, as shown by the IR in Figure 8.1, indicates that the nitrogen within the film is bonded in an unstable form. Also, the
change in C-N and C-O peak intensities upon exposure indicates that the N removal is spontaneous at room temperature. It is presumed that water vapor present in the ambient absorbs into the film and a reaction results in the removal of the nitrogen from the film. Since the IR spectra suggest the nitrogen is bound in primary amines (N-H stretching mode peaks at ~3450 and ~3340 cm⁻¹), it is quite possible that the nitrogen is evolved in the form of ammonia, although N₂ and NOₓ may also be possibilities. The decrease of the C-N grouping and the simultaneous increase of the C-O grouping, suggests that C-N bonds are being converted to C-O bonds through the reaction with water vapor. C-O bond density does not increase with exposure time for the films deposited with O₂-plasma, suggesting that C-O formation is coupled with N elimination in the films deposited from N₂-plasma. Furthermore, assuming similar oscillator strengths for the C-O and C-N bonds, the peak area suggests that for each C-N bond that is broken, one C-O bond is formed. This is shown in Figure 8.6 by the slopes of the C-N and C-O peak area trend lines, which are approximately equal in magnitude and opposite in sign.

8.4.3 Effects of Diluted N₂ Plasma

Although nitrogen was shown to be present in the as-deposited films, stable bonded N is desired to significantly affect film electrical properties. The above results indicate that upon annealing, significant nitrogen is evolved from the surface regions of the films deposited with N₂ plasma, and an Y₂O₃ structure is formed (as indicated by XPS data in Figure 8.7). We therefore investigated post-deposition nitridation as a route to more stable N incorporation. The nitrogen content in Y₂O₃ was seen to increase from ~6 to ~8%, showing that post-deposition nitridation can affect the nitrogen content of as-
deposited films. However, nitrogen evolution upon indicates that the nitrogen is present in an unstable form.

Helium-diluted N₂ plasma has been shown to provide a higher nitrogen content in as-deposited films than pure N₂ plasma.¹⁶ Yttrium oxide films deposited using helium-diluted N₂ plasma, with a He:N₂ ratio of 3:1, did show an increase in the amount of C-N bonding within the film in Figure 8.11. Although the ratio of bonding types does change, the instability of the nitrogen is still a problem. Figure 8.12 shows that annealed films are very stable to post-deposition plasma nitridation.

The instability of N in the deposited films and the resistance of N incorporation into annealed films imply that yttrium oxynitride (O-Y-N) may be inherently unstable, especially in the presence of water. Previous studies of Y-O-N materials formed through high temperature routes,²³,²⁵ indicate that pure Y₃O₅N phases are difficult to achieve. Stable zirconium oxynitride (with N concentration of 3-5 at.%) has been produced by annealing zirconium oxide in ammonia ambient,¹³ suggesting that using ammonia as the nitridation gas, either as a reactant during deposition or as the anneal gas, may be more effective means to produce stable incorporated N in Y-based dielectrics.

8.5 CONCLUSIONS

The use of N₂ as the deposition plasma in place of O₂-plasma excitation for Y-based high-k dielectric deposition from a Y-diketonate precursor does not significantly affect the oxygen content in the deposited film, indicating significant availability and reactivity of the oxygen bond in the precursor. During deposition, the N₂–plasma films had a reduced rate of substrate oxidation. During post-deposition anneals, a slightly
larger apparent activation energy for Si-O bond formation at the substrate interface is observed for films deposited from N2-plasma as compared to films deposited from O2 plasma, consistent with a decreased rate of interface oxidation with nitridation. The hydroxide incorporation rate was approximately the same for N2 and O2-plasma films, indicating similar film density as deposited.

The use of N2 or helium-diluted N2 plasma to deposit films introduces nitrogen in the form of C-N and N-H bonds. The nitrogen in the film is not stable when exposed to the ambient and is evolved via a reaction that results in the decrease of C-N bonding and increase of C-O bonding. Post-deposition nitridation of as-deposited films in N2 plasma increases the nitrogen content of the films, but does not change the inherent instability of the nitrogen. Annealing of films deposited with N2 or diluted N2 plasma removes all nitrogen from the surface regions of the film and produces an Y2O3 structure. Annealed films are quite resistant to N incorporation when in contact with N2 or N2 plasma, and post-anneal nitridation with N2 plasma is not a feasible way to produce an oxynitride structure.

8.6 ACKNOWLEDGEMENTS

The authors thank the funding from SRC/SEMATECH Center for Front End Processes and NSF Grant CTS-0072784. We thank G. Lucovsky for use of his in-situ AES system. R. W. Ashcraft also acknowledges support from the SRC Education Alliance for support of undergraduate research.
8.7 REFERENCES


Figure 8.1 FTIR Spectra of CVD Y$_2$O$_3$ thick films deposited with (1) O$_2$ plasma and (2) N$_2$ plasma and exposed to ambient for various times.
Figure 8.2  O-H peak area (3700-2700 cm$^{-1}$) versus exposure time in ambient for CVD Y$_2$O$_3$ films; (1) film deposited with N$_2$ plasma; (2) film deposited with O$_2$ plasma; peak areas were determined from the IR spectra in Figure 8.1.
Figure 8.3  XPS Si 2p spectra of CVD Y$_2$O$_3$ thin films deposited with O$_2$ and N$_2$ plasma; (1) as-deposited; (2) annealed at 600°C; (3) annealed at 700°C; (4) annealed at 800°C; (5) annealed at 900°C.
Figure 8.4 Arrhenius plot of Si-O/Si peak area ratio versus inverse anneal temperature for films deposited using N\textsubscript{2} plasma (top) and O\textsubscript{2} plasma (bottom) as determined from XPS spectra; the extracted activation energies for each film are displayed.
Figure 8.5 FTIR spectra of CVD Y$_2$O$_3$ films deposited with N$_2$ plasma; (1) as-deposited film exposed to ambient for 4 hours; (2) film annealed at 900°C and exposed to ambient for 21 days; (3) film with an $a$-Si capping layer and exposed to ambient for 6 days.
Figure 8.6  Peak area versus exposure time in ambient for a CVD Y$_2$O$_3$ film deposited with N$_2$ plasma; (1) C-O peaks (1700-1250 cm$^{-1}$); (2) C-N peaks (2250-1950 cm$^{-1}$); peak areas were determined from the IR spectra in Figure 8.1.
**Figure 8.7**  XPS (a) O 1s, (b) N 1s/Y 3s, and (c) Y 3d spectra of CVD Y$_2$O$_3$ thick films deposited with N$_2$ plasma; (1) as-deposited; (2) annealed at 900ºC for 1 min in N$_2$. 
Figure 8.8  AES surface survey spectra of CVD Y$_2$O$_3$ films deposited with N$_2$ plasma. The bottom curve is the spectrum taken after the film was exposed to the air. This film was then transferred in vacuum to a nitridation chamber, and underwent a post-deposition nitridation process at 300°C for 60 minutes in N$_2$ plasma. The resulting spectrum is the middle curve. Finally, the film was annealed *in-situ* at 900°C in N$_2$ for 1 minute and the spectrum is shown by the top curve.
Figure 8.9  AES depth profile of a CVD $\text{Y}_2\text{O}_3$ film deposited with $\text{N}_2$ plasma and annealed ex-situ at 900°C for 1 min in $\text{N}_2$; sputter depth is based on the sputtering rate of $\text{SiO}_2$. 
Figure 8.10  C-V characteristics of CVD Y$_2$O$_3$ films deposited with N$_2$ plasma (solid line) and O$_2$ plasma (dotted line).
Figure 8.11  FTIR spectra of CVD Y$_2$O$_3$ films deposited 
with (1) helium-diluted N$_2$ plasma (3:1 He:N$_2$ 
ratio) and (2) N$_2$ plasma.
Figure 8.12  AES surface survey spectra of CVD Y$_2$O$_3$ films deposited in He-diluted N$_2$ plasma; the bottom spectrum is for a film annealed at 900°C for 1 minute; the top spectrum is for a film that underwent post-annealed nitridation at 400°C in N$_2$ plasma for 30 minutes.

CHAPTER 9

EVIDENCE OF ALUMINUM SILICATE FORMATION DURING CHEMICAL VAPOR DEPOSITION OF AMORPHOUS AL$_2$O$_3$ THIN FILMS ON SI(100)

T. M. Klein, D. Niu, W.S. Epling, and G. N. Parsons

*Dept. of Chemical Engineering, North Carolina State University, Raleigh, NC 27695*

W. Li, and D. M. Maher

*Dept. of Mater. Sci. and Eng., North Carolina State University, Raleigh, NC 27695*

C. C. Hobbs and R. I. Hegde

*Motorola, 3501 Ed Bluestein Blvd. Austin, TX 78721*

I. J.R. Baumvol

*Instituto de Fisica, UFRGS, 91509-900 Porto Alegre, Brazil*

Notes: My contributions to this paper include performing film deposition and involving experimental design.
ABSTRACT

Using narrow nuclear reaction resonance profiling, aluminum profiles are obtained in ~3.5nm Al₂O₃ films deposited by low temperature (<400°C) chemical vapor deposition on Si(100). Narrow nuclear resonance and Auger depth profiles show similar Al profiles for thicker (~18 nm) films. The Al profile obtained on the thin film is consistent with a thin aluminum silicate layer, consisting of Al-O-Si bond units, between the silicon and Al₂O₃ layer. Transmission electron microscopy shows evidence for a two-layer structure in Si/Al₂O₃/Al stacks, and X-ray photoelectron spectroscopy shows a peak in the Si 2p region near 102eV, consistent with Al-O-Si units. The silicate layer is speculated to result from reactions between silicon and hydroxyl groups incorporated in the Al₂O₃ during low temperature deposition.
9.1 INTRODUCTION

The Semiconductor Industry Association roadmap indicates that a sub-1nm oxide will be required for complementary metal oxide semiconductor (CMOS) devices with 50 nm gate widths. However, significant leakage and reliability issues occur with thermal SiO₂ at this thickness, and new high dielectric constant (high-k) materials are being explored. An important factor for any new high-k dielectric is its stability in contact with silicon. Annealing of tantalum oxide thin films [1] on silicon, for example, results in an interfacial SiO₂ layer due to reduction of the Ta₂O₅ [2,3]. An interface layer between the high-k and the silicon can be included to minimize oxidation, but this contributes additional undesired capacitance in the gate stack. Gibbs free energy and ternary phase diagrams can predict oxide compositions that are stable in contact with silicon at elevated temperatures. For example, BeO, MgO, and ZrO₂, are predicted to be stable with silicon at 700°C, consistent with experiments [4,5].

Al₂O₃ is an attractive dielectric because it has a large (9 eV) band gap and large band offsets with silicon, and it is a good barrier to ionic transport. Crystalline Si can be formed on Al₂O₃ without significant reaction between the Si and Al₂O₃ [7], and epitaxial Al₂O₃ films have been deposited on silicon by chemical vapor deposition (CVD) [8] and molecular beam epitaxy (MBE)[9]. A low temperature route to stable high-k/Si interfaces is desired for CMOS devices, but transmission electron microscopy (TEM) analysis of low temperature amorphous Al₂O₃ on Si typically shows a relatively thick intermediate layer [10]. The composition of this layer has not previously been determined. Based on available free energy data for aluminum silicates, including mullite, kyanite, sillimanite, and andalusite [6], the Al₂O₃/Si
interface is expected to be stable to silicate formation. However, kinetics of deposition and interface formation reactions must be considered and analyzed, especially in low temperature processes, to understand interface reactions and achieve optimum material structure.

Advances in ultra-thin high-k/Si interfaces require improved techniques to better understand Si/oxide interface reactions. Depth profiling techniques such as secondary ion mass spectroscopy (SIMS) and sputtered-Auger depth profiling give spatial resolution of 5-10 nm, which is not sufficient for ultra-thin dielectrics. Ion scattering techniques such as Rutherford backscattering spectroscopy and medium energy ion scattering cannot easily distinguish between Al and Si because of their similar atomic mass. This article reports the use of a narrow nuclear reaction resonance profiling (NRP) technique to attain sub-nanometer Al concentration depth profiles in thin Al₂O₃ films deposited on silicon.

9.2 EXPERIMENTAL

Thin Al₂O₃ films were grown by low pressure CVD using triethyldialuminum tri-sec-butoxide (TEDA-TSB) as the Al source [11]. The metal organic was introduced in the reactor by flowing 30 standard cubic centimeters per minute (sccm) of Ar carrier gas through a bubbler heated to 150°C. The reactor pressure was maintained at 0.5 Torr, while 100 sccm O₂ was used as the oxidizing species. The substrates were 1-2 Ω-cm n-type Si(100), cleaned with a J.T. Baker clean solution and dipped in 10:1 buffered HF solution to remove the native oxide prior to deposition. The substrate temperature was 400°C, which resulted in a growth rate of approximately 1 nm/min.
The depth distribution of $^{27}$Al concentration was obtained using the narrow and isolated resonance in the cross sections of the nuclear reaction $^{27}$Al(p, $\gamma$)$^{28}$Si at 405 keV [12]. The measured excitation curves (i.e. $\gamma$-ray yields versus incident proton energy) around the resonance energy ($E_R$) can be converted into concentration versus depth using the SPACES program [13], assuming a density of 3.8 g/cm$^3$ for the stoichiometric Al$_2$O$_3$ film. The width of the nuclear reaction resonance at 405 keV was determined here as being smaller than 40 eV, by measuring the excitation curves for thin and thick aluminum films. For the $^{27}$Al profiling in aluminum oxide thin film on Si, a tilted sample geometry ($\Psi = 55\text{–}65^\circ$) was used to increase the depth resolution. Owing to the combination of an extremely narrow nuclear reaction resonance ($\Gamma \approx 40$ eV), a proton-beam energy stability of 80 eV at 405 keV, and an apparent thickness magnification due to tilting by a factor of 1.7-2.4, a maximum depth resolution of about 0.5 nm near the film surface was obtained [14].

9.3 RESULTS AND DISCUSSION

Figure 9.1a shows the excitation curve of the $^{27}$Al(p,$\gamma$)$^{28}$Si nuclear reaction around the resonance at 405 keV for a thick (18nm) Al$_2$O$_3$ film on Si(100). The inset shows the corresponding aluminum concentration profile with respect to stoichiometric Al$_2$O$_3$, determined by SPACES simulation. A decreasing Al concentration toward the oxide/Si interface is observed, with an average Al concentration less than 50% of the first layer. Figure 9.1b shows the sensitivity and depth resolution of the nuclear resonance technique for a thin (~3.5 nm) Al$_2$O$_3$ film on silicon. The fit to the gamma yield indicates a two-layer Al profile. Figure 9.2 is a sputtered-Auger depth profile of
the same sample shown in Fig 9.1a, showing results similar to the NRP data. Figure 9.3 is a TEM image of the same film, demonstrating contrast between bulk and interface layers. Interface roughness suggests a reaction has occurred at the silicon surface. TEM data of the thin film (not shown) is consistent with the NRP results, indicating a total film thickness of 3.5 nm, made up of two sub-layers of approximately equal thickness.

The near surface region (6-10 nm) of the thick film was characterized using X-ray photoelectron spectroscopy (XPS), resulting in an O/Al atomic ratio of 1.64. For the thin film, the position and shape of the Si 2p peaks shown in Fig. 9.4 are used to probe the composition and structure the Si/Al₂O₃ interface. The peak near 99 and the shoulder near 103.5 eV are assigned to Si⁰ substrate and Si-O bonding in the film, respectively. The peak near 102 eV is assigned to Al-O-Si bonds, confirming that the thin intermediate layer consists of Al-O-Si (silicate) bonding units. The position of the Al 2p peak at 74.7 eV indicates that the Al present in the near-surface region is bound as Al₂O₃. No signal from Al metal is observed. The XPS survey spectrum shows the presence of approximately 20 atomic % carbon. While some carbon is likely residual from the metal organic deposition process, carbon contamination is also expected from the in-air sample transfer to the analysis chamber. This is consistent with the Auger data in Fig. 9.2, where carbon contamination is primarily on the surface. Silicates of Hf and Zr have been shown to have lower dielectric constants than their corresponding Si free oxides [15,16], and electrical analysis of our layers shows similar results for aluminum silicate.
We can speculate on the mechanism for the thin silicate layer formation in the low temperature CVD process. XPS and NRP show excess oxygen in the oxide layer, and infrared indicates OH density is near the detection limit (<0.5at.%). When as-deposited films are annealed, XPS shows an increase in the silicate peak at 102eV, indicating some post-deposition silicate formation. However, substantial silicate formation also occurs during deposition. Excess oxygen available during deposition will tend to oxidize silicon, but the layer is thicker than expected from silicon oxidation kinetics (and from oxidation experiments) at this temperature, suggesting an additional kinetic pathway for oxidation is present during the deposition. Moreover, when the Al₂O₃ deposition is performed on silicon pre-coated with silicon nitride, no silicate interface layer is observed. The metal organic precursor, physisorbed or dissociated chemisorbed on silicon, may present a low temperature kinetic route to oxidation that is not available with only O₂, possibly involving OH formed on the surface during precursor oxidation. Such pathways will be suppressed at higher temperature or low H conditions, consistent with the sharp interface observed using high temperature CVD and MBE. Kinetic processes for interface layer formation are also likely important during low temperature metal organic deposition of other material heterostructures. For example, TiO₂ deposition on silicon using H-free precursors at 280ºC shows formation of an interface layer¹⁷ (presumed to in SiO₂) suggesting that hydrogen elimination is not necessarily sufficient to limit low temperature silicon oxidation.

We acknowledge support from NSF CAREER Program (GNP) and the SRC/SEMATECH Center for Front End Processing.
9.4 REFERENCES


H.S. Kim, G.D.Wilk, M.A.Gribelyuk, W.L.Gladfelter, Chemical Vapor
Figure 9.1a  Narrow resonance nuclear reaction profile (NRP) of 18nm Al$_2$O$_3$ on Si. Model of results (shown in inset) show 2 layers with the first layer having an Al concentration corresponding to Al$_2$O$_3$. 
Figure 9.1b  NRP data for a thin 3.5nm Al$_2$O$_3$ film.
Figure 9.2  Auger depth profile of a AlO / AlSi\textsubscript{x}O\textsubscript{y} film showing the appearance of Si at approximately 100 Å
Figure 9.3 TEM image Al$_2$O$_3$ deposited on silicon at ~400ºC in the as-deposited state. The total film thickness is approximately 18nm. Two distinct layers are observed with approximately equal thickness.
Figure 9.4  XPS spectrum of Al and Si region of a 3.5nm aluminum oxide film deposited on silicon, showing evidence for Al-O-Si silicate bonding.
APPENDICES
APPENDIX A

ELECTRICAL PROPERTIES OF NMOS TRANSISTORS USING Y₂O₃ GATE DIELECTRICS

Appendix A is a compilation of the results from the following papers:


I deposited the Y₂O₃ dielectric films for the NMOS transistors in my reactor; I. Kim, S.K. Han from Dr. C. M. Osburn’s group at NC State University fabricated the NMOS devices and performed the device characterizations.
NMOS transistors using yttrium oxide were fabricated using a non-self-aligned-gate process summarized in Figure A1. The process, developed at NC State University, involves junction formation before the gate stack to allow the use of dielectrics and gate electrodes that cannot withstand normal junction annealing temperatures. Yttrium oxide was deposited in our remote PECVD system using tris(2,2,6,6-tetramethyl-3,5-heptanedionato)yttrium (Y(TMHD)₃) as the Y precursor introduced downstream from an O₂ plasma. Details are described in Chapter 6. The 200 nm poly-silicon (poly-Si) gate was deposited by LPCVD using Si₂H₆ at 630°C for 27 minutes, followed by ion implantation and RTA dopant activation at 950°C for 1 minute. After the device fabrication, capacitance-gate voltage (C-V₉), leakage current-gate voltage (I₉-V₉), drain current-gate voltage (I₉-V₉), and drain current-drain voltage (Iₓ-Vₓ) measurements were performed. Hauser’s program was then used to extract device parameters including equivalent oxide thickness (EOT), metal-to-semiconductor workfunction, substrate doping, channel mobility as a function of electric field, interface states density and the interface roughness scattering parameters (L•H product). After the electrical characterizations, a forming gas anneal (FGA)/post-metallization anneal (PMA) was conducted at 400°C for 20 minutes in an ambient of 10% H₂ with 90% N₂. Same electrical characterizations were performed to study the role of hydrogen during FGA.

Figure A2 shows the electrical characteristics of NMOS transistors. Figure A2a is the C-V₉ curve. The curve is smooth, and EOT is ~2.9 nm. Very low leakage current is attributed to the large EOT, as shown in Figure A2b. Figure A2c shows the drain Iₓ-Vₓ. Figure A2d is the mobility as a function of oxide field. The mobility values are too high
when using EOT extracted from C-V_{g}. Therefore, EOT is adjusted to a lower value from C-V_{g} value according to interface roughness scattering parameter (L H product).

Figure A3 shows the threshold and transconductance shifts under 1.2 V stressing. It can be seen that transconductance is slightly increased after stressing. The threshold voltage decreases under constant-voltage stressing. The threshold shifts are consistent with the generation and trapping of positive charge (or reduction of pre-existing negative charge).

For SiO2, FGA can reduce the interfacial traps and improve the electrical characteristics. Figure A4 shows the effects of FGA on electrical properties of Y2O3 NMOS devices. The C-V_{g} curves before and after FGA in Figure A4a indicate that FGA has very little effect. However, the FGA does increase the leakage current, as evidence in Figure A4b. Although the FGA does not change the flatband voltage, it reduces the threshold voltage by 200 mV, suggesting only a reduction in interface states, and significantly increases the drain current, as shown in Figure A4c. The mobility in Figure A4d is also improved after FGA.
Figure A1  Schematic illustration of non-self aligned gate process; (a) Grow and pattern 100 nm thick oxide and form junction; (b) Deposit 100 nm LPCVD oxide over diffusions and pattern gate and contact regions; (c) Deposit gate dielectric and electrode; (d) Pattern and etch gate electrode/gate dielectric, and deposit and pattern contact metal.
Figure A2  Electrical characteristics of Y$_2$O$_3$ with poly-Si gate NMOS Devices: (a) capacitance vs. gate voltage; (b) leakage current vs. gate voltage.
Figure A2  Electrical characteristics of Y$_2$O$_3$ with poly-Si gate NMOS Devices: (c) drain current vs. gate voltage; (d) device mobility.
Figure A3  Threshold voltage and transconductance shift of Y₂O₃ with NMOS devices under 1.2 V stressing.
Figure A4  Effects of FGA on electrical characteristics of Y$_2$O$_3$ with poly-Si gate NMOS Devices: (a) capacitance vs. gate voltage; (b) leakage current vs. gate voltage.
Figure A4  Effects of FGA on electrical characteristics of Y$_2$O$_3$ with poly-Si gate NMOS Devices: (c) drain current vs. gate voltage; (d) device mobility.
APPENDIX B

COMPARISON OF PROPERTIES OF CHEMICAL VAPOR DEPOSITED YTTRIUM OXIDE WITH AND WITHOUT IN-SITU CAPPING POLY-SI LAYERS

Chapters 4 and 7 report interface structures using x-ray photoelectron spectroscopy (XPS) and high-resolution transmission electron microscopy (HRTEM)/electron energy loss spectroscopy (EELS) for yttrium oxide films deposited for 3 minutes without and with in-situ capping poly-Si layers, respectively. In appendix B, results of uncapped and in-situ capped Y$_2$O$_3$ films deposited for 6.5 minutes will be presented: HRTEM/EELS and Auger electron spectroscopy (AES) depth profile for uncapped films and AES depth profile for a capped film.

Figure B1 shows the HRTEM/EELS results for an uncapped film deposited for 6.5 minutes after an anneal treatment in N$_2$ at 900°C for 1 minute. The TEM image in Figure B1a shows three regions with the total thickness of ~100 Å. The top layer is crystallized, indicating an Y$_2$O$_3$ structure. The middle and bottom layers are amorphous, likely due to the presence of Si. The color transition in the middle layer indicates a change in the film composition, notably the increase of Si concentration. The bottom layer is brighter than the other two layers, implying that it is more SiO$_2$ like, which is confirmed by EELS spectra in Figure 1.b. Region 1 is the silicon substrate with an edge onset at 99 eV and clear periodic fringes in the TEM. Region 2 is dark in the ADF with the edge onset shifted to a higher energy loss (105 eV). Also, the EELS near-edge fine
structure shows peaks near 106, 108, and 115-116 eV, similar to SiO₂. The TEM image indicates the thickness of region 2 is about 2.0 nm, and the yttrium concentration in region 2 is below the detection limit of the method.

Figure B2 is the Auger depth profile of a sample deposited under the same conditions as the sample in Figure B1. The profile was measured using a Scanning Auger Microprobe (Physical Electronics Model 660) at Evans East. Secondary electron images (SEI’s) were obtained from each of the samples prior to AES data acquisition. The SEI's were used to select an analysis area free of particles and/or debris. The incident electron beam with energy of (a) 3 keV and (b) 5 keV was used. A 3 keV Ar⁺ ion beam was used to sputter the film for the depth profile measurement. Due to the lack of Y₂O₃ standard, the sputter rate of SiO₂ that is 42 Å/minute was used for Y₂O₃. The depth is estimated using the oxygen half-maximum intensity as the interfacial marker. These two approximations give a thickness of ~200 Å, shown in Figure B2a, which is twice the value of that obtained from TEM. The profile shows that the ratio of Y to O is around 2:3. No carbon is detected in the film. However, Figure B2b shows a thickness of ~150 Å with Y to O ratio of 7:3. The discrepancy of the concentrations comes from the incident-energy dependence of sensitivity factors. Again, since there is Y₂O₃ standard, sensitivity factors for elemental species are used in both cases, which can introduce significant errors in the concentration calculations. In addition, due to the knock-on effects, AES depth profiling is not suitable for analyzing interfacial structures for ultra-thin dielectrics on silicon.

Figure B3 are the AES profiles of a sample deposited under the same conditions as the sample in Figure B1 but with a 200 Å poly-Si capping layer, and then measured
with incident electron beam energy of (a) 3 keV and (b) 5 keV. The capping layer was deposited \textit{in-situ} with exposing the sample to the atmosphere. The film was also annealed in N$_2$ at 900$^\circ$C for 1 minute. The figure shows the concentration discrepancy due to sensitivity factor effects, similar to that observed in Figure B2. However, comparison between depth profiles using the same incident electron energy is still valid. There are several distinct differences between the sample with and without the capping layer. First, a significant amount of nitrogen (up to 8\%) is present throughout the capped film, as shown in Figure B3; no N is detected in the uncapped film (detection limit 1\%), as shown in Figure B2. The N concentrations are higher at the poly-Si/dielectric and substrate/dielectric interfaces than in the bulk of the film. The reason for significant N incorporation is not understood at this point. One possible source of N is the annealing N$_2$ gas. Second, there is a significant amount of carbon in the capped film, which could lead to poor electrical properties.
Figure B1a  TEM image of a sample deposited for 6.5 minutes and annealed for 1 minute in N₂. The total thickness is ~100 Å.
Figure B1b. EELS spectra of (1) the bulk of the substrate and (2) the bottom layer in Figure B1a for the same sample. The inset is the ADF image.
Figure B2. AES depth profile of a sample deposited under the same conditions as the sample in Figure B1. The incident electron energy is (a) 3 keV and (b) 5 keV.
Figure B3. AES depth profile of a sample deposited under the same conditions as the sample in Figure 1 with a 200 Å poly-Si capping layer. The capping layer was deposited \textit{in-situ} with exposing the sample to the atmosphere. The incident electron energy is (a) 3 keV and (b) 5 keV.