SURFACE CHEMISTRY RESEARCH OF ELECTRONIC PROCESSES AND ELECTRONIC DEVICES

by

Xi Lin

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry and Biochemistry

2018 Summer

© 2018 Xi Lin
All Rights Reserved
SURFACE CHEMISTRY RESEARCH OF ELECTRONIC PROCESSES AND ELECTRONIC DEVICES

by

Xi Lin

Approved: ________________________________
Brian Bahnson, Ph.D.
Chair of the Department of Chemistry and Biochemistry

Approved: ________________________________
George Watson, Ph.D.
Dean of the College of Arts and Sciences

Approved: ________________________________
Douglas J. Doren, Ph.D.
Interim Vice Provost for Graduate and Professional Education
I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed: ______________________________

Robert L. Opila, Ph.D.
Professor in charge of dissertation

Svilen Bobev, Ph.D.
Member of dissertation committee

Andrew Teplyakov, Ph.D.
Member of dissertation committee

Joshua Zide, Ph.D.
Member of dissertation committee
ACKNOWLEDGMENTS

First and foremost, I would like to thank my advisor, Dr. Robert Opila, for all his support and guidance throughout my graduate studies. I am very blessed to have this privilege to work with Dr. Opila. His enthusiasm about science and engineering deeply impact me. His vast knowledge in surface analysis and semiconductor materials has undoubtedly helped with my pursuit of intellectually stimulating research projects. I appreciate all his contribution of mentorship and funding support in my Ph.D. pursuit. I would also like to thank all my committee members: Dr. Svilen Bobev, Dr. Andrew Teplyakov, and Dr. Joshua Zide for their valuable time and insightful comments during accomplishment of this dissertation.

I would like to give special thanks to Air Liquide America for its financial support as well as the internship opportunity, which give me the experience of working in industry. I am grateful to Dr. Rahul Gupta, Dr. Katsuko Higashino and Dr. Venkateswara Pallem for the generous guidance and mentoring. This opportunity has undoubtedly prepared me a professional career in the field of semiconductor fabrication.

I would also like to thank my groupmates: Dan Yang, Jonathan Church, Kevin Jones, Meixi Chen, Bo Yuan, James Hack, Hongfeng Wang, Abhishek Lyer and Zijian Wang, for their professional support and friendship. I really enjoyed all the fun times we spent in and out of the lab. And I special thanks to Kevin Jones for teaching me everything about XPS and Auger.

During my Ph.D. study, I had the chance working with and learning from a great number of talented scientists. I would like to thank Dr. Chaoying Ni, Dr. Fei Deng and
Frank Kriss, for their great patience in building up my skills of SEM, TEM and AFM. I am also grateful to James McCracken and Paul Horng from UD-Nanofab for their guidance and support upon sputtering deposition. Special thanks to Dr. Anderson Jonatti and Wei Li who has been extremely helpful on the DFT simulation with VASP.

In addition to technical support provided by colleges, the support from my friends are equally important. I would like to thank Qingyang Du, Zhengqi Zhang, and all friends in University of Delaware for their priceless friendship which makes my Ph.D. life enlightening and enjoyable.

Finally, I must thank my parents for their persistent understanding and continuous support and encouragement.
# TABLE OF CONTENTS

LIST OF TABLES ................................................................................................................. x
LIST OF FIGURES ................................................................................................................. xi
ABSTRACT ............................................................................................................................. xvi

Chapter

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

1.1 Surface Analysis Methods ............................................................................................ 1

1.1.1 X-ray Photoelectron Spectroscopy ......................................................................... 1
1.1.2 Auger Electron Spectroscopy .................................................................................... 4
1.1.3 Scanning Electron Microscopy .................................................................................. 6

1.2 Fabrication Technique ................................................................................................ 7

1.2.1 Deposition .................................................................................................................. 8
1.2.2 Etching ....................................................................................................................... 9
1.2.3 Atomic Layer Etching ............................................................................................... 11

1.3 Dissertation Objective and Outline .............................................................................. 13

2 PROCESSING CONTROL OF ATOMIC LAYER ETCHING ON TRANSITION METALS ..................................................................................................................... 15

2.1 Introduction .................................................................................................................. 15

2.1.1 Overview of MRAM ................................................................................................. 15
2.1.2 Challenges in Transition Metal Etching .................................................................... 19

2.2 Atomic Layer Etching of Transition Metals .............................................................. 20
2.3 ALE Experiment Setup ............................................................................................... 23

2.3.1 Etching Chamber Setup ............................................................................................ 23
2.3.2 Samples and Etchants ............................................................................................... 24
2.3.3 Characterization ......................................................................................................... 25
2.4 Self-limiting Performance of Etchants ........................................................... 25
  2.4.1 RF Power Dependent Cl₂ Reaction ......................................................... 26
  2.4.2 Temperature Dependent Cl₂ Reaction ................................................... 28
  2.4.3 Performance of Acac on Metal Surfaces .............................................. 29

2.5 Performance of ALE with Cl₂ and Acac ....................................................... 30
  2.5.1 Iron Samples ......................................................................................... 30
  2.5.2 Cobalt, Palladium, Nickel samples ...................................................... 33

2.6 Conclusions .................................................................................................. 35
2.7 Acknowledgment .......................................................................................... 36

3 THE REACTION MECHANISM RESEARCH USING IN SITU XPS ANALYSIS ................................................................. 37

3.1 Introduction .................................................................................................. 37
3.2 Experiment Setup ........................................................................................ 38
  3.2.1 In situ Reaction Chamber .................................................................... 38
  3.2.2 Metal Samples .................................................................................... 40
  3.2.3 XPS Measurements ........................................................................... 40

3.3 Cl₂ Reaction on Clean Fe Samples .............................................................. 41
3.4 Acac Reaction on The Chlorinated Fe Surface .......................................... 43
  3.4.1 Temperature Dependence .................................................................... 43
  3.4.2 Pressure Dependence ......................................................................... 45
  3.4.3 Cyclic Reaction with Cl₂ and Acac ...................................................... 47
  3.4.4 Acac Decomposition During The Reaction ........................................ 47

3.5 Reactions on Cobalt Surface ....................................................................... 50
  3.5.1 Cl₂ Adsorption on Co Surface ............................................................ 50
  3.5.2 Acac Reaction on Cl dosed Co Surface .............................................. 52

3.6 Summary ..................................................................................................... 54
3.7 Acknowledgment ......................................................................................... 55

4 DENSITY FUNCTIONAL THEORY (DFT) SIMULATION OF THE ETCHING REACTION ON FE SURFACE ......................................................... 56

4.1 Introduction: ................................................................................................. 56
4.1.1 Motivation ................................................................. 56
4.1.2 Density Functional Theory (DFT) ................................ 57
4.1.3 Basis Sets and Pseudopotentials ................................ 58
4.1.4 Surface Modelling .................................................... 59
4.1.5 Software ................................................................. 60

4.2 Calculation setup .......................................................... 60
4.2.1 Lattice Parameter Optimization: .................................. 60
4.2.2 Slab Modelling .......................................................... 61
4.2.3 Simulation of Gas Molecule ........................................ 62

4.3 Reaction on Smooth Surface .............................................. 63
4.3.1 Cl₂ gas Adsorption ..................................................... 63
4.3.2 Acac Substitution on Chlorinated Fe Surface .................. 65

4.4 Reaction of Defect Surface ................................................ 66
4.4.1 Isolated Fe Atom on Smooth Surface ......................... 66
4.4.2 Cl₂ Gas Adsorption .................................................... 67
4.4.3 Acac Substitution on Chlorinated Fe Surface ................ 68

4.5 Summary ........................................................................ 69
4.6 Acknowledgment ............................................................. 69

5 SURFACE PHOTO VOLTAGE ANALYSIS FOR BAND BENDING ON
SEMICONDUCTOR SURFACE.................................................. 71

5.1 Introduction .................................................................... 71
5.1.1 Band Bending on Semiconductor Surface .................... 71
5.1.2 Photoelectron Spectroscopy Measurements of SPV .......... 72

5.2 SPV Measurement Setup .................................................. 74
5.3 Dye/Metal Oxide Materials .............................................. 74
5.3.1 Sample Preparation ..................................................... 76
5.3.2 Powder Samples ........................................................ 77
5.3.2.1 F64PcZn/P90 Powder ................................................. 77
5.3.2.2 F16PcZn/P90 powder ................................................. 79
5.3.2.3 F64PcZn/Al₂O₃ powder .............................................. 80
5.3.2.4 F64PcZn/NiO powder ................................................. 81
LIST OF TABLES

Table 2.1 Technique specification of different memories\textsuperscript{38} ........................................... 16
Table 2.2 the sublimation temperature of MCl\textsubscript{x} and M(acac)\textsubscript{x} at 0.6 torr .................. 21
Table 4.1 Total energies of Fe slab and Fe slab with an isolated Fe atom .................. 67
Table 4.2 Cl\textsubscript{2} adsorption energy on defect Fe surface ................................................. 67
Table 5.1 Chemical Shift of F64PcZn/P90 and P90 TiO\textsubscript{2} samples ................................. 77
LIST OF FIGURES

Figure 1.1 Rough schematic of X-ray photoelectron spectroscopy\textsuperscript{5} ........................................ 2

Figure 1.2 Example of C 1s peak for adventitious carbon\textsuperscript{7} ....................................................... 4

Figure 1.3 Mechanism of Auger effect, Auger electrons are excited by incoming electron \textsuperscript{11} .................................................................................................................. 5

Figure 1.4 The AES example of Ni film after first order derivatization, the intensity of an element peak is the peak to peak difference ........................................... 5

Figure 1.5 The emissions resulted from an incoming electron beam\textsuperscript{14} ................................ 7

Figure 1.6 The schematic diagram of sputter deposition ........................................................................... 9

Figure 1.7 Anisotropic etching (left) and isotropic etching (right) ....................................................... 10

Figure 1.8 Comparison of a traditional plasma etch process with an ALE process, in comparison with CVD and ALD.\textsuperscript{21} .......................................................... 12

Figure 2.1. Road map of electronic devices, MRAM is likely the next generation embedded memory\textsuperscript{39} ........................................................................................................ 16

Figure 2.2 Tunneling magnetoresistance application in storage device ........................................ 18

Figure 2.3 MRAM with conventional magnetic field switching (left) and spin tunneling torque switching (right) .................................................................................. 18

Figure 2.4 The reaction processes in an ALE cycle ............................................................................... 22

Figure 2.5 The schematic diagram of the homemade plasma reaction chamber ............................ 23

Figure 2.6 Cross-section of metal samples. There is 100-160 nm metal film (Fe, Co, Ni or Pd) on 15 nm Ti adhesion layer ................................................................. 24

Figure 2.7 Thickness of metal films before and after the exposure of 100 W and 200 W Cl\textsubscript{2}/Ar plasma for 12min .............................................................................. 27
Figure 2.8 AES depth profiles of metal films after the exposure to 100 W Cl₂/Ar plasma for 12 min (a: Fe, b: Co, c: Ni, d: Pd) ......................................................... 27

Figure 2.9 Typical AES depth profiles of metal films after the exposure of 100 W Cl₂/Ar plasma at different temperature for 12 min. (a: Fe, 144 °C; b: Fe, 203 °C; c: Co, 203 °C; Pd: 203 °C) ................................................................. 28

Figure 2.10 The thickness of Fe film etched with different cycles. Black: 100W Cl₂/Ar plasma in step 1, acac flow in step 2, substrate 144°C; Red: 100W Ar plasma in step 1, acac flow in step 2, substrate 88°C; Green: 100W Cl₂/Ar plasma in step 1, N₂ flow in step 2, substrate 144°C; Blue: 100W Ar plasma in step 1, acac flow in step 2, substrate 144°C; Purple: Cl₂/Ar flow without plasma in step 1, acac flow in step 2, substrate 144°C ................................................................. 31

Figure 2.11 Depth profile of Fe samples etched at different temperatures with and without plasma in Cl₂ step ........................................................................................................... 32

Figure 2.12 Surface morphology of etched Fe sample after 10 (left) and 20 (right) ALE cycle at 88 °C with 100W Cl₂/Ar plasma and 88 °C substrate temperature ........................................................................ 33

Figure 2.13 Depth profile of Co, Ni, Pd samples etched by ALE method. a) Co, sample etched by 50-cycles ALE with 100W Cl₂/Ar plasma and 144 °C substrate temperature, b) Ni etched by 50-cycles ALE with 200W Cl₂/Ar plasma and 203 °C substrate temperature, c) Pd etched by 25-cycles ALE with 200W Cl₂/Ar plasma and 203 °C substrate temperature, d) Pd etched by 25-cycles reaction with 200W Cl₂/Ar plasma and 203 °C substrate temperature without acac ........................................... 34

Figure 3.1 a) A picture of the in situ reaction chamber; b) Schematic diagram of the reactor and XPS for surface analysis. The base pressures of the system are 10⁻⁹ Torr for the spectrometer and 10⁻⁶ Torr for the reactor ........................................................................ 39

Figure 3.2 different Fe components in Fe 2p₃/₂ XPS region after dosing Cl₂ at room temperature; ......................................................................................................................... 41

Figure 3.3 The depth profiles of Fe surface layer after dosing Cl₂ at different temperature (a:23 °C, b:80 °C, c:140 °C, d:180 °C) ......................................................................................... 42

Figure 3.4 the Fe 2p (left) and Cl 2p (right) spectra after dosing acac at different temperature (black: before dosing; red:90 °C; blue: 110 °C; green: 135 °C) ............................................................................................................... 44
Figure 3.5 Elemental surface compositions of the chlorinated Fe surfaces after reaction with 100 mtorr acac exposure at 140°C (left) and 180°C (right) ................................................................. 45

Figure 3.6 Elemental surface compositions of the chlorinated Fe surfaces after reaction with acac at 140 °C and different pressures (a, 100 mtorr; b, 200 mtorr; and c, 400 mtorr). Note that time axes vary for each condition. d) The Cl removal rate with various acac pressure at 140 °C. It suggests a first order reaction with the acac pressure. ............ 46

Figure 3.7 XPS depth profile of Fe samples before (left) and after (right) 20 cycles of sequential exposure of Cl₂ and acac at 140°C........................................... 47

Figure 3.8 High resolution photoemission spectra of C 1s, O 1s, and Cl 2p peaks on Fe thin films. The films are Cl-dosed (100 mtorr, 3 min, room temperature) Fe films, heated to 140°C, and following acac exposure of 0 min (bottom), 15 min (middle), and 30 min (top)........................................... 49

Figure 3.9 different Co components in Co 2p XPS region after dosing Cl₂ at room temperature, 140 °C and 180 °C; ................................................................. 51

Figure 3.10 High resolution photoemission spectra of Co 2p, C 1s, O 1s, and Cl 2p peaks on Co films. The films are Cl-dosed (100 mtorr, 3 min, 140 °C) film and the chlorinated Co film after acac exposure (1 torr, 3 min, 180 °C)..................................................................... 53

Figure 4.1 The total energy of Fe crystal bulk and the crystal volume calculated by VASP, the relationship is fitted by Birch–Murnaghan equation of state 61

Figure 4.2 A 5-layer Fe slab with (3x3) super cells and 20.0 Å vacuum layer. The top three layers were relaxed for optimization, and the bottom two layers were fixed. .................................................................................. 62

Figure 4.3 Two stable Fe²⁺ complex with acac ligand after optimization. Left: FeCl(acac); Right: Fe(acac)₂ ................................................................. 63

Figure 4.4 Top views of Cl/Fe(110) (left) and Cl/Fe(110) (right) surface configurations. Green and brown spheres denote Cl and Fe atoms respectively................................................................. 64

Figure 4.5 The acac ligand substitution on smooth chlorinated Fe (100) (left) and Fe (110) (right) surface............................................................................ 66
Figure 4.6 The energy change of acac substitution on chlorinated Fe (100) surface with an isolated Fe atom................................................................. 68

Figure 5.1 The charge transitions on surface photovoltage effect................................. 72

Figure 5.2 surface photovoltage experiment with PES. The binding energy(BE) of VBM can be defined as the energy between the VBM and the fermi level. Light exposure can flatten band bending at the surface. The binding energy will increase for n-type semiconductor and decrease for p-type semiconductor................................................................. 73

Figure 5.3 Relative energy (metal oxide data based on literature\textsuperscript{110}, dye LUMO/HOMO data was provided by The Gorun group) of the valence bands (VB) or highest occupied molecular orbital (HOMO) and conduction band (CB) or lowest unoccupied molecular orbital (LUMO) with respect to the vacuum level................................................................. 75

Figure 5.4 Molecular structure of F64PcZn dye................................................................. 76

Figure 5.5 Schematics of compressed powder film (left) and deposited film (right).................. 77

Figure 5.6 High resolution XPS of O1s, Ti2p\textsubscript{3/2}, and F1s peak in F64PcZn/P90 TiO\textsubscript{2} samples under dark and illuminated condition ........................................... 78

Figure 5.7 High resolution XPS of O1s, Ti2p\textsubscript{3/2} peak in P90 TiO\textsubscript{2} samples under dark and illuminated condition................................................................. 79

Figure 5.8 SPV measurement of F16PcZn/TiO\textsubscript{2} with high resolution XPS on O1s, Ti2p\textsubscript{3/2} and F1s peaks, red line is illuminated condition, black line is dark condition................................................................. 80

Figure 5.9 High resolution XPS of O1s and Al2p\textsubscript{3/2} of F16PcZn/Al\textsubscript{2}O\textsubscript{3} of SPV measurement, the peaks shift to low binding energy with light on the sample.................................................................................................................. 81

Figure 5.10 SPV measurement of NiO and F64PcZn/NiO with high resolution XPS, red line is dark condition, black line is illuminated condition. a) O1s of NiO; b) Ni2p\textsubscript{3/2} of NiO; c) O1s of F64PcZn/NiO; d) Ni2p\textsubscript{3/2} of F64PcZn/NiO ............................................................................. 82

Figure 5.11 Cyclic evolution of peak shifts of major element Ti, O, F. Cycle 1-3 and cycle 7-11 are in the dark, and cycle 4-6 and cycle 12-17 are in the light.................................................................................................................. 84
Figure 5.12 The F components in 10 nm dye layer film (left) and 5 nm dye layer film (right). ................................................................. 85

Figure 5.13 Cyclic evolution of peak shifts of Si. Cycle 1-4, cycle 9-12 and cycle 17-20 are in the dark, and cycle 5-8 and cycle 13-16 are in the light. .... 87

Figure 6.1 An extra port on the top of the in situ reaction chamber which can be used for installation of an electrode of CCP system and wiring of RF generator.................................................................................................................. 95

Figure 6.2 A rough schematic diagram of Kelvin probes by measuring the contact potential difference between two surfaces ........................................... 97
ABSTRACT

Surface chemistry and analysis is important in many different disciplines. In this dissertation, the role of surface chemistry in improving performances of electronic devices is discussed. Two different perspectives are investigated.

In the first topic, atomic layer etching (ALE) of transition metals using Cl\(_2\) and acetylacetone (acac) was studied. Etching of transition metals is one of the major challenges in MRAM fabrication. The etching performance on different metals, including etching rates, self-limiting behaviors, and influence of temperature and RF power, was studied. We successfully etched Fe and Co thin films by forming volatile metal complexes at low temperature with cyclic reactions of Cl\(_2\) and acac.

The mechanism of acac reacting on Cl-modified Fe surfaces was investigated using \textit{in situ} x-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) simulation. The surface was first activated with Cl\(_2\) gas, and then the top layer of metal was removed by acac reaction. The extent of Cl\(_2\) reaction determined the etching rate. At substrate temperatures lower than 135°C the acac could not remove the chlorine. The reaction of acac on chlorinated Fe surface is likely following a complex pathway instead of simple acac substitution for Cl\(_2\). Acac decomposition may play an important role in the process.

The acac reaction on Cl-modified Co surfaces was also investigated by \textit{in situ} XPS. The Cl\(_2\) adsorption on Co surfaces is much weaker than on Fe surface. The remaining organic groups on the Co surface show little carbanion and C-O groups after acac exposure, indicating a different mechanism comparing with the Fe surface.

xvi
In the second topic, surface photovoltage (SPV) measurements using XPS was utilized for measuring the band bending on organic molecule modified semiconductor surfaces. The interaction between the phthalocyanine dye molecule and different metal oxide powders was measured by the SPV analysis. The F64PcZn molecule is likely acting as a p-type semiconductor, and, due to the new charge distribution, changes the band-bending at the substrate surface. The interaction between organic molecule and Si surfaces was also investigated. For n-type Si samples, SPV measurements indicate a downward band bending of benzoquinone (BQ) passivated samples. The BQ-Si sample has the largest band bending, indicating a strong field-effect contribution to eliminate the recombination of electrons and holes on the surface.
Chapter 1

INTRODUCTION

Surface chemistry can be defined as understanding of reactions which occur between adjacent phases, such as solid-gas or solid-liquid etc.\textsuperscript{1} It is an important research for a variety of applications.\textsuperscript{1,2} In this dissertation, we are going to discuss the surface chemistry for electronic applications. Specifically, we want to research the surface chemistry of two different applications: 1) the atomic layer etching of transition metals for magnetic random-access memory (MRAM) and 2) surface photovoltage (SPV) measurement for band bending near the semiconductor surface. The research of surface chemistry will provide a fundamental understanding of the process of metals and surface modification of semiconductors.

1.1 Surface Analysis Methods

Comprehensive surface analytical techniques are necessary tools for understanding the surface physics and chemistry and characterization of the surface morphology and performance. In this dissertation, we have used X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and scanning electron microscopy (SEM) for targeted applications.

1.1.1 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is now a well-established surface analysis technique, which is capable of providing elemental and chemical state information on a solid surface.\textsuperscript{3} The technique is based on the photoelectric effect that
high energy photons cause the emission of electrons from a material. In the 1950s, Kai Siegbahn (Uppsala University, Sweden) first developed a high-resolution X-ray photoelectron spectroscopy by using a Cu Kα X-ray source. And he was also awarded the Nobel Prize for the pioneering work of XPS.

**Figure 1.1** Rough schematic of X-ray photoelectron spectroscopy

Now, most of the XPS equipment uses either Al Kα X-ray sources at 1486.7eV or Mg Kα X-ray sources at 1253.6eV energy. Figure 1.1 shows the interaction between X-ray and electrons. The X-rays will be used to interact with the core shell electrons in an atom. Photoelectrons will be emitted after adsorbing the energy from X-ray. The
kinetic energy ($E_k$) of emitted electrons will be measured by a detector. The binding energy of the core shell electrons ($E_b$) can be calculated by using the following equation:

$$E_b = h\nu - E_k - \Phi_{sp}$$

where $h\nu$ is the energy of the X-ray. $\Phi_{sp}$ is the work function of the spectrometer. All elements except hydrogen and helium have their specific core level binding energies. Thus, peaks observed in the spectra can be used to identify those elements. The intensity is the area under those peaks. Atomic concentration could be calculated by:

$$\sigma_i = \frac{I_i}{s_i} / \sum \frac{I_i}{s_i}$$

$I_i$ is the intensity of the element peak. $s_i$ is the sensitivity factor of the element. The sensitivity factor of one element is an intrinsic property of that element. The values can be found from the handbook or the XPS analysis software.

The binding energy in XPS is sensitive to the chemical environment of atoms. Chemical environments, such as bonding to electron donating or withdrawing groups, valence state, will change charge distribution of the atom, and then influence the binding energies of core electrons. Negatively charging or bonding to electron donating groups will reduce binding energies of electrons in the atom. Conversely, positively charging or bonding to electron withdrawing groups will increase binding energies of electrons in the atom. Based on the chemical shift in XPS, the chemical state information can be extracted. Figure 1.2 shows a typical example of adventitious C 1s peak. The peaks with binding energies 285.0, 286.1, 288.6, 289.6eV are corresponding to C-C, C-O, C=O, O-C=C groups separately. The binding energies of different bonding condition can be found in databases.
1.1.2 Auger Electron Spectroscopy

Auger Electron Spectroscopy (AES) is another important chemical surface analysis tool. The method is based on the electron excitation called “Auger effect”, which is first discovered by Pierre Auger in 1923. \(^\text{10}\) Different from photoelectrons, Auger electrons can be excited by different energy sources such as electron beam, X-Ray, etc. As shown in Figure 1.3, in a commercial AES, a high energy electron beam is used to remove an electron from a core level of an atom with energy \(E_1\). The empty electron position will be filled by another electron from a higher energy orbital and release an energy corresponding to \(\Delta E = E_1 - E_2\). A third electron at level \(E_3\) of the same atom will then absorb this energy and be excited to vacuum level. The detector will measure the kinetic energy of the third electron, which is corresponding to the energies of the three electronic levels and the spectroscopy work function.
Figure 1.3 Mechanism of Auger effect, Auger electrons are excited by incoming electron

Figure 1.4 The AES example of Ni film after first order derivatization, the intensity of an element peak is the peak to peak difference
The element peaks in AES also have specific binding energy and sensitivity factors. Thus, AES can also be used for measuring atomic concentration of different elements like XPS. The sensitivity factor could be found on AES handbooks. But the intensity of Auger electron emission is a little different from XPS. To calculate the atomic concentration, we need to do derivative of raw data, and the intensity is the difference between maximum and minimum peaks in the specific region of an element as shown in Figure 1.4.

1.1.3 **Scanning Electron Microscopy**

Scanning electron microscopy (SEM) is a surface analysis method that uses electron emissions to generate images with topographical information of a sample surface.

Secondary electron (SE) emission is the most important electron emission in SEM, which is widely used for surface morphology imaging. The incoming electron beam in SEM can excited k-shell electrons of the specimen atoms and generate SEs with very low energy. Only those SEs from the sample surface can be excited into the vacuum and captured by the detector. The resolution of SEs is usually close to the resolution of incoming electron beam.

Figure 1.5 shows that the electron-sample interaction will not only generate secondary electrons, but also a variety of signals including characteristic X-rays, backscattered electrons, Auger electrons, etc. From different emissions, we can also get different information. Backscattered electrons come from the reflection of electron in deeper region. It can provide a high contrast image about the distribution of different elements in the sample. Energy dispersive X-ray microscopy (EDX) is often used
together with SEM to analysis the concentration of elements in selected region on the film.

Figure 1.5 The emissions resulted from an incoming electron beam

1.2 Fabrication Technique

Fabrication is a process used to create the integrated circuits or electronic device. It is a multiple-step sequence of physical and chemical surface reaction steps such as photolithographic, deposition, etching, ion implantation, cleaning, polishing and packaging, during which the electronic devices are gradually made on a wafer.
1.2.1 Deposition

Vacuum deposition is a type of processes used to grow films on a solid surface. When the film is grown by direct condensation of the molecules, ions, or atoms in the vapor, the process is called physical vapor deposition (PVD),\textsuperscript{15} such as sputter deposition, e-beam evaporation. When the film is grown by a chemical reaction of gas precursors, the process is called chemical vapor deposition (CVD).\textsuperscript{16} For metal, alloy or metal oxide materials, the most common deposition method is PVD. In our experiment, Fe and TiO\textsubscript{2} films were grown by sputter deposition.

In the sputter deposition, there is no chemical reaction involved. A metal target is placed in the system to serve as the deposition source material. Figure 1.6 shows the schematic of a sputter deposition chamber. The sputtering target (cathode) and the substrate (anode) are put on two electrodes. Sputtering is driven by the plasma between the two electrodes. The plasma can be generated by either DC voltage or Radio Frequency (RF) in the system. In DC sputtering, voltage is set from 3-5 kV. In RF sputtering, the frequency is set at 13.6 MHz. A noble gas, such as Ar, will be leaked into the chamber and ionized by the strong electric field. The ions will bombard the surface of the metal target and eject the metal atoms or ions into the vacuum. The metal atoms in gas phase will then deposit on all surfaces in the chamber. Usually, the wafer used for deposition will be placed right on the top of the sputter target and rotate in a certain speed to make the deposition uniform.
1.2.2 Etching

After growing materials on the wafer by deposition and transferring desired pattern to the thin film by lithography, etching is the next important step to remove unwanted material from the film to create the featured structure. Based on the application, there will be different requirement for the etching process, such as etching rate, selectivity, morphology, isotropy, and so on.

There are two major etching ways -- wet etching and dry etching. Wet etching is a process that uses liquid chemical or solution to remove materials from a wafer. The process based on the liquid – solid surface reaction. The product will dissolve in the liquid phase. This technique is widely used in the Si etching process. HF and KOH are the most common solution. Wet etching requires a simple setup and is highly sensitive to the etchant and the substrate.
Dry etching is a gas phase process, in which the etching product will be evaporated into gas phase. It can also be separated into two types: plasma etching and thermal etching. The major difference between them are isotropy and anisotropy\textsuperscript{18} as shown in Figure 1.7. In the plasma etching, the gas molecules are ionized by a strong electronic or magnetic field. The ions in the plasma will be accelerated by the electronic field to bombard the sample surface. By accelerating ions in certain direction, we can do the anisotropic etching. By tuning the kinetic energy of the ions, the plasma can be used to remove the material by physical interaction such as ion milling, or chemical reaction such as reactive ion etching (RIE). In the ion milling, ions will bombard the sample surface, and directly remove the atoms on the surface. Since it is just a physical process, sputtering can be used on different materials, but on the other hand, it has poor selectivity. In RIE, reactive ions in the plasma could reduce the activation energy of the reaction between etchant and the atoms on the surface and make volatile products. Different materials will react with different etchants, so that RIE shows better selectivity than sputtering.

Thermal etching is using chemical reactions to make volatile compounds and removing compounds on the surface by thermal desorption. The reaction will happen on all surfaces with the same rate, so that we can used thermal etching for the isotropic etching.
1.2.3 Atomic Layer Etching

Atomic layer etching is a next-generation plasma etch technology that enables layer-by-layer etching, which is a similar process technology to atomic layer deposition (ALD).\textsuperscript{19, 20} Figure 1.8 compared the continual process and atomic layer process for deposition and etching.\textsuperscript{21} In the continual plasma etch/deposition processes, all gas precursors are dosed at the same time. A number of reactions happen at the same both on the surface and in the gas phase. It is very difficult to control the process precisely. Atomic layer etching (ALE), a counterpart of ALD, is expected to reproducibly remove single atomic layers of a surface through a series of self-limiting reaction steps.

In a typical ALE cycle, there are two major steps. In the first step, one precursor is dosed to react with the atoms on the clean targeted surface of the film to form a reactive layer. Then the excessive precursor is evacuated by pumping and purging. In the second step, a second precursor reacts with the reactive layer on the surface from the first step to produce volatile compounds. Another pumping and purging process will remove the volatile products and leave a clean surface. The two steps make one cycle in the ALE process. In an ideal condition, both steps should be self-limiting, which means that the gas precursors only react with one atomic layer on the surface. The self-limiting performance is related to specific chemical reactions on the surface, pumping and purging times, or the energy of the plasma which is high enough to modify the surface but low enough to prevent excessive sputtering.

Though ALD has been use in semiconductor fabrication for many years, the development of ALE is much slower. ALE for real applications still needs a lot of improvement on the etch precursors and the processing control. Now, the semiconductor industry has begun working on the 5 nm technology node.\textsuperscript{22} Processes that include ALE or ALE-like technologies will be important for a big inflection point toward getting
these types of capabilities. ALE will not replace the traditional etching in the fab because ALE is time-consuming but be used for the fabrication of the most advanced and challenging structures.

Figure 1.8 Comparison of a traditional plasma etch process with an ALE process, in comparison with CVD and ALD.21

One common application of ALE in industry is to precisely remove targeted materials. People used a gas to active the surface, so that the activated layer on the surface could be removed by low energy plasma sputtering (usually Ar+) in the following step. The plasma energy was so low that makes little damage to the material underneath after removing the activated layer. This method has already been used to remove Si-based materials by Lam research.23,24 Similar methods have been applied for etching of III-V compound semiconductors25, high-K metal oxide26, and polymers27.
Another application is the isotropic etching with thermal ALE for future 3D integration applications. The George group has developed a thermal ALE method for high K metal oxide materials (Al₂O₃, HfO₂) by using ligand-exchange reactions. They first use HF to replace the oxygen on the surface, and then in the second step, a metal acac complex, such as Sn(acac)₂, is used to perform ligand-exchange reactions with the activated surface to form volatile species.

ALE can also be used to etch the materials which are hard to remove by one-step reactions, such as transition metals. The Chang group has successfully etched transition metal films by cyclic etching with Cl₂ and H₂ plasma and ALE with O₂ plasma and organic molecules.

1.3 Dissertation Objective and Outline

The main objective of this dissertation is to investigate the surface chemistry in two different applications: 1) the mechanism of the reactions in atomic layer etching and 2) the band bending on the surface of semiconductors.

Chapter 2-4 are about the surface analysis of the ALE process for transition metals in MRAM device. The work will cover three aspects: process development, mechanism research with in situ XPS, and DFT simulations with VASP. Chapter 2 will investigate the performance of Cl₂ and acetylacetone (acac) ALE method of different parameters (RF power, temperature) and on different metals (Fe, Co, Ni, Pd). We established that this method could only etch Fe film under low temperature conditions. Chapter 3 discusses the reaction mechanism of Cl₂ and acac on Fe and Co surfaces based on in situ XPS analysis. The decomposition of acac plays an important role in the etching of Fe films. Chapter 4 discusses the DFT simulation of Cl₂ and acac reactions.
on different Fe surfaces (Fe (100) and Fe (110)). The different surface reactivity will be the another driving force of the surface reaction in etching process.

Chapter 5 is about surface photovoltage (SPV) measurements for the band bending on semiconductor surfaces modified by organic molecules. Two different materials were investigated, including the phthalocyanine dyes modified metal oxides and benzoquinone passivated Si surfaces.

Chapter 6 summarizes the major contributions of this dissertation and provides some perspectives of the future work.
Chapter 2

PROCESSING CONTROL OF ATOMIC LAYER ETCHING ON TRANSITION METALS

2.1 Introduction

2.1.1 Overview of MRAM

The computer memory is an electronic component used for storage in different electronic devices such as computers, cell phones, and so on. Nowadays, the memory manufacture has become one of the major parts of the semiconductor industry. The memory devices can be divided into two categories: volatile memory (VM) and nonvolatile memory (NVM). For VM devices such as dynamic random-access memory (DRAM) and statistic random-access memory (SRAM), the stored information will be lost if the power is turned off or interrupted. As for NVM such as NOR and NAND flash memories, the stored data can be maintained even if the power is interrupted, but the reading and writing speed of flash memories is much slower than RAM.

With the fast development in new electronic devices, emerging memory technologies are developed to fulfill the different needs by combining functions and features of random accessing, non-volatility, higher write/read speed, lower power consumption, higher density and higher reliability. There are several candidates for future memory such as phase change memory (PCM), magnetic random-access memory (MRAM), and resistance random-access memory (RRAM).
Table 2.1 Technique specification of different memories

<table>
<thead>
<tr>
<th>Attributes</th>
<th>DRAM</th>
<th>NAND</th>
<th>STT-MRAM</th>
<th>PCM</th>
<th>RRAM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell factor($F^2$)</td>
<td>6-10</td>
<td>2-5</td>
<td>4-20</td>
<td>6-12</td>
<td>&lt;4</td>
</tr>
<tr>
<td>Read time (ns)</td>
<td>10-60</td>
<td>50</td>
<td>2-20</td>
<td>2-60</td>
<td>10-50</td>
</tr>
<tr>
<td>Write time (ns)</td>
<td>10-60</td>
<td>104-106</td>
<td>2-20</td>
<td>50-120</td>
<td>10-100</td>
</tr>
<tr>
<td>Endurance</td>
<td>$10^{16}$</td>
<td>$10^5$</td>
<td>$10^{15}$</td>
<td>$10^{10-12}$</td>
<td>$10^{15}$</td>
</tr>
<tr>
<td>Power consumption</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
<td>Med</td>
<td>Low</td>
</tr>
<tr>
<td>Read/write</td>
<td>2pJ</td>
<td>10nJ</td>
<td>0.02pJ</td>
<td>1nJ</td>
<td>2pJ</td>
</tr>
<tr>
<td>Power consumption other than R/W</td>
<td>Refresh power</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Embedded friendly</td>
<td>N(thermal)</td>
<td>N(thermal)</td>
<td>Y</td>
<td>N(Bi-polar)</td>
<td>Y</td>
</tr>
<tr>
<td>Data Retention</td>
<td>N</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
</tr>
</tbody>
</table>

Figure 2.1. Road map of electronic devices, MRAM is likely the next generation embedded memory

Figure 2.1. Road map of electronic devices, MRAM is likely the next generation embedded memory
Comparing with other type of memories, spin tunneling torque magnetic random-access memory (STT-MRAM) is an nonvolatile memory with fastest reading and writing speed, longest endurance and lowest power consumption as shown in Table 2.1. Benefit from these advantage, STT-MRAM will be a perfect candidate for future embedded memory application as shown in Figure 2.1.

MRAM is a magnetic storage device based on a phenomenon called tunneling magnetoresistance (TMR), which was first discovered by M. Jullière in 1975. TMR is an effect that can change the resistance of an electrical device by magnetic interaction. The TMR device is called magnetic tunnel junction (MTJ), which is the basic unit in all MRAMs. The simplest MTJs have two ferromagnetic layers and one barrier layer in the middle. We can use $R_{AP}$ and $R_P$ to stand by the resistance for anti-parallel and parallel magnetization configurations between two ferromagnets layers. The different resistance can be used to standard by 0 and 1 for data storage as shown in Figure 2.2. When the spin directions of two ferromagnetic layers are the same, then resistance $R_P$ will be low, and this state will be data “0”. Conversely, when the spin directions are different, then resistance $R_{AP}$ will be high, and this state will stand by data “1”. the TMR ratio is defined as:

$$\text{TMR} = \frac{(R_{AP} - R_P)}{R_P},$$

For a storage device, a large TMR ratio will be necessary. However, in the early years, the TMR ratio was so low that TMR did not receive enough attention comparing with another similar effect -- giant magnetoresistance (GMR), which was first reported in 1987. The 2007 Nobel Prize in physics was rewarded to Dr. Fert and Dr. Grünberg for this discovery. Until 2004, Yuasa S. and Parkin group reported a revolutionary high TMR above 200% in MTJs with crystalline MgO barrier. In 2008,
CoFeB/MgO/CoFeB device showed up to 604% TMR ratio at room temperature.\textsuperscript{45} Benefited from the significant improvement, the resistance and signal voltage is now much larger and adjustable in MTJs, which allow high-speed read/write operations. TMR is finally able to be used for storage applications.

![Figure 2.2 Tunneling magnetoresistance application in storage device](image)

**Figure 2.2** Tunneling magnetoresistance application in storage device

![Figure 2.3 MRAM with conventional magnetic field switching (left) and spin tunneling torque switching (right)](image)

**Figure 2.3** MRAM with conventional magnetic field switching (left) and spin tunneling torque switching (right)
Early MRAMs were based on the conventional magnetic field switching, which has a complex structure and a large cell size. STT-MRAM has been developed in 2004, based on spin transfer effect that the spin direction can be modified by using a spin-polarized current. STT-MRAM not only have better performance, but also simplify the structure of MRAM cell and made it possible to scale down the size as shown in Figure 2.3. In 2017, Everspin company has successfully commercialized 256M STT-MRAM unit.

To get better performance, the MTJs now have many more layers than the basic structure with only two ferromagnetic layers and one barrier layer mentioned above. The ferromagnetic layers have complex stacks of different magnetic materials as reference and free layers. They are made by different kinds of magnetic and antimagnetic materials including transition metals and their alloys (CoFeB, FeCo, FeNi, CoPt…). New MTJ structures keep increasing the etching difficulty in the fabrication. Etching of the materials in MTJs is going to be the most important step to increase the storage density of MRAM devices. Currently, ion milling is still the major method used in industry, which has poor selectivity and is more difficult to make the devices smaller than 20 nm. In order to catch up the storage density of existing memories, such as DRAM and NAND flash, new techniques will be required for MTJs fabrication to improve the selectivity and device scalability.

### 2.1.2 Challenges in Transition Metal Etching

Etching transition metals such as Fe, Co, Ni, Pt and their alloys is very difficult. Currently, only ion milling has been widely used in industry to etch the magnetic metal in MTJ fabrication, which removes the metal atoms physically from the surface. However, since the solid phase is thermodynamically preferred for metals, the
sputtered metal atoms and ions deposit on all surface inside the chamber and the sidewalls of the insulation layer in the device. Those redeposited metals will lead to short circuits in the device, which require complex cleaning processes.\textsuperscript{52} When the cell size is reduced to 20 nm, ion milling will be difficult in manufacture, and the cost will also significantly increase.

Reactive ion etching (RIE) was also investigated for MRAM devices to overcome metal redeposition. In the past few decades, halogen-based plasmas have been studied for metal etching.\textsuperscript{53-55} They can react quickly to form metal halide complexes on the surface; however, due to their low volatility, a relatively high temperature was required to remove the metal halide product. In addition, the metal chloride residue is hard to remove completely. In some reports, the remaining MCl\textsubscript{x} residues lead to degradation of magnetic properties\textsuperscript{56} or deformation of patterns\textsuperscript{57}. Then, CH\textsubscript{4},\textsuperscript{58-60} CO/NH\textsubscript{3},\textsuperscript{61-63} and CH\textsubscript{3}OH\textsuperscript{64,65} etching has also been studied, hoping that organic ligands can form volatile metal complexes. An organic gas plasma improves the sidewall etching profile and the elemental selectivity comparing with a halogen gas plasma. However, because of lack of direct evidence of volatile coordination complex as etching product, it is still uncertain if the etching is a result from chemical reaction or ion milling. The organic plasma also has another problem in that a carbon layer may form on the surface and passivate the sample surface, limiting further etching.

### 2.2 Atomic Layer Etching of Transition Metals

Given so many problems in the continual etching processes, multi-step processes, such as atomic layer etching (ALE), or quasi-ALE utilizing separate doses of different gases, were developed. Recently, ALE with cyclic reactions with two different etchants on metal surface was reported by the Chang group.\textsuperscript{32, 33} In this work, O\textsubscript{2} plasma was
used to activate the surface of metals into metal oxides, then organic molecules were used to react with metal oxides and make volatile metal complexes. This method benefits from the high reactivity of O$_2$ plasma, and the volatile metal complex made by organic precursors. In addition, the reaction is self-limiting because organic precursors only removed the metal oxide on the surface. Therefore, the process can be precisely controlled.

In our study, we would like to develop an ALE technique to etch metal films. Cl$_2$ and acetylacetone (acac) are chosen as the first and second step precursors, respectively. Cl$_2$ is used to active the Fe surface instead of O$_2$ in previous reports for two reasons. 1) The MO$_x$ residues of O$_2$ etching might lead to the degradation in magnetization of MTJ$^{66}$ and need to be removed by sputtering$^{67}$. 2) Halogen-based etching precursors are commonly used in industry. Acac is used to make volatile metal complexes because metal acac complexes have high vapor pressure.$^{68, 69}$ The thermodynamic data of metal chloride and metal acac complexes are shown in table 2.2.$^{70, 71}$ If acac can have a substitution reaction with metal chlorides, the desorption temperature of the etching product will decrease.

<table>
<thead>
<tr>
<th></th>
<th>FeCl$_3$</th>
<th>CoCl$_2$</th>
<th>NiCl$_2$</th>
<th>PdCl$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sublimation temperature</strong></td>
<td>190$^\circ$C</td>
<td>661$^\circ$C</td>
<td>670$^\circ$C</td>
<td>decompose</td>
</tr>
<tr>
<td>Fe(acac)$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Sublimation temperature</strong></td>
<td>131$^\circ$C</td>
<td>147$^\circ$C</td>
<td>214$^\circ$C</td>
<td>68$^\circ$C</td>
</tr>
</tbody>
</table>
Figure 2.4 shows the steps in one ALE cycle. We first dose chlorine gas/plasma to activate the metal surface and produce a metal chloride layer on the top. Then N$_2$ is purged to remove unreacted etchant molecules on the surface. In the second step, acac is dosed to make volatile metal complex. And then purge N$_2$ again to remove the etching product. This cycle will be repeated for many times to remove the film layer by layer.
2.3 ALE Experiment Setup

2.3.1 Etching Chamber Setup

The home-made etching system we used for the process development is shown in Figure 2.5. The main reaction chamber is made of stainless steel. The chamber wall is heated to 80 °C to eliminate gas adsorption on the chamber wall. There are six gas lines connected to the system for Ar, Cl₂, O₂, N₂, SF₆ and organic precursor. Mass flow controllers (MFC) are used on all gas lines to control the flow rates except the organic precursor line. Since the organic precursor is a liquid under room temperature, it is stored in a stainless steel vessel and dosed by evaporation. A needle valve in this gas line is used to adjust the partial pressure of the organic compound in the chamber. The vacuum is controlled by an oil rough pump. The pressure baseline of the system is ~0.05 torr when the valve to the rough pump is fully open and no gas is flowing into the chamber. A mass spectrometer is used to analyze the background of the chamber and purity of precursors. All valves and MFCs in this system are connected to a computer and controlled by a LabView program.

![Diagram](image)

**Figure 2.5** The schematic diagram of the homemade plasma reaction chamber
In the center of the chamber, there is a capacitively coupled plasma (CCP) setup. The substrate is a four-inch diameter steel plate, and RF power is applied to the substrate as one electrode for the plasma. An ATX 600 AE Advanced Energy RF Matching Network (L type) is used as the RF power resource. Another plate, which is one inch above the substrate, works as a grounded electrode, so a plasma could be generated between the substrate and the plate. There is a heater beneath the substrate to control temperature, and a thermocouple is attached to the heater block with a metal clip. A ½ inch ceramic plate is inserted between the heater and the substrate as an insulation layer. The temperature on the sample surface was calibrated using a feedthrough thermocouple in the same position as used during the process.

2.3.2 Samples and Etchants

![Figure 2.6 Cross-section of metal samples. There is 100-160 nm metal film (Fe, Co, Ni or Pd) on 15 nm Ti adhesion layer](image)

Blanket Fe, Co, Ni, Pd samples were investigated because these metals are essential elements widely used in MTJ stacks. The metal films, which are used in our experiment, were purchased from Advantiv Technologies Inc. They have a metal layer (Fe: ~100 nm; Pd: ~120 nm; Co: ~160 nm; Ni: ~150 nm) on the top of a 15 nm Ti
adhesion layer and Si substrate. The wafers were cut into approximately 1 cm² coupons for etching. A mixture of Cl₂ (flow rate 10 sccm) and Ar (flow rate 30 sccm) is the activation gas/plasma we used to modify the metal surface under either with plasma and without plasma. Acetylacetone (acac, 98% purity) is purchased from Sigma Aldrich and stored in a stainless steel vessel. Before use, the acac was purified by three freeze, pump, and thaw cycles.

2.3.3 Characterization

A JSM -7400F SEM was used to measure the thickness of the films and surface morphology. The chemical composition and depth profiles of the etched films were examined by Auger electron spectroscopy (AES, PHI-610) with 3 kV beam voltage, 1.5 A filament current and 0.6 A emission current. The step size is 1 eV/step for C and Fe and 0.5 eV for Cl, O, Ti, Si with a resolution of ΔE/E of 0.6%. Sputtering in AES was done using an ion gun with voltage 3kV and emission current 25 mA. The sputter rate in the AES chamber on a standard SiO₂ wafer is 7 nm/min. In all AES depth profile data, the x-axis is the sputter time, and the y-axis is the atomic concentration of all elements.

2.4 Self-limiting Performance of Etchants

An ideal ALE process should be based on self-limiting reactions, which means the reactants can only react on the surface without continual removal of the film. Thus, the Cl₂/Ar mixture gas/plasma in step 1 should be optimized that it could only modified the surface instead of etching the film, while the organic gas acac in step 2 should not etch the clean metal surface but only the chlorinated surface. In our experiment, Cl₂/Ar plasma is sensitive to the RF power, pressure, flow rate and temperature. Limited by the capability of the home-made reaction chamber, we only focus on the influence of RF
power and temperature, while pressure and flow rates were fixed. The reaction pressure was set at 0.6 torr. RF power used was 100W and 200 W, while substrate temperature set points were 88, 144, 203 °C. The Cl₂/Ar mixture was dosed for 12 min to evaluate the self-limiting performance of Cl₂ plasma. The self-limiting performance of acac in step 2 is measured by a 20-cycle process with Ar plasma (rule out the influence of Cl₂) and acac exposure.

2.4.1 RF Power Dependent Cl₂ Reaction

RF power has the most important influence on the Cl₂ reaction on metal surfaces. The RF power was varied from 100 W to 200 W to compare the performance under different RF powers, while the temperature was fixed at 88 °C. The thickness of the metal films was measured by SEM in cross sections. As shown in Figure 2.7, the thickness of metal films shows little change with 100 W RF power. However, Fe, Co, Pd films were completely removed after 12 min reaction with 200 W plasma, suggesting that 200 W RF power is too high to have a self-limiting reaction in the Cl₂ step for Fe, Co, and Pd.

The chemical components on the surface after treatment with 100 W Cl₂ plasma were then determined with ex situ AES depth profile shown in Figure 2.8. The total thickness of all metal films did not change after the reaction. However, the reaction between metals and Cl₂ plasma chemically modifies the surface. The thickness of the modified layer on the Fe surface is greater than other metals, indicating that Fe has higher reactivity than the other metals. Fe, Co, Ni surfaces have high oxygen content because the metal surfaces are easily oxidized from ambient environment.
Figure 2.7 Thickness of metal films before and after the exposure of 100 W and 200 W Cl₂/Ar plasma for 12min

Figure 2.8 AES depth profiles of metal films after the exposure to 100 W Cl₂/Ar plasma for 12min (a: Fe, b: Co, c: Ni, d: Pd)
2.4.2 Temperature Dependent Cl\textsubscript{2} Reaction

Based on the previous performance test of Cl\textsubscript{2} plasma at 88 °C, we fixed the RF power at 100 W. Two more temperature set points (144, 203 °C) were used for the temperature dependent experiment. Temperature has less influence on the thickness. AES depth profile was used as the primary analysis method to study the chemical modified layer on the surface.

![Figure 2.9](image)

**Figure 2.9** Typical AES depth profiles of metal films after the exposure of 100 W Cl\textsubscript{2}/Ar plasma at different temperature for 12min. (a: Fe, 144 °C; b: Fe, 203 °C; c: Co, 203 °C; Pd: 203 °C)
After the 144 °C reaction, the depth profiles of metal films are similar to those after 88 °C reactions. The total thickness of all metals remained the same in AES depth profile. However, the thickness of chemical modified layer on the Fe surface increased as shown in AES depth profile (Figure 2.9a), which is different from the other metals. Presumably, the Cl diffusion into the Fe film is easier and makes a thicker FeClₓ layer. The high oxygen concentration on the surface is result from exposure to air. When the substrate temperature was 203 °C, the depth profiles in Figure 2.9b, c show that Fe and Co could be etching by Cl₂ plasma alone. The etching rate of Fe film was the fastest. The thickness of Pd film after dosing Cl₂ at 203 °C increased slightly due to a thicker PdClₓ layer on the top as show in Figure 2.9d. The Ni sample is a very stable when exposed to Cl₂. The AES depth profiles are similar after dosing Cl₂ at 88, 144, and 203 °C. Thus, 100 W Cl₂ plasma could not etch Fe, Co films when the substrate temperature is lower than 144 °C, and Ni, Pd films when the substrate temperature is lower than 203 °C.

2.4.3 Performance of Acac on Metal Surfaces

An ideal reaction gas in step 2 can only react with the Cl-modified layer made in the first step and cannot etch the metals. In this experiment, we tested the influence of acac on blanket metal films. To make the process similar with ALE, acac was dosed cyclically, in which Ar plasma was used in step 1 (RF power 200 W, pressure 0.6 torr, flow rate 30 sccm) and acac was dosed with pressure 0.6 torr in step 2. The process had 20 cycles and doses Ar and acac for 30 s in each step. The thickness of metal films does not change significantly in the depth profile compared with pristine samples, indicating that acac will not etch metal films under these conditions.
2.5 Performance of ALE with Cl\textsubscript{2} and Acac

ALE is based on the self-limiting performance of Cl\textsubscript{2} and acac. For Fe and Co films, the RF power for Cl\textsubscript{2} plasma was set at 0 W and 100 W, and the substrate temperature in the process was set at 88 °C and 144 °C. For Pd and Ni films, 200 W RF power and 203 °C substrate temperature was used. Between two different steps, the chamber was first pump down to 0.05 torr and purged with N\textsubscript{2} for 30 s to remove the volatile molecule on the surface.

2.5.1 Iron Samples

The etch rate was calculated based on the depth profile acquired using AES. Figure 2.7 shows the thickness change of Fe samples as a function of the number of ALE cycles. The RF power was fixed at 100 W for the halogen gas step. The pressure was 0.6 torr for both gases. As shown in Figure 2.10, the thickness of Fe film decreases with the number of cycles at substrate temperatures of 144 °C and 88 °C, (blue diamonds and red squares, respectively). Extracted from linear fits, the etching rates at 144 °C and 88 °C were 2.6 nm/cycle and 1.1 nm/cycle, respectively. As a comparison, single gas etching cycles were also performed at a substrate temperature of 144 °C with the same settings used in ALE experiment. Each gas alone shows little etching of the metal film, (green triangles and crosses respectively). Thus, both Cl\textsubscript{2} and acac play key roles in the surface reactions during ALE.
**Figure 2.10** The thickness of Fe film etched with different cycles. Black: 100W Cl\textsubscript{2}/Ar plasma in step 1, acac flow in step 2, substrate 144°C; Red: 100W Ar plasma in step 1, acac flow in step 2, substrate 88°C; Green: 100W Cl\textsubscript{2}/Ar plasma in step 1, N\textsubscript{2} flow in step 2, substrate 144°C; Blue: 100W Ar plasma in step 1, acac flow in step 2, substrate 144°C; Purple: Cl\textsubscript{2}/Ar flow without plasma in step 1, acac flow in step 2, substrate 144°C.

Given that the structure of MTJ is a stack of metals and alloys, the fabrication of MTJ requires anisotropic etching. The bias of plasma accelerates ions in a perpendicular direction, while the side wall only has thermal etching. We can determine the anisotropy by comparing the etching performance in plasma and thermal processes. In a thermal process, the dosing time of both halogen gas and organic gas are the same as the condition in previous with plasma condition. The number of ALE cycles was
fixed at 30 cycles, and the temperature is varied from 88 °C to 144 °C. The AES depth profiles of etched samples are shown in Figure 2.11. By comparing the thicknesses, the etch rate of thermal etching is much slower than plasma etching. From Fig 2.11c, no etching was evident at 88 °C while the etching rate is 1.1 nm/cycle with plasma, indicating that we can do anisotropic etching at this temperature. Figure 2.11d shows that the film was etched after 30 cycles etch at 144 °C without plasma. But the etching rate is 0.8 nm/cycle, which is also much slower than plasma etching.

![Figure 2.11 Depth profile of Fe samples etched at different temperatures with and without plasma in Cl2 step.](image-url)
The morphology of etched Fe surfaces was studied using SEM based on the samples etched after 10 and 20 ALE cycle at 88 °C with 100 W RF power in the Cl$_2$ step. The SEM images in Figure 2.12 show that the surfaces of etched films are rough. After 10 ALE cycles, small particles, which are the small white dots in the image, were observed on the surface. After 20 cycles, particles grow into larger islands with about 100 nm diameter. They can be result from either the etching products deposited on the surface or a non-uniform etching. Though we can used EDX to analysis the elements in the film, a precise assignment of the chemical components on the surface is not possible at present because the analysis depth of EDX can reach 1 um. In addition, the surface was also damaged by exposure to air.

![Figure 2.12 Surface morphology of etched Fe sample after 10 (left) and 20 (right) ALE cycle at 88 °C with 100W Cl$_2$/Ar plasma and 88 °C substrate temperature](image)

2.5.2 Cobalt, Palladium, Nickel samples

The ALE process on Co films was tested under the self-limiting condition like for Fe films. In the first step, a mixture of Ar (30 sccm) and Cl$_2$ (10 sccm) was dosed.
for 10 s with 100 W RF power. In the second step, acac was dosed for 30 s. The process temperature was 144 °C. However, the thickness of Co did not show significant change even after 50-cycles etching, as shown in Figure 2.13a. Based on the data in Table 2.2, the sublimation temperature of Co(acac)₂ is 147 °C, which is close to the substrate temperature. Presumably, the etching product is not Co(acac)₂ after the reaction of acac on a Cl modified Co surface.

Figure 2.13 Depth profile of Co, Ni, Pd samples etched by ALE method. a) Co, sample etched by 50-cycles ALE with 100W Cl₂/Ar plasma and 144 °C substrate temperature, b) Ni etched by 50-cycles ALE with 200W Cl₂/Ar plasma and 203 °C substrate temperature, c) Pd etched by 25-cycles ALE with 200W Cl₂/Ar plasma and 203 °C substrate temperature, d) Pd etched by 25-cycles reaction with 200W Cl₂/Ar plasma and 203 °C substrate temperature without acac
Ni is more stable than other metals. An ALE process with 200 W RF power in Cl$_2$ plasma and temperature 203 °C was used to etch Ni. However, the thickness of the Ni films also did not change significantly as shown in Figure 2.13b. Limited by the capability of the plasma chamber, Ni could not be etched under any conditions we tested.

As shown in Figure 2.13c, Pd films cannot be etched by ALE process with 200 W RF power in Cl$_2$ plasma and substrate temperature 203 °C too, even though the sublimation point of Pd(acac)$_2$, 68 °C, is much lower than the substrate temperature. However, if we only use Cl$_2$/Ar plasma to do a cyclic etching without acac at the same condition, Pd film was completely removed after 25 cycles as shown in Figure 2.13d. Therefore, acac is likely working as a passivation chemical on the Pd surface, instead of having a substitution reaction with PdCl$_x$.

2.6 Conclusions

In this study, we used Cl$_2$ and acac to perform atomic layer etching of different transition metal films under different substrate temperatures and plasma conditions. When the temperature is lower than 144 °C and RF power is lower than 100 W, either Cl$_2$ or acac will not etch the metal films.

The Fe film can be successfully etched by ALE with Cl$_2$ and acac. Both gases, applied in sequence, are necessary for etching. The ALE method can work not only with halogen plasma, but also without a plasma during chlorine exposure. The etching rate can reach 2.6 nm/cycle at 144 °C, and 1.1 nm/cycle at 88 °C with 100 W plasma, while the etching rate is ~0.8 nm/cycle at 144 °C without plasma. The etching is driven by chemical reaction and the plasma in Cl$_2$ step can highly enhance the etching rate, which can be used for anisotropic etching in MTJ fabrication. The etching rate is much larger
than one atomic layer and highly temperature dependent, which is likely influenced by the Cl diffusion into the metal.

ALE on other metals such as Co Pd, and Ni was also tested. Co could not be etched by the ALE with Cl₂ and acac under self-limiting conditions, even though the sublimation temperature of Co(acac)₂ is close to the substrate temperature. Ni is a more stable material than other metals. It could not be etched in any conditions we tested. For the Pd sample, acac is likely acting as a passivation reagent instead of a reactant to form a Pd(acac)₂ complex. The different performance on Fe, Co, Ni, Pd films indicates different acac reaction mechanisms on different chlorinated metal surfaces.

2.7 Acknowledgment

I would like to thank the funding support from the Delaware Research and Technology Center, American Air Liquide.
3.1 Introduction

In previous process development, we successfully etched an Fe film with cyclic reactions of Cl₂ and acac. However, the mechanism of Cl₂ and acac surface reaction is not clear. Understanding the reaction mechanism will be important to improve the performance of ALE and precursors, such as precisely control of etching rate, and capability to etch different metals (Fe, Co, Ni...).

It was difficult to study the mechanism with the previous experimental strategy, in which we performed the ALE process at Air Liquide and characterized the surfaces in University of Delaware. First, we were not able to trace the activated chemical component on metal surface during the process, such as the native metal oxide layer, chamber contamination, remaining etching intermediates and so on. Second, the surface analysis is ex situ, in which the sample surface will be altered by the oxygen, moisture and adventitious carbon in atmosphere during the sample transport.

Therefore, an in situ analysis system was necessary to overcome these issues, and in situ methods have been widely used for mechanism research of surface reaction. For example, the Hess group has used in situ XPS to study the reaction of β-diketone on FeOₓ surface²⁴; the George group used in situ quartz crystal microbalance to monitor the mass of the sample throughout the ALE process²⁸; the Masel group used in situ
temperature programmed desorption (TPD) to analysis the decomposition of acac on Ni (100) surface.\textsuperscript{75,76}

In this chapter, \textit{in situ} XPS analysis will be used to research the reaction of Cl\textsubscript{2} and acac on Fe and Co surface.

### 3.2 Experiment Setup

#### 3.2.1 \textit{In situ} Reaction Chamber

The structure of the home-made \textit{in situ} reactor is shown in Figure 3.1. The reactor is modified from a stainless steel six-way cross. The reactor is connected to the XPS main chamber through a manual gate valve. Samples were loaded from the XPS main chamber by a transfer arm and then placed on a stainless steel heating stage with a Heatwave Lab 101130 UHV cartridge heater inside. The heater was connected to a DC power supply through a vacuum feedthrough. The temperature was monitored by a K-type thermocouple attached to the stage. Sample surface temperature vs. thermocouple temperature was calibrated at the operating pressures of the reaction. An oil rough pump and an Edwards all-in-one turbo pump are used to control the pressure. A thermal gauge (10\textsuperscript{3}torr~10\textsuperscript{-4}torr) and an ion gauge (<10\textsuperscript{-4}torr) are used to monitor the chamber pressure. The background pressure is 10\textsuperscript{-9} torr in the XPS main chamber and 10\textsuperscript{-6} torr in the reaction chamber.

In order to determine the contamination in chamber background, we placed a clean sputtered Fe sample in the chamber and heated it to 140°C for 2h without dosing any gases. The atomic concentrations of adventitious C, O and Cl found on the surface were 17, 10, and 8 atom percent respectively. Therefore, the etching experiment is considered to be finished when the Cl atomic concentration approaches 8 atom percent.
Figure 3.1 a) A picture of the \emph{in situ} reaction chamber; b) Schematic diagram of the reactor and XPS for surface analysis. The base pressures of the system are $10^{-9}$ Torr for the spectrometer and $10^{-6}$ Torr for the reactor.
Acetylacetone (acac, 99.5% purity) were purchased from Aldrich Sigma and stored in a Pyrex tube. Before use, the acac went through three freeze, pump, and thaw cycles. Acac was delivered to the reaction chamber by evaporation through a leak valve. Cl₂ gas (99.9% purity) was purchased from Keen Gas. The pressure of Cl₂ and acac were controlled by needle valves and leak valves.

### 3.2.2 Metal Samples

400 nm sputtered iron metal (Fe⁰) thin film was deposited on 150 mm diameter Si (100) wafers by sputter PVD in UD Nano-Fab. The Co sample was provided by Air Liquide. A 300 nm Co film on top of 50 nm Ta and 500 nm thermal SiO₂. The samples were cut into 1cm by 1cm coupons. For a fundamental understanding purpose, the surfaces were sputter cleaned with 3 kV argon ions gun until the native oxide was removed as verified by XPS, then Cl₂ gas was dosed in the reaction chamber for 3min at room temperature at 100 mtorr. *In situ* XPS was used to analyze the chemical composition of the surface and near-surface regions during the etching reaction.

### 3.2.3 XPS Measurements

XPS studies were carried out using a PHI-5600 electron spectrometer. All XPS spectra were acquired using monochromatic Al Kα radiation (hv=1486.6 eV) with 23 eV pass energy and 0.05 eV/step. Ar sputtering used a 3kV ion gun and emission current at 25 mA. All of the binding energies were determined by reference to the Fe 2p₃/₂ peak at 706.8 eV. The sputter rate was calibrated by sputtering a 100 nm SiO₂ thin film. Peak fitting was done with CASA XPS software. A Shirley-type background subtraction was subtracted from each C 1s, O 1s, Cl 2p peak, and a mixture of Gaussian and Lorentzian functions was used for the fit. For the determination of iron valence state,
the Fe 2p$_{3/2}$ peak, Lorentzian Asymmetric (LA) convoluted line-shapes were also used.$^{77, 78}$

### 3.3 Cl$_2$ Reaction on Clean Fe Samples

![Fe$^{2+}$ peak multiplex](image)

**Figure 3.2** different Fe components in Fe 2p$_{3/2}$ XPS region after dosing Cl$_2$ at room temperature;

Cl$_2$ adsorbed on Fe surfaces at room temperature was first studied by XPS. The Cl$_2$ exposure was fixed at 100 mtorr pressure for 3 min. Figure 3.2 displays Fe 2p$_{3/2}$ XPS traces for Cl$_2$ dosed on the Fe surface. The Fe peaks are fitted with Gupta and Sen (GS) multiplets.$^{77, 78}$ The peak at 706.8 eV is the Fe$^0$ component, which is from the unreacted Fe layer under the FeCl$_x$. The broad peak is fitted into the 709.5, 710.1, and 711.2 eV peaks, which are corresponding to the Fe$^{2+}$ components split by spin-orbit
coupling interactions. The peak at 712.1 eV corresponds to the small amount of Fe\(^{3+}\) surface components, likely resulting from defects on FeCl\(_2\) surfaces. Finally, the peak at 715.1 eV corresponds to the Fe\(^{2+}\) satellite peak resulting from metal ligand charge transfer. The ratio between atomic concentration of Fe\(^{2+}\) and Cl is close to 1:2, suggesting that the major product of Cl\(_2\) adsorption on the surface is FeCl\(_2\).

Figure 3.3 The depth profiles of Fe surface layer after dosing Cl\(_2\) at different temperature (a:23 °C, b:80 °C, c:140 °C, d:180 °C)
The effect of temperature on Cl₂ adsorption was then studied. The thickness of the FeClₓ layer after dosing Cl₂ at room temperature is around 0.5 nm as shown by the XPS depth profile in Figure 3.3a and increases to 1 nm at 80°C (Figure 3.3b), 4.5 nm at 140°C (Figure 3.3c), and 8 nm at 180°C, which is much thicker than one atomic layer. The interface between FeClₓ and Fe substrate also appears broader at higher temperature. Similar with the Cl diffusion into Cu films in literatures, Cl₂ gas also activates Fe surfaces by diffusing into the metal film. Based on the Fick’s diffusion law,

\[ \frac{\partial c_x}{\partial t} = D \frac{\partial^2 c_x}{\partial x^2} \]

where x is the depth, cₓ is the Cl concentration at depth x, t is the diffusion time, and D is the diffusion coefficient which is temperature dependent. When the depth is \(4\sqrt{Dt}\), the Cl concentration will reduce to 0.08 of the Cl concentration on the surface. As a result, the diffusion depth is influenced by the temperature and the Cl₂ exposure time. The Cl₂ reaction has poor self-limiting performance.

### 3.4 Acac Reaction on The Chlorinated Fe Surface

#### 3.4.1 Temperature Dependence

The second step in the ALE process is the reaction of acac with Cl-modified Fe surfaces. The Fe sample was first dosed with 100 mtorr Cl₂ at room temperature for 3 min, and then acac vapor was dosed at different condition. In order to determine the optimum reaction temperature, we dosed 1 torr of acac at different temperatures for 3 min. Figure 3.4 shows the change of Fe 2p and Cl 2p photoemission peaks after dosing acac at different temperatures. When increasing reaction temperate from 23°C to 110°C, the intensity and components of Fe 2p and Cl 2p peak show little change compared to the spectra acquired before acac exposure. Changes in the XPS spectra are observed.
when the reaction temperature reached 135°C. The Cl 2p peak, Fe²⁺ components and the satellite peak all diminish after reaction, while the intensity of Fe⁰ component increases significantly. Thus, most of the Cl⁻ and Fe²⁺ are removed from the surface with acac as temperatures approach 135 °C.

![Spectra](image)

**Figure 3.4** the Fe 2p (left) and Cl 2p (right) spectra after dosing acac at different temperature (black: before dosing; red:90 °C; blue: 110 °C; green: 135 °C)

When the temperature is higher than 135 °C, the reaction rate is no longer sensitive to the temperature. Figure 3.5 shows the atomic concentration changes during the acac reaction with different acac pressure and temperature. The Cl removal rate is not a constant during the process and increases with acac exposure time at first and then slows when the Cl fraction is lower than 20 atom percent. The removal of Cl can be the result of several processes involving the acac reaction on the surface including 1) the desorption of HCl, 2) volatilization of an organic chloride product, or 3) a volatile metal complex. Removal of Cl is a necessary step for the further reactions between Fe²⁺ and
organic groups, including either the formation of volatile complex or reducing Fe$^{2+}$ to Fe$^0$ by the organic molecule. If we assume that the etching rate follows the rate of Cl removal, we can estimate the reaction rate. The average Cl removal rate is taken to be the time required for the Cl fraction to decrease from 40 atom percent to 20 atom percent.

![Figure 3.5](image)

**Figure 3.5** Elemental surface compositions of the chlorinated Fe surfaces after reaction with 100 mtorr acac exposure at 140°C (left) and 180°C (right)

### 3.4.2 Pressure Dependence

The influence of acac pressure was then studied at 140°C. Figure 3.6 shows the change of surface atomic concentration of all elements with acac exposure time under different pressures. The reaction follows similar trends at 100 mtorr, 200 mtorr and 400 mtorr, but the remaining organic groups on the surface after reaction are slightly different as shown in Figure 5a, b, c, respectively. At 100 mtorr acac pressure, the remaining carbon fraction is more than 50 atom percent after 40 min exposure. But when using 400 mtorr acac pressure, only 40 atom percent carbon remains after 20 minutes. In this part of the reaction cycle the reaction appears to be a first order reaction in acac
pressure, since the average removal rate of Cl ratio is proportional to the acac pressure (see Figure 3.6d). Thus, a higher acac pressure is preferred for this process, yielding a shorter reaction time and less organic residue in one reaction cycle.

**Figure 3.6** Elemental surface compositions of the chlorinated Fe surfaces after reaction with acac at 140 °C and different pressures (a, 100 mtorr; b, 200 mtorr; and c, 400 mtorr). Note that time axes vary for each condition. d) The Cl removal rate with various acac pressure at 140 °C. It suggests a first order reaction with the acac pressure.
3.4.3 Cyclic Reaction with Cl₂ and Acac

To prove that an Fe film can be etched by the two successive reactions, we dosed 100 mtorr Cl₂ for 3 min and 1 torr acac for 3 min at 140°C sequentially for 20 cycles. The thickness of the Fe film before and after etching was measured by XPS depth profiling. The thickness of Fe film decreases from about 450 nm to about 350 nm (sputter depths are determined by sputter rates in know thickness SiO₂ films) as shown in Figure 3.7. This etching rate is 5 nm/cycle, which is close to the thickness of the FeClₓ layer formed in each cycle (~4.5 nm in Figure 3d). Presumably, the extent of the Cl₂ reaction determined the etching rate, and the acac reaction only occurred with FeClₓ. Based on this result, a self-limiting ALE process could be developed by using a suitable halide precursor and optimized conditions.

Figure 3.7 XPS depth profile of Fe samples before (left) and after (right) 20 cycles of sequential exposure of Cl₂ and acac at 140°C.

3.4.4 Acac Decomposition During The Reaction

To study the reaction mechanism of the acac reaction on the Cl-dosed Fe surface, the chemical shifts in the C 1s photoemission spectra were acquired at high resolution.
Figure 3.8 presents the data for Cl-dosed samples dosed for different acac exposure times, showing the chemical states of C 1s after the reaction. Based on the surface composition with acac exposure at 140°C, 100 mtorr (Figure 3.6a), three time-points, 0, 15, 30 min, were selected for conditions corresponding to before acac reaction, during the acac reaction and after acac reaction conditions.

When a Cl$_2$ dosed Fe film was placed in the reaction chamber and heated to 140°C without dosing any acac, C 1s peaks were observed at 284.6 eV, 283.5 eV, 286.2 eV, and 287.5 eV which correspond to hydrocarbon bonded only to hydrogen and carbon, C-Fe bonding, C-O and C=O groups respectively. Only a weak O 1s peak at 531.9 eV was observed, which corresponds to C-O single bonds (e.g. alcohol or ether oxygen). These organic groups can be attributed to the chamber background contamination. Following 15 min exposure of acac the C 1s and O 1s showed different carbon and oxygen peak distributions compared to those observed without acac treatment. In the C 1s region, the intensity of the C 1s peaks at 284.6, 286.2 and 288.7 eV has increased, while the intensities of the carbide-like peak at 283.5 eV and the C=O peak at 287.5 eV remained similar to those observed before dosing acac. In the O 1s region, peaks with binding energies of 530.3, 532.6 and 534.6 eV were observed, which correspond to O$^{2-}$, C=O and carboxyl groups, respectively. The intensity of Cl peak decreased during the process. The remaining Cl peak shift from 199.1 eV to 199.5 eV, suggesting that either organic chloride compound was forming, or other electronegative groups coordinated with Fe and decrease the charge transfer from the Fe to the Cl. After dosing acac for 30 min, the binding energy of remaining Cl on the surface shifted back to 199.1 eV due to the FeCl$_3$ residues. The atomic concentration of Cl is close to the Cl baseline 8% from the chamber background, indicating the ending of acac reactions.
Comparing the spectra of samples after 15 min and 30 min acac exposure in Figure 3.8, several things are obvious. First, the Cl has been removed from the surface. The intensity of C 1s and O 1s peaks only increased slightly. Second, the intensity of C-Fe bonding peak, which increased after 15 min acac exposure, diminished after 30 min acac exposure. Third, comparing with the literature, acac should only have two C 1s contributions: methyl and C=O group with ratio 3:2. However, the intensity of the hydrocarbon peak increased much faster than the C=O group after 15 min and 30 min acac exposure in our experiment.

![Figure 3.8](image.png)

**Figure 3.8** High resolution photoemission spectra of C 1s, O 1s, and Cl 2p peaks on Fe thin films. The films are Cl-dosed (100 mtorr, 3 min, room temperature) Fe films, heated to 140°C, and following acac exposure of 0 min (bottom), 15 min (middle), and 30 min (top).
The decomposition of acac is likely to occur at high temperatures and increase the relative concentrations of O\(^2^-\), hydrocarbon and C-Fe bonding.\(^{82}\) C-Fe bonding can result from either background contamination or acac decomposition. The O\(^2^-\) or OH\(^-\) groups already present on the surface can also react with acac and lead to beta C-C bond scission.\(^{83}\) When most of the FeCl\(_x\) was removed, the ratio of C-Fe bonding decreased. The C-Fe peak originally is probably a result of reaction of the chlorinated surface with adventitious carbon before exposure with acac. During exposure to acac, the chlorinated surface may react further with acac leading to the formation of C-Fe bonding. Once the Cl is removed from the surface, acac (or adventitious carbon) no longer forms C-Fe bonds. This mechanism implies that the C-Fe species is an intermediate in the formation of a volatile etching product.

Due to the decomposition of acac, the etching mechanism does not appear to simply follow the proposed reaction. The acac decomposition products, including C-Fe bonding, O\(^2^-\) and C-O groups, could be either important intermediates in the process, or ligands in the volatile organometallic complex instead of acac. However, a precise assignment of the intermediate and etching product is not possible at present.

### 3.5 Reactions on Cobalt Surface

#### 3.5.1 Cl\(_2\) Adsorption on Co Surface

300 nm Co films provided by Air Liquide were exposed to 100 mtorr Cl\(_2\) gas for 3 min after removal of the CoO layer by the ion gun sputter. The Co peak at 778.1 eV is the Co\(^0\) component, which is from the unreacted Co layer under the CoCl\(_x\). The broad peak at 781.7 eV peaks corresponds to the Co\(^{2+}\) components from the Cl reaction. The peak at 787.4 eV corresponds to the Co\(^{2+}\) satellite peak resulting from metal adsorbate
charge transfer. The ratio between atomic concentration of Co\(^{2+}\) and Cl is close to 1:2, suggesting that the major product of Cl\(_2\) adsorption on the surface is CoCl\(_2\).

**Figure 3.9** different Co components in Co 2p XPS region after dosing Cl\(_2\) at room temperature, 140 °C and 180 °C;

The effect of temperature on the Cl\(_2\) adsorption was studied. The Co components on the Co surface after Cl\(_2\) reactions (room temperature, 140°C and 180°C) are shown in Figure 3.9. The Cl\(_2\) adsorption on Co surfaces is temperature dependent, but the Cl atomic concentration is much lower than seen on the Fe surface with the same Cl\(_2\) exposure. The Co\(^0\)/Co ratio on chlorinated Co surface is 0.87, 0.30, and 0 after Cl\(_2\) exposure at 23°C, 140°C and 180°C respectively. The different crystal lattice can be one of the reasons which lead to the difference between the Cl diffusion into Fe and Co surfaces. Cobalt crystals have hcp/fcc lattice, where the atomic packing factor (APF) is
0.74. Cobalt is more close-packing than iron which has bcc lattice (APF is 0.68). The Cl diffusion into Co films is more difficult.

3.5.2 Acac Reaction on Cl dosed Co Surface

To study the reaction mechanism of the acac reaction on chlorinated Co surfaces, the XPS chemical shifts were acquired at high resolution. Given that the Co film was not able to be etched at 144 °C in the process development experiment, the substrate temperature was then raised to 180 °C for surface reactions. Figure 3.10 compares all element components on the surface of chlorinated samples before and after the acac exposure (180 °C, 1 torr, 3 min). Changes in the XPS are observed after the reaction. The intensity of Cl 2p peaks and the Co$^{2+}$ component peak is reduced after the acac reaction, while the intensity of the Co$^0$ component increases significantly. Similar with the Fe reaction, the remaining Cl peak shifts from 199.3 eV to 199.7 eV, suggesting that either organic chloride compounds were forming, or electron-withdrawing groups coordinated with Co and weaken the bonding between Co and Cl. The removal of CoCl$_x$ can be the result of several processes involving the acac reaction on the surface including formation of volatile metal complexes or removal of an organic chloride product. The change of the CoCl$_x$ is less than the change of FeCl$_x$ when the acac exposure pressures and temperature are the same. (180 °C, 1 torr, 3 min)

Before the acac exposure, C 1s peaks were observed at 284.6 eV, which correspond to the hydrocarbon bonded only to hydrogen and carbon. The O 1s peak is too weak to be measured. The organic groups can be attributed to the chamber background contamination. After 3 min exposure of 1 torr acac, the C 1s and O 1s showed different carbon and oxygen peak distributions compared to those observed before the acac treatment. In the C 1s region, the intensity of the hydrocarbon group
peaks at 284.6 eV has increased and a peak at 287.1 eV appeared which corresponds to the C=O group bonded to the metal. In the O 1s region, peaks with binding energies of 530.2, 532.0 and 533.4 eV were observed, which correspond to O\(^2\), C=O and O-C=O, respectively.

**Figure 3.10** High resolution photoemission spectra of Co 2p, C 1s, O 1s, and Cl 2p peaks on Co films. The films are Cl-dosed (100 mtorr, 3 min, 140 °C) film and the chlorinated Co film after acac exposure (1 torr, 3 min, 180 °C)

The remaining organic components during the acac reaction on the chlorinated Co surface were quite different from Fe. First, the atomic concentration of carbon and
oxygen from organic groups is much lower on the Co surface. This can be a reason why the acac on the Co surface is less reactive than on the Fe surface. Second, the decomposition of acac is not significant on the Co surface. The carbanion group at 283.6 eV and C-O group at 286.1 eV were not observed on the Co surface. The different organic components may have two reasons. 1) Acac does not decompose on the Co surface; 2) products of the acac decomposition desorb from the Co surface faster than the Fe surface. It is difficult to identify the two reasons only with XPS.

3.6 Summary

We chemically etched Fe films by successively dosing Cl₂ and acac and investigated the influence of several conditions by using in situ XPS. Fe surfaces were activated by Cl₂ gas. XPS of the Fe 2p₃/₂ peak and the ratio between Fe and Cl components indicates that the major reactant on the surface is FeCl₂. The thickness of FeClₓ layer and the breadth of the FeClₓ/Fe interface is highly temperature dependent, indicating that the Cl₂ step has poor self-limiting performance at high temperature. To achieve precise control, an activation gas or plasma with better self-limiting performance may be needed to replace Cl₂.

Acac reactions were then carried out at various temperatures and pressures to identify the etching conditions. Acac was able to remove the FeClₓ layer at temperatures higher than 135°C, and the removal rate is proportional to the acac pressure. The mechanism of acac reaction on Cl-dosed Fe surfaces was studied by in situ XPS, showing that the reaction does not follow the acac substitution pathway. During the reaction, the acac molecule was not the major organic species on the surface. Instead, it is likely that the decomposition of acac plays an important role in this reaction. Species containing C-O, carboxyl or carbanion groups, which resulted from the acac
decomposition, likely participated in the formation of a volatile metal complex. It is important to determine which volatile complex formed after acac decomposition.

We also had preliminary results of the Cl$_2$ and acac reactions on Co surfaces. The Cl$_2$ adsorption on the Co surface is also temperature dependent. However, the Cl$_2$ adsorption on the Co surface is lower comparing with the Fe surface. The hcp lattice of Co crystalline, which is a more close-packing structure than bcc lattice of Fe, can be contribute to the weak Cl$_2$ adsorption on the Co surface. The acac reaction on chlorinated Co surfaces required higher temperatures (>180°C) than the Fe sample but removed less CoCl$_x$ on the Co surface than on the Fe surface. The different surface organic components can be a reason for the lower acac reactivity on the Co surface. The remaining organic groups on the Co surface show little carbanion and C-O groups after acac exposure. The difference can have two possible reasons. 1) acac does not decompose on the chlorinated Co surface; 2) acac decomposition products desorb from the Co surface faster than the Fe surface.

3.7 Acknowledgment

I would like to thank the funding support from the National Science Foundation and Delaware Research and Technology Center American Air Liquide.
Chapter 4

DENSITY FUNCTIONAL THEORY (DFT) SIMULATION OF THE ETCHING REACTION ON FE SURFACE

4.1 Introduction:

4.1.1 Motivation

In previous chapters, we studied the etching process by a series of experiments and surface analyses. A fundamental study of reaction mechanisms in the etching process can also be made by computational studies. The advancement of computational quantum mechanics such as density functional theory (DFT), has been widely used to identify different chemical reactions. DFT provides an effective way to predict molecular structures and energies including structure stability, surface morphologies\(^8\), surface electronic structures\(^5\), work functions\(^6\), structural reconstructions\(^7\), and adsorbate interactions\(^8\).

In this chapter we ask two questions based on previous experiments. 1) the uniformity of surface reaction. From the \textit{in situ} XPS studies, we found that the interface between FeCl\(_x\) and Fe was rough. Given that sputter deposited Fe films are polycrystalline films, the major surface is Fe (110) and other crystal orientations will exist on grain boundaries. The influence of different crystal orientations and defects to the surface reaction will be investigated. 2) Acac substitution reaction on chlorinated Fe surface. From the \textit{in situ} XPS studies, decomposition of acac is observed, and it is likely necessary for the formation of a volatile complex. However, it is uncertain if direct acac...
substitution is the major reaction on chlorinated Fe surface. By using DFT simulation, the thermodynamic energies in each proposed step can be calculated to explain these results.

4.1.2 Density Functional Theory (DFT)

In quantum mechanics, the Schrödinger equation is a mathematical equation that describes the changes over time of a quantum mechanical system. The simple form of time-independent Schrödinger equation can be described as:

\[ H \Psi = E \Psi \]

where \( H \) is the Hamiltonian operator, \( \Psi \) is wave function, and \( E \) is the eigenstate energy of wave function \( \Psi \). The eigenstate energies and wave functions are independent of time. In real systems, multiple electrons need to be considered. The interaction between multiple electrons and nuclei can be simplified by Born-Oppenheimer approximation, where the wavefunctions of nuclei and electrons in a molecule can be separated. The wavefunction of electrons can be solved by the equation described as:

\[
\left[ -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} V(r_i) + \sum_{i=1}^{N} \sum_{j<i} U(r_i, r_j) \right] \Psi = E \Psi
\]

where \( m \) is the electron mass, \( N \) is the number of electrons. This equation is the sum of the electron kinetic energy, the interaction energy between the electrons and the nuclei, and the interaction energy between different electrons. Directly solving this many-body Schrödinger equation is impossible.

DFT provides an effective way to simplify the many-body problem by solving the ground-state electron density instead of solving for the individual electrons based on the Hohenberg-Kohn theorem\(^{89}\) and the Kohn-Sham equation.\(^{90}\) The Hohenberg-Kohn theorem proves that the correct ground state electron density can minimize the
total energy of the system, and uniquely determine the ground state properties including energy and the wave function. The Hohenberg-Kohn theorem uses the functional of the electron density and makes a theoretical foundation for reducing the many-body problem of N electrons with 3N spatial coordinates to three spatial coordinates. Based on the Hohenberg-Kohn theorem, the Kohn-Sham DFT was further developed to simplify the calculation. The Kohn-Sham equation is a one-electron Schrödinger equation of a fictitious system with non-interacting particles (typically electrons) that generate the same density as any given system of interacting particles. The Kohn-Sham equations can be described as:

\[ -\frac{\hbar^2}{2m} \nabla^2 + V(r) + V_H(r) + V_{\text{xc}}(r) \Psi_i(r) = E_i \Psi_i(r) \]

The electron potential includes external potential \( V(r) \), Hartree potential \( V_{\text{H}}(r) \) and exchange-correlation potential \( V_{\text{xc}}(r) \). In this Schrödinger-like equation, it only involves a single electron and the electron potential \( V(r)+V_{\text{H}}(r)+V_{\text{xc}}(r) \) is related to the electron density.

### 4.1.3 Basis Sets and Pseudopotentials

In DFT, basis sets are important for solving the Kohn-Sham equation. The two commonly used basis sets are localized functions and planewaves.\(^{91,92}\) Localized basis sets, also known as atomic basis sets, are based on atomic centered electron orbitals. For a single molecule or cluster structure with limiting numbers of atoms, localized basis sets use fewer basis functions and have higher efficiency. However, localized basis sets are not suitable for infinite structure due to basis set superposition error (BSSE). The most well-known localized basis sets are Gaussian basis sets.
Planewaves basis sets are delocalized periodic basis functions in the whole space which do not have the BSSE. They are widely used in the simulation of infinite structures, such as metal surfaces and band structures. The accuracy and computational time can be determined by setting a cut-off energy value and the number of planewaves needed. The core electrons of atoms are not involved in bonding interactions and have little influence on the total electron structure. The pseudopotential approximation was used to replace the complicated effects of core electrons coupled to nuclei to increase computational efficiency.

4.1.4 Surface Modelling

The two most common models for simulations of crystalline surface structure are the cluster models and the slab models. The major difference between these two methods is the result of the basis sets used. The cluster model usually uses localized basis sets. The surface is represented as a small isolated cluster of atoms. The major challenge in this method is reducing the influence of cluster edges. The choice of cluster size and shape is important for reducing the influence of the cluster edge. The slab model, which has an infinite two-dimension slab with a periodic structure, is commonly used for planewave basis sets. Given that the slab unit is repeated along x, y, z direction, a vacuum layer is inserted into the system to minimize the interaction between two slabs along z direction. In this model, the choice of the vacuum layer thickness and the slab thickness are essential to the time consumption and calculation accuracy. The slab modelling is a more common way to simulate the metal surface.
4.1.5 Software

There are several commercially available DFT software packages, using different basis sets. Gaussian developed by Dr. Pople is one of the most widely used DFT software packages that uses localized basis sets. The Vienna \textit{ab-initio} simulation package (VASP)\textsuperscript{92, 94} from the Theoretical Physics Department at the University of Vienna, is another widely used DFT software package based on planewaves basis sets.

4.2 Calculation setup

In this thesis, the theoretical calculation of total energies and structural optimizations of selected products were performed for Fe surfaces using VASP. Spin polarized calculations using the Perdew-Burke-Ernzerhof (PBE)\textsuperscript{95} functional and projector augmented plane wave (PAW) potentials\textsuperscript{96} were used for all calculations.

DFT was employed for two types of calculations: (1) Cl adsorbate energy on Fe surface and (2) geometry of adsorbed molecules and total energy of molecules and the surface in the acac reaction.

4.2.1 Lattice Parameter Optimization:

The construction of Fe surface slab is based on bcc Fe crystal. The lattice parameter was optimized according to the Birch–Murnaghan equation of state\textsuperscript{97} to get the lowest total energy as shown in Figure 4.2. The equation of state (EOS) describes the relationships among thermodynamic variables such as energy and volume.

\[
E_{\text{tot}}(a) = E_0 + \frac{9V_0B_0}{16} \left[ \left( \frac{a_0}{a} \right)^2 - 1 \right] ^3 B_0' + \left( \frac{a_0}{a} \right)^2 \left( 6 - 4 \left( \frac{a_0}{a} \right)^2 \right)
\]

In this equation, \( E_0 \) is total energy at the equilibrium state; \( a_0 \) is the equilibrium lattice constant; \( V_0 \) is the equilibrium volume; and \( B_0 \) is the bulk modulus. For the thermodynamic calculation, the calculated Fe lattice constant is 2.804 Å for the
minimum total energy of the Fe bulk. Calculated values for the lattice constant compare well with corresponding experimental measurements.\textsuperscript{98}

![Graph showing the total energy of Fe crystal bulk and the crystal volume calculated by VASP, the relationship is fitted by Birch–Murnaghan equation of state](image)

**Figure 4.1** The total energy of Fe crystal bulk and the crystal volume calculated by VASP, the relationship is fitted by Birch–Murnaghan equation of state

### 4.2.2 Slab Modelling

A 5-layer Fe slab with a (3x3) super unit cell was used in the calculations in which the three top-most layers were relaxed for surface structure optimization while the bottom two layers were fixed at their bulk positions to simulate the influence from the bulk. A 20.0 Å vacuum layer was inserted into unit cells along the z-direction. Calculations were carried out using an energy cutoff of 400 eV and integrations over the Brillouin zone were performed using a 6x6x1 mech of Monkhorst-Pack\textsuperscript{99} k-points.
Two low index Fe surfaces were examined in this thesis: 1) Fe (110), the lowest energy surface of the bcc lattice, and 2) Fe (100), a higher energy surface that may be present locally. The total energies of different structures were calculated by VASP.

Figure 4.2 A 5-layer Fe slab with (3x3) super cells and 20.0 Å vacuum layer. The top three layers were relaxed for optimization, and the bottom two layers were fixed.

4.2.3 Simulation of Gas Molecule

A single molecule (such as Cl₂, HCl, acac and hypothetical etching products) is placed in a 20*20*20 Å³ cubic vacuum cell to simulate the molecule in gas phase. Calculations were carried out using an energy cutoff of 400 eV and integrations over the Brillouin zone were performed using a 1x1x1 mesh of special k-points.

Based on the in situ XPS results, the major component on chlorinated Fe surface is FeCl₂. The hypothetical product of acac substitution in this chapter is also Fe²⁺ complex. Two Fe²⁺ complexes with acac ligands are shown in Figure 4.3. Both have
stable molecular structures after optimization in this calculation. FeCl(acac) has an Fe metal center with one Cl and one acac ligand. Fe(acac)$_2$ is a square planar structure with two acac ligands. The total energies of FeCl(acac) and Fe(acac)$_2$ are -95.5 eV and -177.9 eV. Both molecules are produced by replacing a Cl atom on the surface with an acac molecule. We will focus on the surface structure with one acac molecule on the surface in the following calculations. If the reaction is exothermic, it will be considered thermodynamically preferred. If not, the substitution mechanism between acac and chlorinated Fe surface might not occur.

![Figure 4.3 Two stable Fe$^{2+}$ complex with acac ligand after optimization. Left: FeCl(acac); Right: Fe(acac)$_2$](image)

### 4.3 Reaction on Smooth Surface

#### 4.3.1 Cl$_2$ gas Adsorption

The change of enthalpy, $E_1$, in Cl$_2$ adsorption is calculated according to:

$$E_1 = \frac{1}{n} \left[ E_{Cl/\text{slab}} - \left( E_{\text{slab}} + \frac{n}{2} E_{Cl_2} \right) \right]$$
where $n$ is the number of chlorine atoms adsorbed on the simulated portion of the slab. $E_{\text{Cl/Slab}}$, $E_{\text{slab}}$, and $E_{\text{Cl}_2}$ stand for the total energies of the Cl-dosed Fe surface, clean Fe surface, and an isolated chlorine molecule, respectively.

![Figure 4.4](image)

**Figure 4.4** Top views of Cl/Fe(110) (left) and Cl/Fe(110) (right) surface configurations. Green and brown spheres denote Cl and Fe atoms respectively.

On the Fe (100) surface, the Cl coverage can reach 100% with a mixture of hollow site and bridge site bonding. The average adsorption energy $E_1$ for each Cl atom is -2.05 eV (-198 kJ/mol). Fe (110) surface is the close-packed surface on bcc lattice. The adsorption of Cl in the simulation is unstable for a coverage of one Cl for each surface Fe. The maximum stable coverage is then found to be 0.67 with adsorption energy $E_1$ -2.23 eV (-215 kJ/mol) for each Cl atom.

In the Cl$_2$ reaction step, the calculated Cl$_2$ adsorption energy and highest coverage on Fe (100) and Fe (110) surfaces are quite different, indicating different
exothermicity on Fe (100) and Fe (110) surfaces. Due to this reactivity difference, presumably, Cl\textsubscript{2} will react mostly at grain boundaries or defects on the Fe surface.

4.3.2 Acac Substitution on Chlorinated Fe Surface

In order to form FeCl(acac), an acac molecule will react with one Cl atom on the surface and produce an HCl molecule. After replacing one Cl\textsuperscript{-} with acac\textsuperscript{-} anion in this reaction, the energy \( E_2 \) is calculated according to:

\[
E_2 = E_{acac/stab} + E_{HCl} - E_{Cl/stab} - E_{acac}
\]

where \( E_{acac/Slab} \), \( E_{Cl/Slab} \), \( E_{acac} \), and \( E_{HCl} \) represent the total energies of the Cl-dosed Fe surface after an acac\textsuperscript{-} ligand replaced a Cl\textsuperscript{-}, a Cl-dosed Fe surface, an isolated acac molecule and an isolated HCl molecule; respectively. \( E_2 \) was first calculated based on the optimized Cl dosed smooth Fe surfaces.

On the Fe (100) surface, replacing a Cl atom with acac will rearrange the surface structure. A Fe atom can be withdrawn from the surface after optimization, and the substitution energy \( E_2 \) is 0.31 eV (30 kJ/mol). On the Fe (110) surface, replacing a Cl atom with acac does not withdraw any Fe atoms from the surface. The energy needed for this reaction is 1.98 eV (191 kJ/mol), which is much higher than the energy on the Fe (100) surface. In addition, the structure, in which the acac has bidentate coordination with an Fe atom, is unstable in the structure optimization. Therefore, it is very difficult to form a FeCl(acac) complex on a smooth surface. The acac substitution for Cl is not thermodynamically preferred on either Fe (110) or Fe (100) smooth surfaces.
4.4 Reaction of Defect Surface

4.4.1 Isolated Fe Atom on Smooth Surface

The influence of defects on surface reactions was also considered, where we used an isolated Fe on a smooth Fe surface to simulate a defect site. The energy change can be described as:

$$\Delta E = E_{\text{def}} - E_{\text{slab}} - E_{\text{Fe gas}}$$

where $E_{\text{def}}$ and $E_{\text{slab}}$ are the total energies of defect surface and smooth surface. $E_{\text{Fe gas}}$ is the energy of free Fe atom. The total energies of defect Fe surface and smooth Fe surface are listed in table 4.1.

The energy of a free Fe atom is -3.37 eV (-325 kJ/mol) and the total energy of an isolated Fe on the smooth Fe (100) surface can be reduced by -6.63 eV (-399 kJ/mol). The total energy of isolated Fe on Fe (110) surface can be reduced by -4.86 eV (-293 kJ/mol).
kJ/mol). The energy differences on the surfaces proved that the defect surfaces are more stable thermodynamically. The reaction between this isolated Fe atom and gas molecules will be calculated by the influence of surface defect.

Table 4.1 Total energies of Fe slab and Fe slab with an isolated Fe atom

<table>
<thead>
<tr>
<th></th>
<th>Fe (100)</th>
<th>Fe (110)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smooth surface</td>
<td>-357.62 eV</td>
<td>-367.08 eV</td>
</tr>
<tr>
<td>Surface with isolate Fe atom</td>
<td>-367.63 eV</td>
<td>-374.32 eV</td>
</tr>
<tr>
<td>Free Fe atom</td>
<td>-3.37 eV</td>
<td>-3.37 eV</td>
</tr>
<tr>
<td>Energy change</td>
<td>-6.63 eV</td>
<td>-4.86 eV</td>
</tr>
</tbody>
</table>

4.4.2 Cl₂ Gas Adsorption

Table 4.2 compares the energy of the Cl₂ adsorption on both defect and smooth Fe (100) and Fe (110) surfaces. The defect Fe atom only reduced the adsorption energy slightly on the Fe (100) surface from -2.05 eV (-202 kJ/mol) to -2.13 eV (-205 kJ/mol). The configuration of Cl atoms on the defect Fe (100) surface is similar with the smooth Fe (100) surface. Because the isolated Fe atom occupies a hollow site on the Fe (100) surface, one of the hollow site Cl atoms moves to the top of the isolated Fe atom.

Table 4.2 Cl₂ adsorption energy on defect Fe surface

<table>
<thead>
<tr>
<th></th>
<th>Fe (100)</th>
<th>Fe (110)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smooth surface</td>
<td>-2.05 eV</td>
<td>-2.23 eV</td>
</tr>
<tr>
<td>Surface with isolate Fe atom</td>
<td>-2.13 eV</td>
<td>-2.29 eV</td>
</tr>
</tbody>
</table>

The Cl atoms configuration on the defect Fe (110) surface changed a lot after optimization -- three Cl atoms bridge to the isolated Fe atom. However, the adsorption energy did not have significant change too. The defect atom only reduced the adsorption energy on the Fe (110) surface from -2.23 eV (-215 kJ/mol) to -2.29 eV (-221 kJ/mol).
4.4.3 Acac Substitution on Chlorinated Fe Surface

On surfaces with defect, the acac molecule is able to bidentately coordinate with the isolated Fe atom. On the Fe (100) surface, the surface configuration with a FeCl(acac) complex on the surface, which can be a product of acac substitution, was stable after DFT optimization. The acac substitution energy will be -1.51 eV (-146 kJ/mol) on the Fe (100) surface as shown in Figure 4.6. The desorption of this FeCl(acac) complex required 1.26 eV (122 kJ/mol), which is close to the sublimation energy of some metal acac complexes.\(^7\)

![Figure 4.6 The energy change of acac substitution on chlorinated Fe (100) surface with an isolated Fe atom](image)

However, on the Fe (110) surface, the acac substitution reaction is still difficult to occur. There are three Cl atoms bridged between the isolated Fe atom and surface Fe atoms, which makes a stable Cl-dosed Fe surface. Though we can get a stable structure after replacing one of the bridging Cl atoms with acac, the reaction energy is 2.07 eV (200 kJ/mol), which is still a very high barrier for a reaction. Given that the main surface of a Fe crystal is Fe (110), the direct acac substitution for Cl is unlikely the major etching reaction on a polycrystalline Fe film, even though the defect can assist the substitution reaction on the Fe (100) surface.
4.5 Summary

Using DFT simulation, the reaction of Cl$_2$ adsorption and acac substitution on chlorinated surfaces are compared on Fe (100) and Fe (110) smooth and defect surfaces. Based on the discussion presented above, we can reach several conclusions.

First, the adsorption energies of Cl$_2$ calculated by DFT simulation varies a lot on different crystal surfaces. The Cl coverage can reach 100% on the Fe (100) surface, while the maximum stable coverage is then found to be 0.67 on the Fe (110) surface. Cl$_2$ is found to react more exothermally on defect sites or less energetically favorable surface orientations (Fe (100) surface). The different surface reactivity can explain the Cl diffusion in previous experiments.

Second, the DFT calculations also indicated that the acac substitution for Cl is not thermodynamically preferred on Fe surfaces. The hypothetical etching product in this dissertation is FeCl(acac). The acac substitution can only remove the isolated Fe atom from Fe (100) by forming the FeCl(acac) complex. However, similar reactions are not likely to happen on both smooth chlorinated Fe surfaces and the defective Fe (110) surface. On smooth surfaces, the acac bidentate coordination structure is not stable on either Fe (100) or Fe (110) surfaces during the structure optimization. The direct acac substitution energies are 0.31 eV (30 kJ/mol) on the Fe (100) surface, 1.98 eV (191 kJ/mol) on the smooth Fe (110) surface and 1.26 eV (122 kJ/mol) on the defect Fe (110) surface, which are high energy barriers for the reaction. Therefore, the direct acac substitution is difficult on the Fe surface.

4.6 Acknowledgment

I would like to thank the funding support from the National Science Foundation and Delaware Research and Technology Center American Air Liquide, the help from
Professor Anderson Janotti and computer clusters technical support from chemistry and biochemistry department, University of Delaware.
Chapter 5
SURFACE PHOTO VOLTAGE ANALYSIS FOR BAND BENDING ON SEMICONDUCTOR SURFACE

5.1 Introduction

5.1.1 Band Bending on Semiconductor Surface

Band bending exists on semiconductor surfaces due to the different chemical environment between the surface and bulk, such as the termination of lattice periodicity at the surface, adsorption of molecules, contact with other materials, and so on.\textsuperscript{100} The surfaces of semiconductors are often depletion regions (or space-charge regions) where the built-in electric field, due to defects at the surface, has swept out mobile charge carriers. This reduced carrier density means that the electron energy band of the majority carriers is bent away from the Fermi level and generates a surface potential. As shown in Figure 5.1, for n-type semiconductors, the Fermi level in the bulk is closer to the conduction band, so that the surface will be negatively charged and generate a building potential to reach an equilibrium, and the bands bend upward near the surface. For p-type semiconductors, the Fermi level in the bulk is closer to the valence band, and the band bends downward on the surface.

Surface photovoltage (SPV) involves monitoring the change in the electrical potential of a semiconductor surface after generating electron-hole pairs with a light source.\textsuperscript{101, 102} When excited by light, the extra conduction electrons in n-type materials
are repelled from the surface by the built-in potential and, conversely, the holes are trapped near the surface with the net result of flattened bands.

**Figure 5.1** The charge transitions on surface photovoltage effect

5.1.2 **Photoelectron Spectroscopy Measurements of SPV**

The band bending at solid interfaces can be estimated by different optical and electrochemical measurements. In photoelectron spectroscopy (XPS or UPS), the electrical potential at the surface is measured by shifts in the photoelectron binding energy. In Kelvin probe, the potential at the surface is measured using a capacitive technique. Recently, the Suzer group reported using X-ray photoelectron spectroscopy (XPS) to study the surface photovoltage (SPV) under ultra-high vacuum (UHV). They studied the SPV on Si surfaces and at Si/SiO₂ interfaces and developed a dynamical XPS technique to measure the light bias by measuring the charging condition of the surface. Since XPS is a very surface-sensitive technique (probe depth < 10 nm), the change in the band bending coming from the surface photovoltage will result in the XPS binding energy (BE) shifts, as illustrated in Figure 5.2. They used the shifts in
elements core level peaks to detect the charging from the light exposure. The binding energy shift is repeatable when turning the light on and off. Based on the light-induced peak shifts, they discovered that SiO$_2$ layer on Si surfaces can increase the band bending in the p-type Si and decrease the band bending in the n-type Si.

![Diagram of surface photovoltage experiment with PES.](image)

**Figure 5.2** surface photovoltage experiment with PES. The binding energy (BE) of VBM can be defined as the energy between the VBM and the fermi level. Light exposure can flatten band bending at the surface. The binding energy will increase for n-type semiconductor and decrease for p-type semiconductor.
5.2 SPV Measurement Setup

The binding energy was measured on a Phi-5600 X-ray photoelectron spectrometer, using monochromatic Al Kα excitation ($h\nu = 1486.7$ eV). The spectrometer binding energy (BE) scale was calibrated by measuring core level spectra from sputter-cleaned Au, Ag and Cu foils. High-resolution core level spectra were acquired at pass energy $E_{\text{pass}} = 46$ eV with a step-size of 0.05 eV. This data was collected without a neutralizer.

An OSRAM Sylvania 69263 XBO 1000W/HS Xenon arc-lamp was used for white-light biasing. The beam from this lamp was directed into the chamber with mirrors through a quartz viewport. A blocking metal panel was placed over the viewport as a shutter to control the light on and off manually. The other viewports on the vacuum chamber were blocked to prevent the interference of ambient room light.

5.3 Dye/Metal Oxide Materials

Dye sensitized thin film solar cells (DSSCs) have attracted attention for application in solar energy conversion since the Gratzel group first reported a high overall solar-to-electric conversion efficiency. One of the most widely used materials in DSSCs is metal phthalocyanine (Pc), offering the following advantages: (i) better energy conversion efficiency, (ii) highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies that can be finely tuned by changing the Pc ring substituents and the central metals, (iii) excellent chemical, thermal and light stability, and (iv) HOMO/LUMO energy levels that lie close to the conduction band and valence band in large band gap semiconductors like TiO$_2$. 
Figure 5.3 Relative energy (metal oxide data based on literature\textsuperscript{110}, dye LUMO/HOMO data was provided by The Gorun group) of the valence bands (VB) or highest occupied molecular orbital (HOMO) and conduction band (CB) or lowest unoccupied molecular orbital (LUMO) with respect to the vacuum level.

Band alignment between the dye and the semiconductor is crucial in device design since it plays an important role in charge separation, transfer and recombination between the dye and the semiconductor.\textsuperscript{111, 112} In conventional designs, both the dye LUMO and HOMO are a little higher than the semiconductor conduction band (CB) and valence band (VB) edge. How well the LUMO of the dye molecules match the conduction band determines the dye-to-semiconductor electron injection rate.
5.3.1 Sample Preparation

The 29H,31H,1,4,8,11,15-18,22,25-octafluoro-2,3,9,10,16,17,23,24-octakis-perfluoroisopropyl phthalocyanine Zinc(II) (F64PcZn) dye, shown in Figure 5.5, is synthesized by the Gorun group in Seton Hall University.\textsuperscript{113}

P90 TiO\textsubscript{2} Powder (average size: 14 nm), F64PcZn/P90 TiO\textsubscript{2}, F16PcZn/P90 TiO\textsubscript{2}, F64PcZn/Al\textsubscript{2}O\textsubscript{3}, and F64PcZn/NiO powder samples were also provided by the Gorun group in Seton Hall University. The powder samples were attached to carbon tape and compressed into a pellet with glass slide manually for further XPS measurement as shown in Figure 5.6. Atomic concentration of all elements will be provided in following sections.

Anatase TiO\textsubscript{2} films were grown on Si wafers by Sputter PVD in the Nano Fab of University of Delaware. Sputtering was done with a 1.5 kV by 0.4 A power source at 400 °C, 500mTorr in Ar+O\textsubscript{2} atmosphere (20% oxygen).\textsuperscript{114} The thickness of the TiO\textsubscript{2} layer was 72 nm after 30min growth as measured by ellipsometry. A 10 nm dye layer was further deposited on the TiO\textsubscript{2} film by the Gorun group of Seton Hall University.

![Figure 5.4 Molecular structure of F64PcZn dye](image-url)
5.3.2 Powder Samples

5.3.2.1 F64PcZn/P90 Powder

XPS results show that the atomic concentrations of F64PcZn/P90 powders pressed on a carbon tape are 16.4% Ti, 44.4% O, 29.4% C, 9.2% F, 0.4% N and 0.1% Zn. Since the concentration of the dye was very low (Zn ~0.1%), the high component of C mostly likely comes from the carbon tape. We choose F as the major element to track the light-induced binding energy shift of the dye, which has relatively higher intensity. And O and Ti peak were used to track the light-induced binding energy shift of TiO$_2$.

Table 5.1 Chemical Shift of F64PcZn/P90 and P90 TiO$_2$ samples

<table>
<thead>
<tr>
<th></th>
<th>Light</th>
<th>O 1s</th>
<th>Ti 2p$_{3/2}$</th>
<th>C 1s</th>
<th>F 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>F64PcZn/P90</td>
<td>On</td>
<td>530.8eV</td>
<td>459.5eV</td>
<td>285.6eV</td>
<td>689.4eV</td>
</tr>
<tr>
<td></td>
<td>Off</td>
<td>530.3eV</td>
<td>459.1eV</td>
<td>285.1eV</td>
<td>688.8eV</td>
</tr>
<tr>
<td></td>
<td>Shift</td>
<td>0.5eV</td>
<td>0.4 eV</td>
<td>0.5eV</td>
<td>0.6eV</td>
</tr>
<tr>
<td>P90</td>
<td>On</td>
<td>529.9eV</td>
<td>458.6eV</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Off</td>
<td>529.8eV</td>
<td>458.5eV</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Shift</td>
<td>0.1eV</td>
<td>0.1eV</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As shown in Figure 5.7, the peak shift upon illumination in the F64PcZn/P90 powder sample is approximately 0.4–0.6 eV to higher binding energy. The increasing
binding energy indicates that the valence and conduction bands of TiO\textsubscript{2} bend upward at the surface and are flattened upon the exposure to light.

Figure 5.6 High resolution XPS of O1s, Ti2p\textsubscript{3/2}, and F1s peak in F64PcZn/P90 TiO\textsubscript{2} samples under dark and illuminated condition.

To determine if there is any interaction between the dye and TiO\textsubscript{2}, a pure P90 TiO\textsubscript{2} sample was measured separately to compare the different binding levels. N-type semiconductors usually have upward band bending at the surface. The peak shift of the pure P90 TiO\textsubscript{2} sample upon illumination is approximately 0.1 eV (shown in Figure 5.8),
which is much smaller than the 0.4~0.6 eV shift seen for the F64PcZn/P90 sample, as listed in Table 5.1. The different peak shifts are likely caused by the increasing band bending at the interface between F64PcZn and TiO$_2$. Presumably, F64PcZn can act as a p-type semiconductor, which increases the negative charging on the surface of TiO$_2$.

**Figure 5.7** High resolution XPS of O1s, Ti2p$_{3/2}$ peak in P90 TiO$_2$ samples under dark and illuminated condition

### 5.3.2.2 F16PcZn/P90 powder

As shown in Figure 5.9, the SPV results of the F16PcZn/P90 powder sample are similar to those with the F64PcZn/P90 powder sample. The chemical shift in F16PcZn/P90 sample is 0.2~0.4 eV to higher binding energy when illuminated by the white light. The peak shift also matches with the band bending on the TiO$_2$ surface region, which is upward as an n-type semiconductor. The smaller band bending may result from a weaker interaction with TiO$_2$ comparing the F16PcZn with the F64PcZn dye.
Figure 5.8 SPV measurement of F16PcZn/TiO$_2$ with high resolution XPS on O1s, Ti2p$_{3/2}$ and F1s peaks, red line is illuminated condition, black line is dark condition.

5.3.2.3 F64PcZn/Al$_2$O$_3$ powder

As shown in Figure 5.10, SPV of the F64PcZn/Al$_2$O$_3$ powder sample is different from F64PcZn/P90 TiO$_2$ powders. The binding energy is much larger than the theoretical values due to the surface charging of Al$_2$O$_3$. Binding energies of all elements reduced about 0.6 eV under illuminated condition. As an insulator, the band gap of Al$_2$O$_3$ is approximately 9 eV, which is too large to be excited by the light with the wavelength larger than 140 nm. Presumably, the peak shift of the F64PcZn/Al$_2$O$_3$ is
resulted from the dye molecule, which works as a p-type semiconductor and generates a built-in voltage on the surface.

**Figure 5.9** High resolution XPS of O1s and Al2p\textsubscript{3/2} of F16PcZn/Al\textsubscript{2}O\textsubscript{3} of SPV measurement, the peaks shift to low binding energy with light on the sample

### 5.3.2.4 F64PcZn/NiO powder

We also compared the SPV of p-type semiconductor NiO and F64PcZn/NiO powder samples, as shown in Figure 5.11. However, the peak shift in both samples is
not significant (<0.1 eV), indicating that the NiO powder has a flat band near the surface and a weak surface interaction with the dye.

Figure 5.10 SPV measurement of NiO and F64PcZn/NiO with high resolution XPS, red line is dark condition, black line is illuminated condition. a) O1s of NiO; b) Ni2p\(_{3/2}\) of NiO; c) O1s of F64PcZn/NiO; d) Ni2p\(_{3/2}\) of F64PcZn/NiO

So far, SPV results show that the dye molecule can interact differently with an n-type, p-type semiconductor and insulator. The F64PcZn is likely serving as a p-type
semiconductor, which can increase the band bending of the n-type TiO$_2$ powder samples and decrease the binding energy of the Al$_2$O$_3$ samples when exposure to the light. For the F16PcZn dye, we only research a F16PcZn/P90 TiO$_2$ powder sample. Similar with the F64PcZn dye, the F16PcZn can increase the band bending of the n-type TiO$_2$ powder. The bending of the F16PcZn/P90 TiO$_2$ sample is smaller than the F64PcZn/P90 TiO$_2$ sample due to the weaker electron withdraw ability of F16PcZn.

5.3.3 F64PcZn/Anatase TiO$_2$ Film

In powder samples, some dye molecules may be compressed inside the pallet, which can also be excited when exposed to the light. In addition, the thickness, density and uniformity of the pallet may be different. To further understand the interaction between the dye and TiO$_2$, we investigated a thin film sample (5-10 nm dye film on the top of 72 nm TiO$_2$ film).

The atomic concentration of the thin film sample with 10 nm F64PcZn dye layer on the top of a 72 nm TiO$_2$ is found out to be 31.8% F, 41.4%C, 3.6%N, 0.4%Zn, 17.3%O, and 5.6%Ti in XPS. The F:N:Zn ratio is close to the ratio in F64PcZn molecule. The ratio of C and O is a little higher due to the contamination from the ambient. The O and Ti signals indicate that the analysis depth is deeper than the thickness of the dye layer. The major different between this sample and powder samples is that the peak shifting process is much slower for the thin film sample. The peak shifts of major element peaks (Ti, O, F) with the alternating light condition are depicted as shown in Figure 5.12. Each light condition lasts about 40 min. For the first illumination step, the peak shift of all elements is very small (<0.05 eV). And the peak shifted back when the light bias was removed in cycle 7-11. But in the second illumination step, the peak of all elements continues to shift to higher binding energy.
The SPV performance of the film is quite different than the powder samples. The peak shift is much smaller than powder samples, and the cyclic evolution of peak shift is not reproducible.

There are several possible factors that be attributed to this photo-induced shift. 1) A photocatalytic reaction occurs at the TiO$_2$/dye interface. Anatase TiO$_2$ is also known to be an active photocatalyst.$^{115}$ In Figure 5.13, we can see that there are two F 1s components in both films. The stronger peak at 689.5 eV is from the C-F group (F bonded to C) of the dye. The smaller peak at 685.1 eV is consistent with a M-F bond,
which may result from F64PcZn decomposition. The intensity of M-F component is much weaker in the 10 nm dye film than 5 nm film, suggesting that decomposition of dye occurs on the TiO$_2$ surface. This decomposition may change the interaction between dye layer and TiO$_2$ layer, or the conductivity and charging on the surface. In either event different peak shifts would be expected in the thin film and powder samples. 2) The dye layer (5-10 nm) in the thin film sample is thicker than powder samples. The light induced charge redistribution in the dye layer (excitation, surface charging, dipole rearrange and so on) instead of the SPV on the interface may contribute to the different chemical shift when exposed to the light.

![Figure 5.12](image)

**Figure 5.12** The F components in 10 nm dye layer film (left) and 5 nm dye layer film (right).

### 5.4 Passivated Si Samples

Reducing the recombination of excited electrons of Si surfaces is increasingly important for Si solar cells. As the recombination rate is related to the surface defect density, different materials have been used to reduce the number of surface defect sites including organic molecules and inorganic thin films. $^{117,118}$ Benzoquinone in methanol solutions (BQ/ME) is one of the organic passivants that has been utilized by our group, providing a surface recombination velocity as low as 1.6 cm/s. Meixi Chen in our group
has found that the BQ/ME passivation is driven by a light-induced radical reaction on the Si surface. The semiquinone radical HO-C₆H₄–O∙, and methanol radical CH₃O∙ are responsible for bonding to the silicon surface defect sites. The bonding of organic groups on n-type Si surfaces will also change the electron distribution, which may introduce an electrical passivation effect.

The work function is the key to explore the electronic structure of the BQ modified Si surface. It is determined by a combination of the surface band bending, electronic structure, and electron affinity. XPS SPV measurement was used to measure the combination of the surface band bending and electron affinity on the BQ modified Si surface.

5.4.1 Sample Preparation

The Si wafers were double side polished n-type silicon (100) wafers with a resistivity of 1–5 Ω*cm and 280 μm thickness. The wafers were cleaned by following steps to make a hydrogen terminated surface: first, a piranha clean consisting of a 5 min bath in a 4:1 solution of sulfuric acid and hydrogen peroxide. Piranha solutions were freshly made and cooled to room temperature for 10 min before use. Then, the wafers were given a 5 min DI water submersion and immersed in a HF (2%) solution for 2 min to make H-Si wafers. In the end, H-Si wafers were rinsed with DI water and dried by N₂ purging. The cleaned H–Si wafers were quickly placed in different solutions (0.01 mol/L BQ/ME solution for BQ termination, or pure methanol solution for ME termination) and sealed in plastic bags. Samples were kept in the BQ/ME solution before the SPV testing.
5.4.2 SPV of Passivated n-Si Sample

Figure 5.13 Cyclic evolution of peak shifts of Si. Cycle 1-4, cycle 9-12 and cycle 17-20 are in the dark, and cycle 5-8 and cycle 13-16 are in the light.

As shown in Figure 5.14, all n-type Si samples treated by BQ, ME and H have a repeatable energy shift to a lower binding energy in the illuminated condition, which indicates a downward band bending. The bending direction is different from SiO₂/Si surfaces, which has an upward band bending. This suggests that the bonding between organic groups and the Si surface creates a significant field-effect contribution to the surface potential. For all three samples, BQ-Si has the largest band bending (~0.23 eV) while H terminated Si has the smallest band bending (~0.05 eV).
5.5 Summary

Surface photovoltage measurements using XPS were utilized for measuring the band bending on organic molecule-modified semiconductor surfaces.

The interaction between the phthalocyanine dye molecule and different metal oxide powders was measured by the XPS SPV analysis. The F64PcZn molecule on the powder surfaces can increase the binding energy on n-type TiO$_2$ powders by approximately 0.5 eV and reduce the binding energy on insulating Al$_2$O$_3$ powders by approximately 0.6 eV. The F64PcZn is likely acting as a p-type semiconductor, and, due to the new charge distribution, changes the band-bending at the substrate surface. However, the SPV performance on a thin film sample is different from the performance on powder samples. The peak shift is less than 0.1 eV, and the cyclic evolution of peak shift is not reproducible. The mechanism of the photo induced chemical shift at the dye/TiO$_2$ thin film sample is more complex than powder samples where the decomposition of dye or charge redistribution in the organic layer also likely influences the XPS chemical shift.

For n-type Si samples, surface photovoltage measurements indicate a downward band bending of H, BQ and ME treated samples. The BQ-Si sample has the largest band bending, indicating that the bonding between BQ and Si generated a significant field-effect contribution to eliminate the recombination of electrons and holes on the surface.

5.6 Acknowledgment

I would like to thank the funding support and the sample preparation from the Gorun group in Seton Hall University.
Chapter 6

SUMMARY AND FUTURE WORK

6.1 Summary of Results

6.1.1 ALE Process Research

6.1.1.1 Process Development

In this dissertation, we used Cl\(_2\) and acac to perform cyclic etching on transition metal films under different substrate temperatures and plasma RF powers. The etching performance, including the self-limiting behaviors, anisotropic etching, and etching rates at different conditions, was studied.

The Fe films are successfully etched by ALE with Cl\(_2\) and acac. When the temperature is lower than 144 °C and the RF power is lower than 100 W, Cl\(_2\) or acac could not remove Fe from the surface independently. The adsorption of each single gas can reach a saturation on the surface. The Fe layers removed in each cycle are more than one atomic layer and highly temperature dependent. The surface morphology of the etched samples is rough. Both etching rates and surface morphologies suggest that the self-limiting performance of Cl\(_2\) and acac is not good enough for an atomic layer process.

The performance of thermal and plasma processes demonstrates that the etching rate can be significantly enhanced by the plasma in Cl\(_2\) step. In addition, at 88 °C, Fe films could not be etched by Cl\(_2\) and acac in a thermal process but can be etched in a
plasma process. The different etching rates at plasma and thermal conditions can be utilized for the anisotropic etching in MTJ fabrication.

The ALE performance on other metals, such as Co, Pd, and Ni, suggests different reaction mechanisms on different metal surfaces. Co could not be etched by the ALE with Cl\textsubscript{2} and acac with a substrate temperature lower than 150 °C, even though the sublimation temperature of Co(acac)\textsubscript{2} is lower than 150 °C. The etching products might be some different cobalt complexes. Ni could not be etched under any conditions we tested. On the Pd films, acac performed as a passivation reagent instead of making a Pd(acac)\textsubscript{2} complex.

6.1.1.2 Mechanism study

The etching rate per cycle is determined by the thickness of FeCl\textsubscript{x} layer -- the product of the Cl\textsubscript{2} reaction in the first step. The Fe 2p\textsubscript{3/2} peak and the ratio of Fe and Cl components in XPS spectra indicates that the major chemical on the surface is FeCl\textsubscript{2}. The thickness of FeCl\textsubscript{x} layer and the breadth of the FeCl\textsubscript{x}/Fe interface is highly temperature dependent, indicating that the Cl\textsubscript{2} can diffuse into the Fe films and the Cl\textsubscript{2} reaction on Fe surfaces is not uniform. The adsorption energy of Cl\textsubscript{2} was calculated by DFT simulations. Cl\textsubscript{2} is found to react more exothermally on defect sites or less energetically favorable surface orientations. To achieve a more precise control, a less reactive gas or plasma such as NF\textsubscript{3}, ICl, or IBr\textsuperscript{120} might be used to replace Cl\textsubscript{2} and reduce the adsorbate diffusion for better self-limiting performance.

The lowest etching temperature is determined by the acac reaction on metal surfaces. The acac was able to remove the FeCl\textsubscript{x} layer with a temperature higher than 135°C, and the removal rate is proportional to the acac pressure. Both the in situ XPS and the DFT simulation suggest that the mechanism of the acac reaction on chlorinated
Fe surfaces does not follow the classical acac substitution pathway. Instead, the decomposition of acac is likely playing an important role in this reaction. From the XPS spectra, acac was not the major organic species on the surface during the reaction. Surface species containing C-O, carboxyl or carbanion groups, which result from the acac decomposition, likely participate in the formation of volatile metal complexes instead of a pure acac substitution. DFT calculations also indicate that the acac substitution for Cl is not thermodynamically preferred on Fe surfaces.

The reaction on Co surfaces is different comparing with that on Fe surfaces. In the Cl\(_2\) reaction, the CoCl\(_x\) on Co surfaces is less than the FeCl\(_x\) on Fe surfaces. The acac reaction on chlorinated Co surfaces required a higher temperature than on Fe surfaces but removed less CoCl\(_x\) when using the same acac pressure as in the acac reaction on Fe surfaces. The remaining organic groups on the Co surface show little carbanion and C-O groups after the acac exposure, indicating that acac reaction mechanism on the chlorinated Co surface may be different from the chlorinated Fe surface.

6.1.2 Surface Photovoltage (SPV) Analysis of Organic Molecule Modified Semiconductor Surface

We have adopted a method to measure surface photovoltage on semiconductor surfaces using XPS. XPS SPV have been successfully used to measure the band bending near the semiconductor surface, which are modified by adsorption of organic molecules. In metal oxide powder samples, the band bending resulting from interaction between a phthalocyanine dye molecule and the metal oxide was observed. F64PcZn and F16PcZn act as p-type semiconductors, and, due to the new charge distribution, changes the band-bending at the surface of TiO\(_2\) powders. On n-type Si films, surface photovoltage
measurements indicate a downward band bending of H-Si, Benzoquinone(BQ)-Si and Me-Si samples. BQ-Si samples has the largest band bending, indicating that the bonding between BQ and Si generated a strong field-effect contribution to eliminate the recombination of electrons and holes on the surface.

However, the SPV performance on a deposited organic film is different. The peak shift of deposited F64PcZn/TiO$_2$ films (F64PcZn layer 5-10 nm, TiO$_2$ layer 72 nm) is less than 0.1 eV, and the cyclic evolution of peak shift is not reproducible. The mechanism of the photo induced chemical shift is more complex in samples with a thick organic layer, where the decomposition of the organic molecule or charge redistribution in the organic layer may also influence the XPS chemical shift.

6.2 Future Work

6.2.1 ALE Process Development

The study of Cl$_2$ and acac reactions on pure metal films in this dissertation has opened a door to ALE for MRAM fabrications. Further research will focus on how to improve ALE performance on metal films and fulfill the needs of the MRAM fabrication. In the future, we will continue working in three directions for this project: 1) utilize ALE in MRAM device fabrication, such as the alloy film etching and the performance on patterned samples (selectivity, anisotropic etching, etc.); 2) based on the mechanism, study more precursors and choose the best one; 3) improve in situ experiments to get more information of the surface reactions.

6.2.1.1 Application for Real MRAM System

First of all, we need to apply ALE to those materials which are widely used in MRAMs. So far, the most common material in ferromagnetic layers is the FeCoB alloy
for commercial MRAMs. In addition, FePt and CoPt alloys with the L1\textsubscript{0} structure are widely used alloys in perpendicular magnetic tunneling junction (p-MTJ) devices for next generation MRAMs which have a lower power consumption and faster reading/writing speed. The alloys mentioned above contain Fe or Co which have been successfully etched with Cl\textsubscript{2} and beta-diketone cyclic reactions in our experiments. Based on our results, we will try to etch FeCoB and CoPt films with similar reactions.

Second, the structure of MTJs is a complex stack of metals and alloys. In the fabrication of these devices, the anisotropic etching capability and selectivity between metals and mask materials on pattern samples will be necessary for real applications. In the future, the plasma etching condition will be finely optimized for anisotropic etching on patterned metal samples. The SEM will be used to research the morphology of the surfaces and device side walls. We will also compare the etching rates on metals and other materials to research the etching selectivity.

Third, the last goal of ALE is a precise etching control. In the meantime, the etching rate is much more than a single atomic layer per cycle, so that it cannot be used for the precise etching based on the cycles. Because the removal of metal atoms is determining by the thickness of the MCl\textsubscript{x} layer from the Cl\textsubscript{2} reaction, we will finely tune the etching conditions (such as gas pressures, plasma bias, RF power, gas flows) to control the etching rate and the surface morphology.

6.2.1.2 Looking for new etchants

The etchants in our ALE methods are Cl\textsubscript{2} gas/plasma and beta-diketone gases. The results from Chapter 3 and 4 of Cl\textsubscript{2} and acac reactions have provided some valuable information for choosing new etchants.
In the surface activation step, the thickness of metal chloride layer determines the etching rate. However, Cl\textsubscript{2} gas/plasma is so reactive that the thickness of metal chloride layer is much more than a single atomic layer. Cl\textsubscript{2} gas will be replaced by different gases or plasmas to improve the etching performance. To achieve a more precise control, a less reactive gas or plasma such as NF\textsubscript{3}, ICl, or IBr\textsuperscript{120} might reduce the adsorbate diffusion for better self-limiting performance. To increase the anisotropy of ALE for patterned samples, the plasma which could provide side wall protections such as SiCl\textsubscript{4}/Cl\textsubscript{2}/Ar can also be used to replace Cl\textsubscript{2} gas.\textsuperscript{122}

In the second step, the decomposition of acac is playing an important role in the etching reaction instead of the acac substitution for Cl. A possible decomposition mechanism is the beta C-C bond cleavage\textsuperscript{83}, which has several potential decomposition products, including carbanion, ketone, CO or CH\textsubscript{2}=C=O groups. We will test the influence of those decomposition products with both in situ analysis and DFT simulation. The suitable molecule should be able to etch the metal more efficiently and eliminate by-products remaining on the surface in the XPS analysis. In the DFT simulations, the reaction of a suitable molecule on metal surfaces should also have lower thermodynamic energies for replacing a Cl atom on the surface and removing the organometallic complexes.

6.2.1.3 Improvement of in situ characterization

First, XPS can only provide the information of the chemicals remaining on the surface. We are not able to analyze those leaving molecules, especially in the acac reaction on the chlorinated surface. To research those chemicals in the gas phase, we will cooperate with the Teplyakov group in University of Delaware to do the temperature programed desorption (TPD) measurement. TPD can analyze the gas-phase
molecules desorbed from the surface under UHV conditions and provide the information regarding the products and byproducts of the surface reaction and their desorption temperatures. The TPD chamber in the Teplyakov group is able to dose organic precursors for an in situ surface reaction on chlorinated metal surfaces. In the future, we will prepare the chlorinated metal surface in our lab and transfer the sample to Dr. Teplyakov’s lab to do the in situ TPD analyses for the acac reaction on the chlorinated surface as soon as possible.

Figure 6.1 An extra port on the top of the in situ reaction chamber which can be used for installation of an electrode of CCP system and wiring of RF generator

Second, the in situ reaction chamber now can only do the thermal etching. However, if we would use some organic chloride precursors to make a chlorinated metal
surface, a plasma system will be necessary. A capacitively coupled plasma (CCP), which is similar with the system in Air Liquide, is suitable for this reaction chamber. To construct a CCP system, the six-way cross will be replaced by a larger chamber. The sample holder can work as an electrode which is grounded. Another electrode will be fixed on the top of the reaction chamber, which is connected to an RF generator. An extra port on the top and extra spaces have been left for this modification.

6.2.2 SPV Analysis

6.2.2.1 SPV Measurement with Kelvin Probe

Different SPV methods will be utilized as a reference to the XPS SPV measurement. The Kelvin probe is another commonly used method for measuring the relative change of the Fermi level. Unlike XPS, Kelvin probes can work under ambient conditions or in a solution. In the Kelvin probe measurement, two surfaces of different materials are considered as two sides of a parallel capacitor as shown in Figure 6.2. The vacuum between the metal and semiconductor electrodes in the circuit works as a dielectric layer. The contact potential difference ($V_{cpd}$) will be affected by the surface band bending of the semiconductor. The light-induced $V_{cpd}$ shift can be used for the surface photo voltage measurement of the semiconductor.

The measurements can be done by the scanning Kelvin probe microscopy (SKPM). The SKPM is usually installed on an atomic force microscopy (AFM), so that it can do high spatial resolution scans on the surface. The SKPM SPV measurement can be done in a specific small area on the surface. It can also study the surface morphology and the charge distribution at the same time, which is suitable for some non-uniform samples.
6.2.2.2 DFT Simulation for SPV Measurement

DFT simulations have been used for explaining the reactions in the ALE process. Another student in our group, Meixi Chen, also used the DFT simulation to predict the structure of organic groups on benzoquinone passivated Si surfaces. DFT simulations are an important tool for the theoretical study of the organic molecule on the semiconductor surface.

The DFT simulations is also able to predict the band structure near the surface. We can first simulate the bonding condition and the configuration of organic molecules on the surface. The bonding on the surface can be used to explain the reaction mechanism and the interaction between organic molecules and the semiconductor. Based on the surface structure, DFT software (such as VASP) can calculate the band

---

Figure 6.2 A rough schematic diagram of Kelvin probes by measuring the contact potential difference between two surfaces
structure of the materials from the bulk to the surface and provide the information such as electrostatic potential and charge distributions,\textsuperscript{125} which can help us to predict the XPS chemical shift in the SPV measurement.
REFERENCES


https://en.wikipedia.org/wiki/Scanning_electron_microscope


38. Lichtman, B. “Complimentary Memory Technologies to Reform the Homogeneity, Energy Landscape, and Volatility of Future Memory Hierarchies.” 2015,


68. Basova, T.V. “Volatile Precursors for Films Deposition: Vapor Pressure, Structure and Thermodynamics.” 2011, Ch. 20


76. Nigg, H.L. and R.I. Masel. “Surface reaction pathways of 1,1,1,5,5,5-hexafluoro-2,4-pentanediene on clean and pre-oxidized Ni(110) surfaces.” *Journal of Vacuum Science & Technology A*, 1999, 17, 3477-3480


103. Gorgoi, M. and D.R.T. Zahn. “"Band bending" in copper phthalocyanine on hydrogen-passivated Si(111).” *Organic Electronics, 2005, 6, 168-174*


Order Completed

Thank you for your order.

This Agreement between Xi Lin ("You") and AIP Publishing ("AIP Publishing") consists of your license details and the terms and conditions provided by AIP Publishing and Copyright Clearance Center.

Your confirmation email will contain your order number for future reference.

<table>
<thead>
<tr>
<th>printable details</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>License Number</td>
<td>4302550450833</td>
</tr>
<tr>
<td>License date</td>
<td>Jul 19, 2018</td>
</tr>
<tr>
<td>License Publisher</td>
<td>AIP Publishing</td>
</tr>
<tr>
<td>Licensed Content Title</td>
<td>In situ XPS study on atomic layer etching of Fe thin film using Cl2 and acetylacetone</td>
</tr>
<tr>
<td>Licensed Content Author</td>
<td>Xi Lin, Meixi Chen, Anderson Janotti, et al</td>
</tr>
<tr>
<td>Licensed Content Date</td>
<td>Sep 1, 2018</td>
</tr>
<tr>
<td>Licensed Content Volume</td>
<td>36</td>
</tr>
<tr>
<td>Licensed Content Issue</td>
<td>5</td>
</tr>
<tr>
<td>Requestor type</td>
<td>Author (original article)</td>
</tr>
<tr>
<td>Format</td>
<td>Print and electronic</td>
</tr>
<tr>
<td>Portion</td>
<td>Figure/Table</td>
</tr>
<tr>
<td>Number of figures/tables</td>
<td>8</td>
</tr>
<tr>
<td>Requestor Location</td>
<td>Xi Lin</td>
</tr>
<tr>
<td></td>
<td>1 Wenham Dr Apt 5</td>
</tr>
<tr>
<td></td>
<td>Newark, DE 19713</td>
</tr>
<tr>
<td></td>
<td>United States Attn:</td>
</tr>
<tr>
<td>Billing Type</td>
<td>Invoice</td>
</tr>
<tr>
<td>Billing address</td>
<td>Xi Lin</td>
</tr>
<tr>
<td></td>
<td>1 Wenham Dr Apt 5</td>
</tr>
<tr>
<td></td>
<td>Newark, DE 19713</td>
</tr>
<tr>
<td></td>
<td>United States Attn:</td>
</tr>
<tr>
<td></td>
<td>Xi Lin</td>
</tr>
<tr>
<td>Total</td>
<td>0.00 USD</td>
</tr>
</tbody>
</table>

Copyright © 2018 Copyright Clearance Center, Inc. All Rights Reserved. Privacy statement. Terms and Conditions. Comments? We would like to hear from you. E-mail us at customerservice@copyright.com.
This is a License Agreement between Xi Lin ("You") and IOP Publishing ("IOP Publishing") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by IOP Publishing, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

<table>
<thead>
<tr>
<th>License Number</th>
<th>4373661191364</th>
</tr>
</thead>
<tbody>
<tr>
<td>License date</td>
<td>Jun 21, 2018</td>
</tr>
<tr>
<td>Licensed content publisher</td>
<td>IOP Publishing</td>
</tr>
<tr>
<td>Licensed content title</td>
<td>Journal of Physics D : Applied Physics</td>
</tr>
<tr>
<td>Licensed content date</td>
<td>Jan 1, 1970</td>
</tr>
<tr>
<td>Type of Use</td>
<td>Thesis/Dissertation</td>
</tr>
<tr>
<td>Requestor type</td>
<td>Academic institution</td>
</tr>
<tr>
<td>Format</td>
<td>Print, Electronic</td>
</tr>
<tr>
<td>Portion</td>
<td>chart/graph/table/figure</td>
</tr>
<tr>
<td>Number of charts/graphs /tables/figures</td>
<td>1</td>
</tr>
<tr>
<td>The requesting person/organization is:</td>
<td>Xi Lin</td>
</tr>
<tr>
<td>Title or numeric reference of the portion(s)</td>
<td>Chapter 1, Figure 1.8.</td>
</tr>
<tr>
<td>Title of the article or chapter the portion is from</td>
<td>N/A</td>
</tr>
<tr>
<td>Editor of portion(s)</td>
<td>N/A</td>
</tr>
<tr>
<td>Author of portion(s)</td>
<td>N/A</td>
</tr>
<tr>
<td>Volume of serial or monograph.</td>
<td>N/A</td>
</tr>
<tr>
<td>Page range of the portion</td>
<td>12</td>
</tr>
<tr>
<td>Publication date of portion</td>
<td>2018/8/31</td>
</tr>
<tr>
<td>Rights for</td>
<td>Main product and any product related to main product</td>
</tr>
<tr>
<td>Duration of use</td>
<td>Life of current edition</td>
</tr>
<tr>
<td>Creation of copies for the disabled</td>
<td>no</td>
</tr>
<tr>
<td>With minor editing privileges</td>
<td>no</td>
</tr>
<tr>
<td>For distribution to</td>
<td>Worldwide</td>
</tr>
<tr>
<td>In the following language(s)</td>
<td>Original language of publication</td>
</tr>
</tbody>
</table>
TERMS AND CONDITIONS

The following terms are individual to this publisher:

These special terms and conditions are in addition to the standard terms and conditions for CCC’s Republication Service and, together with those standard terms and conditions, govern the use of the Works. As the “User” you will make all reasonable efforts to contact the author(s) of the article which the Work is to be reused from, to seek consent for your intended use. Contacting one author who is acting expressly as authorised agent for their co-author(s) is acceptable.

User will reproduce the following wording prominently alongside the Work:

- the source of the Work, including author, article title, title of journal, volume number, issue number (if relevant), page range (or first page if this is the only information available) and date of first publication. This information can be contained in a footnote or reference note; and
- a link back to the article (via DOI); and
- if practicable, and IN ALL CASES for new works published under any of the Creative Commons licences, the words “© IOP Publishing. Reproduced with permission. All rights reserved”

Without the express permission of the author(s) and the Rightsholder of the article from which the Work is to be reused, User shall not use it in any way which, in the opinion of the Rightsholder, could: (i) distort or alter the author(s)’ original intention(s) and meaning; (ii) be prejudicial to the honour or reputation of the author(s); and/or (iii) imply endorsement by the author(s)
Title: Semiconductor Logic Technology
Innovation to Achieve Sub-10 nm Manufacturing

Authors: Klaus Schwegler

Publication: IEEE Journal of the Electron Devices Society

Publisher: IEEE

Date: March 2013

Copyright © 2013, IEEE

Thesis / Dissertation Reuse

The IEEE does not require individuals working on a thesis to obtain a formal reuse license, however, you may print out this statement to be used as a permission grant:

Requirements to be followed when using any portion (e.g., figure, graph, table, or textual material) of an IEEE copyrighted paper in a thesis:

1) In the case of textual material (e.g., using short quotes or referring to the work within these papers) users must give full credit to the original source (author, paper, publication) followed by the IEEE copyright line © 2011 IEEE.

2) In the case of illustrations or tabular material, we require that the copyright line © [Year of original publication] IEEE appear prominently with each reprinted figure and/or table.

3) If a substantial portion of the original paper is to be used, and if you are not the senior author, also obtain the senior author's approval.

Requirements to be followed when using an entire IEEE copyrighted paper in a thesis:

1) The following IEEE copyright/credit notice should be placed prominently in the references: © [year of original publication] IEEE. Reprinted, with permission, from [author names, paper title, IEEE publication title, and month/year of publication]

2) Only the accepted version of an IEEE copyrighted paper can be used when posting the paper or your thesis on-line.

3) In placing the thesis on the author's university website, please display the following message in a prominent place on the website: In reference to IEEE copyrighted material which is used with permission in this thesis, the IEEE does not endorse any of [university/educational entity's name goes here]'s products or services. Internal or personal use of this material is permitted. If interested in reprinting/republishing IEEE copyrighted material for advertising or promotional purposes or for creating new collective works for resale or redistribution, please go to http://www.ieee.org/publications_standards/publications/rights/rights_link.html to learn how to obtain a License from RightsLink.

If applicable, University Microfilms and/or ProQuest Library, or the Archives of Canada may supply single copies of the dissertation.
This Agreement between Xi Lin ("You") and John Wiley and Sons ("John Wiley and Sons") consists of your license details and the terms and conditions provided by John Wiley and Sons and Copyright Clearance Center.

License Number: 4382176323354
License date: Jul 04, 2018
Licensed Content Publisher: John Wiley and Sons
Licensed Content Publication: Surface & Interface Analysis
Licensed Content Title: Interactions of CO2 and CO at fractional atmosphere pressures with iron and iron oxide surfaces; one possible mechanism for surface contamination?
Licensed Content Author: D. J. Miller, M. C. Biesinger, N. S. McIntyre
Licensed Content Date: Mar 8, 2002
Licensed Content Volume: 33
Licensed Content Issue: 4
Licensed Content Pages: 7
Type of use: Dissertation/Thesis
Requestor type: University/Academic
Format: Print and electronic
Portion: Figure/table
Number of figures/tables: 1
Original Wiley figure/table number(s): Figure 2
Will you be translating?: No
Title of your thesis / dissertation: SURFACE CHEMISTRY RESEARCH OF ELECTRONIC PROCESSES AND ELECTRONIC DEVICES
Expected completion date: Aug 2013
Expected size (number of pages): 1
Requestor Location: Xi Lin
1 Wenark Dr, Apt 5
Newark, DE 15713
United States
Attn:
Publisher Tax ID: EU826007151
Total: 0.00 USD

Terms and Conditions
Figure 1.1

Summary

| Description | English: This schematic depicts the process known as the "Photo-electric Effect" as it pertains to XPS. |
| Date | 10 June 2010 |
| Source | Own work (Original caption: "I created this work entirely by myself.") |
| Author | Bvcrist |

Licensing

This work has been released into the public domain by its author, Bvcrist at English Wikipedia. This applies worldwide. In some countries this may not be legally possible; if so: Bvcrist grants anyone the right to use this work for any purpose, without any conditions, unless such conditions are required by law.

Figure 1.3

Summary

| Description | This is a series of schematic drawings of the Auger effect. Panel (a) provides a sequential view of Auger transitions in terms of atomic orbital energy (increasing radially) while panel (b) provides the same information in condensed format using spectroscopic notation. |
| Date | 15 October 2007 |
| Source | Own work |
| Author | A. Carlson |

Permission

I, the copyright holder of this work, release this work into the public domain. This applies worldwide. In some countries this may not be legally possible; if so: I grant anyone the right to use this work for any purpose, without any conditions, unless such conditions are required by law.
Figure 1.5

Summary

<table>
<thead>
<tr>
<th>Description</th>
<th>English: Illustration of the phenomena that occur from the interaction of highly energetic electrons with matter, also depicting the pear shape interaction volume which is typically observed in this type of interactions.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date</td>
<td>17 December 2013</td>
</tr>
<tr>
<td>Source</td>
<td>Own work</td>
</tr>
<tr>
<td>Author</td>
<td>Claudionico-commonswiki</td>
</tr>
</tbody>
</table>

Licensing

I, the copyright holder of this work, hereby publish it under the following license:

This file is licensed under the Creative Commons Attribution-Share Alike 4.0 International license.

You are free:
- to share — to copy, distribute and transmit the work
- to remix — to adapt the work

Under the following conditions:
- attribution — You must attribute the work in the manner specified by the author or licensor (but not in any way that suggests that they endorse you or your use of the work).
- share alike — If you alter, transform, or build upon this work, you may distribute the resulting work only under the same or similar license to this one.