Spring 1-1-2011

ALD Enabled Wafer Level Polymer Packaging for MEMS

Yadong Zhang
University of Colorado at Boulder, pentazhanghalle@gmail.com

Follow this and additional works at: https://scholar.colorado.edu/mcen_gradetds

Part of the Mechanical Engineering Commons, and the Polymer and Organic Materials Commons

Recommended Citation
https://scholar.colorado.edu/mcen_gradetds/19

This Dissertation is brought to you for free and open access by Mechanical Engineering at CU Scholar. It has been accepted for inclusion in Mechanical Engineering Graduate Theses & Dissertations by an authorized administrator of CU Scholar. For more information, please contact cuscholaradmin@colorado.edu.
ALD Enabled Wafer Level Polymer Packaging for MEMS

by

Yadong Zhang

B.S., Materials Science and Engineering, Beihang University

M.S., Materials Science and Engineering, Beihang University

A thesis submitted to the

Faculty of the Graduate School of the

University of Colorado in partial fulfillment

of the requirements for the degree of

Doctor of Philosophy

Department of Mechanical Engineering

2011
This thesis entitled:
ALD Enabled Wafer Level Polymer Packaging for MEMS
written by Yadong Zhang
has been approved for the Department of Mechanical Engineering

______________________________________________________
Ronggui Yang

______________________________________________________
Y.C. Lee

Date___________________________

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.
Yadong Zhang (Ph.D., Mechanical Engineering, 2011)

ALD Enabled Wafer Level Polymer Packaging for MEMS

Thesis directed by Professor Ronggui Yang and Professor Y.C. Lee

Abstract

Wafer level polymer packaging for MEMS is a cost-effective approach that is also compatible with microelectronic packaging technologies. However, polymer packages are not hermetic and cannot be used for MEMS devices, which usually demand vacuum or low moisture environment inside the packages. This problem can be solved by applying atomic layer deposition (ALD) of nano-scaled Al$_2$O$_3$ or other inorganic materials over the polymer packages. Defects and mechanical cracks in ALD coatings are major concerns for hermetic/vacuum sealing. Several techniques have been developed to inspect such defects and cracks. Assisted by the electroplating copper technique, we have reduced the defect density by 1000 times for an ultra-thin, 2-nm ALD Al$_2$O$_3$ film. Such an ultra-thin coating is essential to enhance coating’s mechanical toughness. The toughness is usually determined by monitoring coating’s crack initiation and growth in a bending test. A real-time, non-destructive inspection technique has been developed for in-situ characterization of an ALD film coated on a surface or buried in a multilayer structure. With the knowledge and technology established, we have successfully demonstrated a wafer-level polymer packaging process for MEMS using a Pirani gauge as the vacuum sensor. The leak rate through the polymer package has been reduced by 100 times by the ALD Al$_2$O$_3$ coating. More importantly, we have developed models and identified issues that are critical to ALD-enabled wafer level polymer packaging for MEMS.
Dedication

To my parents, my wife, and my son.

“Love never fails.” (Corinthians 13:8)
Acknowledgements

I would like to express my sincere gratitude and appreciation to the people who made this thesis possible.

First of all, I would like to thank my advisors prof. Ronggui Yang and prof. Y.C. Lee. They jointly gave me advice, help, and influence throughout this thesis. Their attitudes towards research and delivering high quality work have been impressed and influenced me. Special thanks to prof. Steven George for his invaluable guidance and support on the study of ALD thin films in this thesis. Special thanks to my thesis committee members: prof. Martin Dunn and prof. Victor Bright for their invaluable inputs and suggestions to this study.

I would also thank my colleagues, collaborators, and group members for their support, discussions, and suggestions. I am glad to be part of them and enjoyed the experience working with them. They include some of the current and former members from different groups, and people from the university facilities, and company. They together made this thesis possible. They are Aziz Abdulagatov, Jacob Bertrand, Dr. Dragos Seghete, Dr. Shih-Hui Jen, Dr. Arrelaine Dameron, Andrew Cavanagh, Zachary Gibbs from prof. Steven George’s group; Dr. David Miller from prof. Martin Dunn’s group; David Boetler, Ching-Yi Lin, Dr. Mu-Hong Lin, Ming Kong, Hsin-Ray Wu, Yunda Wang, Dr. Li-Anne Liew from prof. Y.C. Lee’s group; Dr. Wei Wang and Xiaobo Li from prof. Ronggui Yang’s group; Dr. Joe Brown, Harris Hall, Chris Oshman from prof. Victor Bright’s group; Xinhui Liu from prof. Scott Bunch’s group; Dr. Xinhua Lian from prof. Weimers’ group. Special thanks to Dr. Yu-Zhong Zhang from Invitrogen Inc.. Special thanks to Dan Fitzstephens from iMINT; Paul Rice and Kittery Barrows from NCF; Jan Van Zeghbroeck and Mark Leonas from CNL, at the University of Colorado at Boulder.
## Contents

Chapter 1 Introduction ........................................................................................................... 1  
  1.1 Preface .......................................................................................................................... 1  
  1.1.1 Background and Motivation ....................................................................................... 1  
  1.1.2 Problem Statement and Objectives ........................................................................... 5  
  1.1.3 Contributions and Publications ............................................................................... 7  
  1.1.4 Dissertation Organization ....................................................................................... 10  
  1.2 Background Overview ................................................................................................. 10  
  1.2.1 MEMS Packaging .................................................................................................. 10  
  1.2.2 Thin Film Barriers ............................................................................................... 17  

Chapter 2 Defect Visualization Techniques ........................................................................... 23  
  2.1 Introduction .................................................................................................................. 23  
  2.2 Background ................................................................................................................ 23  
  2.2.1 Defect Modeling .................................................................................................... 23  
  2.2.2 Defect Characterization ......................................................................................... 25  
  2.3 Defect Estimation ....................................................................................................... 26  
  2.4 Defect Visualization Techniques and Experiment ..................................................... 27  
  2.4.1 Electroplating Decoration ..................................................................................... 28  
  2.4.2 Fluorescent Tagging ............................................................................................ 30
2.5 Results and Discussion........................................................................................................33
  2.5.1 Defect Density in ALD Al₂O₃ on Ni Substrates ......................................................33
  2.5.2 Defect Size Characterization ................................................................................36
  2.5.3 Discussion on Causes for Defects .............................................................................41
  2.5.4 Defect Visualization in ALD Al₂O₃ on Polymer Substrates ................................43
  2.6 Chapter summary.............................................................................................................48

Chapter 3 Ultra-Thin ALD Films ..........................................................................................49
  3.1 Introduction ..................................................................................................................49
  3.2 Background ..................................................................................................................50
  3.3 Theoretical Analysis .....................................................................................................51
  3.4 Experiment ...................................................................................................................55
  3.5 Results and Discussion .................................................................................................57
    3.5.1 Defect Densities in Ultra-Thin ALD .................................................................57
    3.5.2 Effect of Electroplating Conditions on Defect Density Characterization ......59
    3.5.3 Effect of Substrate Surface Conditions on Defect Reduction ......................63
    3.5.4 Barrier Structure Consists of Ultra-Thin ALD Layers ..................................66
  3.6 Chapter Summary ..........................................................................................................68

Chapter 4 ALD Film Mechanical Robustness and Real-Time Cracking Inspection.........70
  4.1 Introduction ..................................................................................................................70
  4.2 Background ..................................................................................................................71
  4.3 Methods .......................................................................................................................73
    4.3.1 LSCM-Based Inspection .....................................................................................73
    4.3.2 Deflection Bending .............................................................................................76
4.3.3 ALD Sample Preparation ................................................................. 79

4.4 In-Situ Inspection of ALD Cracking .................................................. 79
  4.4.1 Channel Cracking of Single Layer Films ........................................ 79
  4.4.2 Cyclic Loading Test and Sensitivity of the Inspection ....................... 81
  4.4.3 Channel Cracking of Buried ALD Films ......................................... 84

4.5 Merits of the LSCM Based Optical Inspection ................................... 86
  4.5.1 Versatility ......................................................................................... 86
  4.5.2 In-situ Characteristics ....................................................................... 87
  4.5.3 Resolution ......................................................................................... 87

4.6 Chapter Summary .................................................................................. 89

Chapter 5 Design and Fabrication of Sensors for MEMS Packaging Study .......... 91
  5.1 Introduction ......................................................................................... 91
  5.2 Background ......................................................................................... 91
  5.3 Pirani Gauge Design and Fabrication .................................................. 94
    5.3.1 Design and Analysis ....................................................................... 94
    5.3.2 Designs for Different Packaging Schemes ......................................... 98
    5.3.3 Fabrication ....................................................................................... 99
  5.4 Pirani Gauge Calibration ................................................................. 100
    5.4.1 Test Setup ....................................................................................... 100
    5.4.2 Test Methods .................................................................................. 101
    5.4.3 Test Results .................................................................................... 104
  5.5 Chapter Summary ............................................................................... 107

Chapter 6 Critical Issues for ALD-Enabled Polymer MEMS Packaging ............... 109
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1</td>
<td>Introduction</td>
<td>109</td>
</tr>
<tr>
<td>6.2</td>
<td>Background</td>
<td>109</td>
</tr>
<tr>
<td>6.3</td>
<td>Polymer Packaging Based on Encapsulant</td>
<td>111</td>
</tr>
<tr>
<td>6.4</td>
<td>Polymer Packaging Based on Dry Film Adhesive</td>
<td>113</td>
</tr>
<tr>
<td>6.4.1</td>
<td>Material for Packaging</td>
<td>113</td>
</tr>
<tr>
<td>6.4.2</td>
<td>Packaging Process</td>
<td>116</td>
</tr>
<tr>
<td>6.4.3</td>
<td>Test of the Polymer Package</td>
<td>119</td>
</tr>
<tr>
<td>6.4.4</td>
<td>Modeling on ALD-Coated Polymer Package</td>
<td>128</td>
</tr>
<tr>
<td>6.4.5</td>
<td>Test on ALD-Coated Polymer Package</td>
<td>133</td>
</tr>
<tr>
<td>6.4.6</td>
<td>Buffer Layer to Address ALD Cracking</td>
<td>135</td>
</tr>
<tr>
<td>6.5</td>
<td>Chapter Summary</td>
<td>143</td>
</tr>
</tbody>
</table>

**Chapter 7 Summary and Future Work**

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1</td>
<td>Summary</td>
<td>144</td>
</tr>
<tr>
<td>7.2</td>
<td>Future Work</td>
<td>146</td>
</tr>
<tr>
<td>7.2.1</td>
<td>Inspection on ALD Thin Film Coating</td>
<td>146</td>
</tr>
<tr>
<td>7.2.2</td>
<td>ALD-Enabled Polymer MEMS Packaging</td>
<td>148</td>
</tr>
</tbody>
</table>

**Bibliography**

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
</tr>
</tbody>
</table>
Tables

Table 2. 1 Defect density estimation for various barrier films ................................................................. 27
Table 3. 1 Tolerable defect densities for different ALD/MLD thicknesses ............................................. 54
Table 3. 2 Barrier performance prediction for different ALD/MLD thicknesses .............................. 68
Table 4. 1 LSCM objectives and scanning parameters ............................................................................. 75
Table 4. 2 Approaches to improve the mechanical reliability of ALD barrier films under bending ..................................................................................................................................... 90
Table 6. 1 Desired vacuum level for packaging a number of MEMS devices and their market size .......................................................................................................................................................... 110
Table 6. 2 Comparison of the major concepts in literatures for the aspects for wafer level packaging of MEMS ...................................................................................................................................................................... 110
Table 6. 3 Physical properties of PerMX3000 (after cured at 150 °C, 30 min) ..................................... 114
Table 6. 4 OTR of various polymer films ................................................................................................. 127
Table 6. 5 E_a of various polymer films for OTR ................................................................................... 128
Table 6. 6 Ranges of the pressure change inside the ALD coated polymer package for different years of use .................................................................................................................................................. 133
Table 6. 7 CTEs and Young’s moduli of ALD Al_2O_3, dry film substrate, and PI buffer layers .. 136
Table 6. 8 Comparison of mechanical properties between different types of PI ............................... 140
Figures

Figure 1. 1 Wafer level capping of MEMS for hermetic sealing .............................................. 2
Figure 1. 2 SEM image of a polymer packaged micro-resonator demonstrated by Joseph et al.... 3
Figure 1. 3 ALD/MLD enabled hermetic polymer packaging of MEMS .................................. 5
Figure 1. 4 Schematic diagram of localized heating for bonding (left) and the SEM image of the
packaged μ-resonator using localized heating after the glass cap was forcefully
broken away (right) ......................................................................................................................... 12
Figure 1. 5 Schematic of the fabrication process flow for epitaxial polysilicon encapsulation .. 13
Figure 1. 6 Cross section showing the epitaxial polysilicon encapsulated and sealed interdigitated
com-drive fingers ......................................................................................................................... 13
Figure 1. 7 Process for manufacturing Ni vacuum package using electroplating ...................... 14
Figure 1. 8 Microshell process for packaging MEMS switch ..................................................... 15
Figure 1. 9 Polymer packaging process for MEMS via thermal decomposition of a sacrificial
polymer ........................................................................................................................................... 16
Figure 1. 10 Summary of the barrier performance of various types of coatings and the
corresponding applications ......................................................................................................... 18
Figure 1. 11 Oxygen transmission rate as function of defect density (left) and coating thickness
of PECVD SiO₂ and SiN on PET substrate .................................................................................. 19
Figure 1. 12 ALD Al₂O₃ growth using sequential, alternating exposures to trimethylaluminum
Figure 1. 13 Summary of the development of barrier performance of ALD barrier coatings over recent years .................................................................................................................. 20

Figure 2. 1 Characteristics of ALD coatings and a SEM image of the surface condition for ALD Al$_2$O$_3$ coated on PEN substrate ................................................................................................................................. 28

Figure 2. 2 Schematics of electroplating decoration mechanism ................................................................................................................................. 29

Figure 2. 3 Function of the fluorescent tag, which binds solely to the polymer substrate, based on its greater hydrophobicity. .................................................................................................................. 31

Figure 2. 4 Defect decoration results for ALD Al$_2$O$_3$ film on (a) Cu, (b) Au and (c) Ni substrates ................................................................................................................................................. 33

Figure 2. 5 Change of copper bump size and density with electroplating time for (a) 20 minutes and (b) 100 minutes. ................................................................................................................................. 34

Figure 2. 6 Copper bump densities as a function of electroplating time for two samples. ........ 35

Figure 2. 7 Copper bump size distribution of electroplated ALD Al$_2$O$_3$ on Ni for 100min. .... 37

Figure 2. 8 Process to remove the copper bump exposing its footprint and an example of before and after a copper bump being removed .................................................................................................................. 38

Figure 2. 9 Etching process of a copper bump in copper etchant followed by further undercutting of the Ni substrate. ................................................................................................................................. 39

Figure 2. 10 SEM image of the footmark left by a copper bump with size of ~300 µm (a) and ~60 µm (b). ......................................................................................................................................................... 39

Figure 2. 11 Mechanism to use FIB for defect characterization ................................................................................................................................. 40

Figure 2. 12 A FIB milled copper bump (a) and the cross section of the corresponding defect site (b). ......................................................................................................................................................... 40
Figure 2. 13 Examples of the causes for defects in ALD coatings. ................................................................. 41

Figure 2. 14 Comparison of defect densities of ALD Al₂O₃ deposited on a rough copper pad and a PVD copper film coated on a silicon wafer ................................................................. 42

Figure 2. 15 Fluorescence images showing: (a) PEN substrate with no ALD Al₂O₃ film; (b) PEN polymer substrate coated with a native ALD Al₂O₃ film; and (c) ALD Al₂O₃-coated PEN substrate with scratches intentionally formed to produce defects in ALD Al₂O₃ film................................................................. 43

Figure 2. 16 Fluorescence images displaying cracks in ALD Al₂O₃ film: (a) series of channel cracks generated after tensile strain of 5%; and (b) cracks formed at edge of sample by cutting. ................................................................. 45

Figure 2. 17 FESEM image showing width of crack caused by cutting the sample......................... 46

Figure 2. 18 (a) Confocal microscope image of prescribed markers and various defect sites close to markers. (b) FESEM image of defect at site #1. (c) FESEM image at site #2..... 47

Figure 3. 1 A schematic diagram of effective thickness l which is determined by the defect spacing in the inorganic barrier layer (AlOₓ) and results into a much longer diffusion path than the organic layer................................................................. 52

Figure 3. 2 Lag time as a function of number of bilayers (Dyads) and its dependency on defect density or defect spacing ................................................................. 53

Figure 3. 3 Use thinner layers to build up a higher number of ALD/MLD bilayers for multilayer barrier structure................................................................. 54

Figure 3. 4 Comparison of the defect densities of Al₂O₃ deposited on Ni substrates and Ni substrates with a 15nm ALD W buffer layer as a function of Al₂O₃ thickness ....... 58

Figure 3. 5 Comparison between the SEM images of 2nm-thick Al₂O₃ ALD deposited on the Ni
substrate (a) and the Ni substrate with a 15nm-thick tungsten ALD seed layer (b).

Figure 3.6 The change of the copper bump density as a function of electrolyte concentration (EC: CuSO4 and H2SO4) (a) and electroplating time (ET) (b) .......................................................... 60

Figure 3.7 SEM images of typical electroplated 2nm Al2O3 samples after (a) 5 minutes, (b) 10 min, (c) 30min, and (d) 60 min plating.......................................................... 61

Figure 3.8 (a) XPS intensities of characteristic Al 2s and W 4d peaks of three samples of 2nm Al2O3 on 15nm W which underwent exposure in the 0.03mol/L electrolytic solution for 0, 30 and 60 minutes respectively; (b) XRR results for Al2O3 film thickness reduction as a function of exposure time in the 0.03mol/L electrolytic solution. ..... 63

Figure 3.9 (a) A typical cross section image of the focus ion beam milled copper bumps grown on 2nm Al2O3 on the Ni substrate; (b) Close-up view of (a) at the location where the copper bump grew up from revealing an incomplete coverage site in the Al2O3 film due to less efficient nucleation; (c) Close-up view of a typical cross section image of the copper bumps grown on 2nm Al2O3 on the 15nm ALD W revealing particle contamination on the substrate. ................................................................. 65

Figure 3.10 Concept to use buffer layer to achieve low defect 2nm-thick ALD Al2O3 for creation of multilayer barrier structures ................................................................. 67

Figure 4.1 An example of cracking of ALD Al2O3/SiO2 multilayers encapsulated thermal ground plane test vehicle under 100 °C ...................................................................................... 72

Figure 4.2 Schematics of the crack inspection principle using laser scanning confocal microscopy ........................................................................................................... 74

Figure 4.3 Example of the intensity dip triggered by a crack ...................................................... 75

Figure 4.4 Deflection bending apparatus and crack measurement locations for in-situ inspection
of film cracking.................................................................................................................. 76

Figure 4. 5 Example of cracking at three locations across the width of the sample strained to
2.5% .................................................................................................................................. 77

Figure 4. 6 Comparison between the analytical solution and the measurement of the deflection as
a function of the displacement for a PEN strip............................................................... 78

Figure 4. 7 Crack densities as a function of the bending radius of curvature (a) and bending strain
(b) of ALD Al₂O₃ films coated on PEN substrate............................................................ 80

Figure 4. 8 Crack density change during cyclic loading test of ALD Al₂O₃ film on PEN........... 82

Figure 4. 9 (a) Intensity dips and the corresponding detection contrast values produced by the
cracks on 5nm ALD Al₂O₃ films at different strain levels; (b) Detection contrast of
cracks for ALD Al₂O₃ films with different thicknesses at different strain levels. ..... 83

Figure 4. 10 Crack densities as a function of the bending radius for 40nm ALD Al₂O₃ film and
the films coated by SU8 layers. ......................................................................................... 85

Figure 4. 11 Schematics of the principle using cover-coat to shift the neutral plane where the
strain equals zero to the ALD film..................................................................................... 86

Figure 5. 1 Design of pirani gauge for fabrication using polymumps process...................... 95

Figure 5. 2 Modeling results of the operational curves of two beam designs ....................... 97

Figure 5. 3 Two packaging schemes for pirani gauge......................................................... 98

Figure 5. 4 PolyMUMPs .................................................................................................... 99

Figure 5. 5 SEM images of the released sensors for scheme I (left) and scheme II (right)....... 100

Figure 5. 6 Test setup for the pirani gauge sensor............................................................. 101

Figure 5. 7 FRCs of pirani gauge with 250 µm beam as function of vacuum level with different
current inputs. .................................................................................................................... 102
Figure 5. 8 Measurement of thermal impedance as a function of vacuum level of pirani gauge with 250 µm beam. ................................................................. 103
Figure 5. 9 Repeatability of the pirani gauge at 10 Torr for 7 days using two test methods. ..... 104
Figure 5. 10 Comparison between the modeling and experiment data of FRC as a function of pressure for the pirani gauges with 250 µm and 500 µm beams. .......................... 105
Figure 5. 11 Experiment calibration curves for the 250 µm beam gauges with/out poly-cap. .... 106
Figure 5. 12 Experiment calibration curves for the 250 µm beam gauges with/out poly-cap. .... 107
Figure 6. 1 Critical issue I: device damage during polymer curing. .................................... 112
Figure 6. 2 Cross section of pirani gauge with poly-cap structure: initial design (left) and improved design (right) with posts. ......................................................... 113
Figure 6. 3 PerMX 3000 dry film structure and the diagram for lamination process ............... 115
Figure 6. 4 PerMX 3000 dry film enclosed pirani gaue sensor ............................................ 115
Figure 6. 5 Deflection of 50 µm dry film above a package cavity caused by one atmospheric pressure difference ................................................................. 116
Figure 6. 6 Major steps for dry film-based wafer level packaging process for MEMS. ........ 118
Figure 6. 7 A dry film package fabricated on a 2mm×2mm chip with a pirani gauge sensor inside. .................................................................................................. 119
Figure 6. 8 Test setup for polymer package ........................................................................ 120
Figure 6. 9 Test results on pressure change as a function of time of the PerMX 3000 dry film package ........................................................................................................... 121
Figure 6. 10 Critical issue II: cracking of the dry film package ............................................ 123
Figure 6. 11 Comparison of cracking of the dry film structure with and without acetone rinse 124
Figure 6. 12 Test results on pressure change as a function of time of the dry film package with
elimination of cracks (left) and comparison on air leak rate in the release region for
the packages without and with cracks (right) .......................................................... 125
Figure 6. 13 Critical issue III: temperature effect on leak rate of the dry film polymer package 126
Figure 6. 14 Linear fit of ln (L) as a function of 1/θK to derive the activation energy for air leak
through the dry film package .................................................................................. 128
Figure 6. 15 Air leak through the defects in the ALD Al₂O₃ coated polymer package .......... 129
Figure 6. 16 Modeling results on the pressure change as a function of time for the ALD coated
dry film polymer package at room temperature and 100 °C ................................. 131
Figure 6. 17 Test results on the dry film package before and after 25nm ALD Al₂O₃ coated... 134
Figure 6. 18 Critical issue IV: ALD Al₂O₃ cracking on dry film package due to CTE mismatch.
........................................................................................................................................ 135
Figure 6. 19 Stress generated at ALD with/out buffer layer when it cools down from 115 °C to
room temperature ...................................................................................................... 137
Figure 6. 20 Critical issue V for package test: a long lag time after the ALD coating .......... 139
Figure 6. 21 Breaches found at the PI buffer layer surround the chip substrate, which become the
opennings for air leak and yield a long lag time due to long diffusion distance to the
package cavity ............................................................................................................... 139
Figure 6. 22 Optical microscope images show the encapsulation quality of PI 2545 on a dummy
dry film package ...................................................................................................... 140
Figure 6. 23 LSCM images of an ALD coated dummy dry film package buffered by ELC-2500.
........................................................................................................................................ 141
Figure 6. 24 Test results on 25nm ALD coated on ELC-2500 epoxy encapsulated dry film
package ......................................................................................................................... 142
Chapter 1 Introduction

1.1 Preface

1.1.1 Background and Motivation

Micro-electro-mechanical systems (MEMS) technology has developed numerous micro sensors, actuators and the related systems for diverse applications. Some notable examples include pressure/tilt sensors, accelerometers, gyroscope, chemical sensors and micro biomedical devices, lab-on-a-chip, resonators, displays, optical switches and radio frequency (RF) switches, printer heads, energy harvesting and storage, and data storage [1]. Recently, the MEMS market has grown dramatically with some exciting applications in consumer electronics. For example, an accelerometer gears every iPhone with the function of detection of rotation for the proper display of contents. Qualcomm’s MEMS display for mobile devices offers low power consumption and superb viewing quality in a wide range of environmental conditions, including bright sunlight. Tire Pressure Monitoring System (TPMS) became a standard feature equipped in tens of millions of automobiles. Nintendo’s Wii game console uses accelerometers to detect accelerations in three dimensions of the handheld pointing device.

To bring all these MEMS devices from development to commercialized products, packaging is usually a major consideration. MEMS devices consist of fragile and movable structures and packaging is a critical step to provide physical protection and connection to the external environment. MEMS devices also require a controlled ambient, usually at vacuum, to operate properly. Very often, the performance of the MEMS devices are determined by the packaging quality [2-5]. In addition, packaging has to adapt to a diversity of applications, device
structures, and requirement of MEMS and microsystems. For all these reasons, packaging is one of the most costly parts for MEMS manufacturing.

Many types of packaging techniques have been developed for MEMS. These techniques generally fall into two categories: device-level packaging and wafer-level packaging [1], [3]. For device-level packaging, the wafer is diced before packaging and each MEMS device is packaged individually. Device-level packaging increases the cost and the probability of damage. In comparison, wafer-level packaging has the potential to significantly reduce the cost, increase the packaging density, and improve the reliability. In wafer-level packaging, the devices are packaged in batch on the wafer before being diced. Currently, most studies have focused on wafer-level capping [1], [5-9]. As shown in Figure 1.1, MEMS devices are fabricated on one wafer while silicon/glass caps are made on another wafer. The two wafers are then bonded together to achieve hermetic/vacuum sealing. The capped MEMS devices are then diced and packaged through injection plastic molding in the next level.

![Figure 1.1 Wafer level capping of MEMS for hermetic/vacuum sealing](image-url)
This capping approach has been successfully demonstrated and implemented to many MEMS devices. However, the silicon/glass capping technique usually associates with high temperature bonding process and the caps are bulk and potentially reduce the packaging density. The cost of capping technique is comparatively high.

Over the recent years, new techniques and concepts have been continuously developed [3], [4], [10-14]. One of the new developments for wafer level MEMS packaging relies on low cost polymer materials that can reduce packaging size and increase packaging density on a wafer. The polymer packaging approach is also compatible with the standard wafer level packaging process used in microelectronics industry, which is usually polymer-based. Figure 1.2 shows a polymer packaged micro-resonator demonstrated by Joseph et al. [14].

![Polymer packaged micro-resonator](image)

Figure 1.2 SEM image of a polymer packaged micro-resonator demonstrated by Joseph et al. [14]
Compared with silicon or glass capping, polymer-based packaging has the advantages listed below

- No silicon/glass cap and bonding ring;
- Minimized package size and freeform geometry;
- Low packaging processing temperature;
- Standard MEMS process and no double-wafer alignment;
- Low cost per device;

Polymer packaging is very attractive. However, two issues have to be considered. Hermetic/vacuum sealing is essential for most MEMS devices, but polymer materials are porous in micro-scale and not hermetic. Outgassing from polymers is another issue that can degrade the hermeticity/vacuum and cause damage of the device by generating particles. To provide hermetic/vacuum sealing, extra barrier coatings have to be applied onto the polymer package. Such barrier coatings have been developed for organic light emitting diodes (OLEDs) encapsulation [15-18]. One of the techniques is called atomic layer deposition (ALD), which has been demonstrated as an ideal approach to produce high quality conformal gas/moisture diffusion barriers [19-28]. Recent studies found that ALD Al₂O₃ thin films with only 25 nm thickness coated on polymers can reduce the water vapor/oxygen transmission rate by more than 1000 times [19], [20]. Further reduction can be achieved by multilayer structures combining ALD Al₂O₃ layers with other ALD oxides or organic layers [24-28]. Compared with the common thin film deposition techniques, such as physical vapor deposition (PVD) and chemical vapor deposition (CVD), ALD has appealing features listed below [29-32]:

- Low temperature deposition (as low as 33 °C, compatible with polymer substrates);
- Pinhole-free deposition (high quality barrier films);
• Conformal deposition (compatible with various package geometries);
• Excellent step coverage;
• Precise thickness control;
• Extendible to large substrates;
• No particle generation;
• Nano-scale multi-layer structures

Using ALD to enable wafer level polymer packaging of MEMS presents a great opportunity for development of new techniques for MEMS packaging and new applications for ALD thin film barriers. Figure 1.3 shows the concept for ALD enabled wafer level polymer packaging of MEMS.

![ALD Hermetic Sealing](image)

Figure 1. 3 ALD/MLD enabled hermetic polymer packaging of MEMS

1.1.2 Problem Statement and Objectives

The purpose of this research is to study the feasibility of using ALD Al₂O₃ barrier coatings to hermetically seal wafer level polymer packages for MEMS applications. This work primarily focuses on two topics: quality of ALD thin film coatings and critical issues for
ALD-enabled polymer packaging. For the quality of ALD coatings, we address the issues associated with defects and cracks. For ALD-enabled packaging, we address the design and fabrication of the test vehicle and the process development and identification of critical issues for packaging.

For hermetic/vacuum sealing applications, the integrity of ALD Al₂O₃ coatings in terms of pinhole defects is one of the major issues. The defects in the coating are the leak source for gas/water vapor and the coating’s barrier performance is directly determined by the number of defects and their distribution. Defects could be related to various reasons such as particle contamination, bad nucleation, substrate surface roughness, and the issues for deposition process. The characteristics of ALD Al₂O₃ coatings, such as extremely small thickness, optical transparency, and homogeneity, makes it challenging to evaluate and analyze defects in the coatings. However, the knowledge and the ability to know the defect existence and defect density in the ALD coatings is essential for hermetic/vacuum sealing development. The knowledge can guide the design and develop barrier coating for better performance. We also need to know the defect information to define the barrier coating quality to reach the hermetic sealing target.

Mechanical cracking is another major issue for ALD Al₂O₃ coatings on polymer substrates. With the existence of cracks, the barrier performance of the coating can be significantly degraded or completely damaged. Mechanical cracks can be generated by mechanical and thermal-mechanical stressing during coating processing, handling, and using. The film cracks generated in the ultra-thin ALD coating can be hundreds microns in length, but as small as few nanometer in width. The cracks can also be in “close” state and “unseen” when the polymer substrate in elastic recovery. To understand the mechanical robustness and reliability of the ALD barrier coatings, we have to characterize and study the cracking phenomenon.
For ALD Al₂O₃ sealed polymer packages for MEMS application, no available test vehicle can be used for the test and evaluation. The standard helium leak test for electronic packages can not be applied for most of the MEMS packages with a cavity volume less than 10⁻³ cc. We have to design and fabricate an appropriate test vehicle based a wafer level polymer packaging process. Using this test vehicle, we can then evaluate the ALD sealed polymer packages. It is very important to understand the associate problems for packaging and identify the critical issues.

1.1.3 Contributions and Publications

Contributions to ALD thin films:

- Developed key techniques for defect visualization/characterization of ALD thin film coatings grown on a variety of substrates; These techniques enable the evaluation of defects in ALD barrier coatings and guide the barrier coating’s design;
- Demonstrated the defect densities in ultra-thin (2~10 nm) ALD Al₂O₃ films and achieved defect reduction of more than 1000 times for 2nm-thick ALD Al₂O₃ films; This demonstration shows the feasibility to use ultra-thin ALD Al₂O₃ layers, such as 2nm, for barrier and hermetic sealing applications;
- Developed the first real-time non-destructive inspection technique for cracking of thin film barrier coating on surface and in buried/multilayer structures; This technique provide an effective and efficient method to evaluated the mechanical robustness and flexibility of ALD Al₂O₃ films on polymer substrate;

Contributions to MEMS packaging:

- Developed a major wafer level polymer packaging process for MEMS; This process enables low temperature, low package size, and low cost;
- Developed a test vehicle to study ALD-enabled polymer MEMS packaging and identified the critical issues for packaging and ALD vacuum sealing.
- Demonstrated about 100X reduction of the leak rate by the ALD sealed polymer package.

**Peer reviewed journal publications resulting from this project**


**Referred conference proceedings resulting from this project**

- “Real-Time Inspection of a Moisture Barrier Film Buried by a Protective Layer for


- “Defect Visualization of Atomic Layer Deposition Enabled Polymer Barriers Using Fluorescent Tags”, Y. Zhang, Y.-Z. Zhang, D. C. Miller, J. A. Bertrand, R. Yang, M. L.
1.1.4 Dissertation Organization

This thesis is organized into seven chapters. Chapter 1 provides a brief overview and the scope of this project, followed by a literature review of the background. The review covers the recent development of MEMS packaging techniques, an introduction on thin film barriers for packaging and the related theories and experimental techniques, the technique for hermetic/vacuum test of MEMS packages. Chapter 2, 3, and 4 expand on the study of ALD thin film barriers. Chapter 2 focuses on thin film defects and the technique development to characterize the defects. Chapter 3 examines defect densities and defect reduction for ultra-thin ALD films (i.e. 2~10nm), and the feasibility to use 2nm-thick ALD Al₂O₃ to for barrier application with optimized performance. Chapter 4 concerns the mechanical robustness of ALD films on polymers under stress/strain, and the development of real-time, nondestructive inspection technique for ALD Al₂O₃ cracking. Chapter 5 and 6 covers the study on packaging. Chapter 5 presents the development of MEMS-based pirani gauge sensor for MEMS packaging study, including pirani gauge design and analysis, fabrication, and test. Chapter 6 develops the wafer level polymer packaging process for MEMS, identifies the critical issues, and presents the tests results for ALD-enabled polymer MEMS packaging. Lastly, chapter 7 summarizes the project and gives the thoughts and recommendation for future work.

1.2 Background Overview

1.2.1 MEMS Packaging

As introduced in section 1.1.1, wafer-level MEMS packaging is desired since it allows
low cost with batch production, small package size, and improved reliability. This section will introduce the development of MEMS packaging techniques and discuss the associated problems with several examples.

A common practice for wafer-level MEMS packaging is to use a silicon/glass cap wafer to bond with the MEMS device wafer to achieve hermetic/vacuum sealing as shown in Figure 1. Different bonding techniques have been utilized such as anodic bonding, eutectic bonding, fusion bonding, soldering, and glass frit bonding [2], [5], [10]. A common problem for these bonding techniques is high temperature (from several hundreds to thousand °C) to ensure good bonding quality with short bonding time. It can be difficult to achieve hermetic/vacuum sealing of a high percentage of devices on a wafer. Polymer adhesives, such as epoxy and BCB [33-38], were also used to make the bonding ring to lower the bonding temperature. But, polymer is non-hermetic and usually used for the applications where the requirement for hermeticity and vacuum is low. To reduce the thermal load of bonding process to the device, localized heating has been developed to confine the heating region around the bonding ring [5], [6]. The localized heating is achieved by using a micro-heater fabricating on top of the device substrate and patterned in the shape of bonding ring. An input current to the micro-heater and the joule heating helps to form a strong bond to a silicon or glass cap. As an example, a group from University of Michigan demonstrated localized aluminum/silicon to glass bonding [6]. Figure 1.4 shows the schematic diagram of the localized heating for bonding and the SEM image of the packaged μ-resonator after the glass cap was forcefully broken away. Using this approach, they reported the heating region was confined locally within 15μm of the heating source of above 1000 °C. This technique, however, is difficult to be applied to wafer-level packaging, since it has to put resistive micro-heater around every device and the total power consumption should be high and therefore
rises up the substrate temperature.

Figure 1. Schematic diagram of localized heating for bonding (left) and the SEM image of the packaged μ-resonator using localized heating after the glass cap was forcefully broken away (right) [6]

Another approach for MEMS packaging is to encapsulate the whole device by thin film deposition [3], [4], [12], [13], [39]. Sacrificial layer is used in between the device and the encapsulation layer and then released to create gap. One advantage of this encapsulation approach is that it avoids bulk silicon/glass caps and produces minimal package size. It is also compatible with standard semiconductor fabrication process. As one example, a group from Stanford University developed a wafer level encapsulation approach using epitaxial polysilicon process [3], [4], [12], [13], as shown in Figure 1.5. This process involves HF release of the device through vent hole followed by deposition of 20-50 µm thick polysilicon at 980°C to seal the vent holes. Using this approach to encapsulate a resonator, they demonstrated that no measurable pressure change could be detected of the encapsulated cavity at room temperature and the pressure increase rate is 5-10mTorr/year when tested at 100°C.
Figure 1.5 Schematic of the fabrication process flow for epitaxial polysilicon encapsulation [4].

Figure 1.6 shows the cross section of the epitaxial polysilicon encapsulated interdigitated comb-drive fingers [13].

Figure 1.6 Cross section showing the epitaxial polysilicon encapsulated and sealed interdigitated comb-drive fingers [13].

This approach fully integrated the MEMS fabrication and packaging processes, and eliminated the boundary between the device fabrication and packaging using capping technique.
After the MEMS device fabrication, the encapsulation can be done at any semiconductor foundries. However, the high temperature of the encapsulation process is a concern for packaging of MEMS for different applications and integrating with the control circuits.

Similar approach has been developed by using electroplating to fabricate the encapsulation layers [10], [11]. This electroplating encapsulation process offers a low temperature approach (<250 °C) to do wafer level vacuum packaging. In this process, a sacrificial spacer layer is applied before the electroplating. After electroplating, a metal encapsulation layer is created above the sacrificial layer and the sacrificial layer is then removed through an etch tunnel. In the final step, the etch tunnel is closed by a variety of ways to achieve vacuum sealing. Figure 1.7 shows one example using electroplated Ni to create the vacuum package by a group from the University of Michigan. In this example, the way to seal the etch tunnel is critical for vacuum sealing. Different ways were employed including localized welding, evaporation/sputtering seal, and solder bumping. The vacuum sealing was demonstrated only using solder bumping to encapsulate the whole structure. Nevertheless, this approach presents an opportunity of manufacturing high yield, low cost vacuum packages at low temperature.

Figure 1.7 Process for manufacturing Ni vacuum package using electroplating [10].
Another example demonstrated by a group from Intel is based on electroplated microshell process as shown in Figure 1.8 [11]. Gold and copper were used for manufacturing the MEMS device and package. Since both gold and copper layers can be manufactured by electroplating, the process temperature and cost can be substantially reduced. To seal the package, a stamping process was developed by using a stamp wafer. The temperature for the stamping process is less than 350°C. Although this approach is device specific and the use of stamp wafer may increase the complexity of the process and bring extra cost, it provided a concept for manufacturable, low cost, and low temperature vacuum packaging process.

Figure 1.8 Microshell process for packaging MEMS switch [11]

Recently, the use of polymer materials for MEMS packaging arouses as an appealing
topic, since it is low cost, low process temperature, and compatible with the wafer level packaging process developed for microelectronics packaging. Figure 1.2 shows an example of this polymer packaging for MEMS resonator [14]. The package cavity was fabricated by an epoxy-based polymeric overcoat on a sacrificial polymer and thermal decomposition of the sacrificial polymer. The highest temperature happened during the decomposition process and it was kept below 300 °C. Figure 1.9 shows the detail for the polymer packaging process. Other examples include using LCP [40-42], BCB [43], and SU8 [44] to fabricate the package. As mentioned, polymers are non-hermetic materials and the high gas/moisture permeability makes them difficult to be used for hermetic/vacuum package. In addition, outgassing of polymers is problematic for vacuum packaging applications. In recent years, the development of thin film barrier technology emerges as a potential solution to address these issues for polymer MEMS packaging. Next section will briefly review the thin film barrier technology and the use of ALD for barrier applications.

![Polymer packaging process for MEMS via thermal decomposition of a sacrificial polymer](image)

Figure 1.9 Polymer packaging process for MEMS via thermal decomposition of a sacrificial polymer [14]
1.2.2 Thin Film Barriers

The development of thin film barriers is attributed to the trend to use polymer as packaging materials. Polymers are usually low-cost, flexible, and light-weight compared with traditional glass and metal materials. However, polymers have relatively high gas/moisture permeability and cannot provide enough barrier protection for various applications. Additional inorganic thin film coatings such as AlOx, SiOx and SiNx have been used to reduce the polymer permeability. The single layer coatings deposited on polymers can reduce the permeability by at most two to three orders of magnitude [16]. Traditionally, thin film barrier coated polymers have been used for food and pharmaceutical packaging. Nowadays, thin film barriers have become essential to protect flexible organic light emitting diodes (OLEDs), organic solar cells, and other thin film devices from moisture- and oxygen-aided degradation [16], [17], [45], [46]. For example, OLEDs require the water vapor transmission rate (WVTR) < 1×10^{-6} g m^{-2} day^{-1}. The stringent requirement leads to continuous efforts to suppress the defects or pinholes in the barrier films, which includes the improvement of the thin film deposition process, material selection, and the development of multilayer/hybrid film structures [24-28], [47-49].

Typical thin film barriers on polymers are single layer films of oxides and nitrides, such as SiOx, SiNx, AlOx, that are deposited using thermal or electron beam evaporation, sputtering and reactive magnetron sputtering, chemical vapor deposition (CVD) and plasma enhanced chemical vapor deposition (PECVD) [16], [17], [50]. Recently, atomic layer deposition (ALD) has been proposed as an ideal approach to produce barrier films due to its low defect density and low temperature process [19-23], [32]. It has been reported that with only 25nm ALD Al2O3 coating on polymer the permeability can be reduced by more than three orders of magnitude [22], [23]. With multilayer ALD structures, the barrier performance can be improved by another
several orders of magnitude [24-26]. So far, the best barrier performance has been achieved by ALD barrier films. Figure 1.10 summarizes the barrier performance (WVTR) of various types of coatings and the corresponding applications.

Figure 1.10 Summary of the barrier performance of various types of coatings and the corresponding applications.

Ideally, a perfect inorganic coating has very low permeability and is virtually impermeable for gas/moisture [16], [49]. However, since no coating is perfect, there are always defects or pinholes that are associated with the deposition process, the imperfection of the substrate, and the materials [16-18], [49-51]. Some common reasons for the coating defects are particle contamination, substrate surface imperfections, grain boundary, and columnar growth of the film. Also, cracks and buckling could be caused by mechanical and thermo-mechanical stressing [16], [17], [47], [52-62]. These surface imperfections either significantly reduce the barrier protection or completely damage it. Many experimental and theoretical studies have
provided compelling evidence for the defect driven mechanism to explain the gas/moisture permeation in thin film barriers [47, 49-51, 63-66]. Figure 1.11 (a) gives the oxygen transmission rate (OTR) as function of defect density (left) and coating thickness of PECVD SiO2 and SiN on polyethylene terephthalate (PET) substrate [51]. Figure 1.11 clearly shows from the left figure that the defect dependency of the oxygen permeation through the barrier film from the left figure. It also shows from the right figure that the oxygen permeation is not inversely proportional to the coating thickness. A substantial decrease of the permeation happens at a critical thickness, after which the improvement of barrier performance becomes saturated with the thickness increase due to combination of various types of defects in the thicker film. To further improve the barrier performance, multilayer layer structures consisting of alternating inorganic layer and organic layer have been developed. In multilayer structures, the organic layers decouple defects in the inorganic layers and make the path for gas/moisture permeation become tortuous and therefore substantially improve the barrier performance [49].

![Figure 1.11 Oxygen transmission rate as function of defect density (left) and coating thickness of PECVD SiO2 and SiN on PET substrate [51]](image)

Due to the low defect deposition process, Al2O3 barrier coatings deposited by ALD demonstrated superior barrier performance. In addition, ALD technique bears many other
advantages such as low temperature, conformal deposition, excellent step coverage, and no particle generation. ALD process also enables nanoscale multilayer structures. With all these merits, ALD has become increasingly attractive for barrier coating and hermetic sealing applications. ALD is based on sequential, self-limiting surface reactions and grows thin films with atomic level control of thickness [29-32], [67]. Al₂O₃ is one of the most attractive ALD materials because of its chemical and thermal stability, excellent dielectric properties, and good adhesion to many materials [67]. ALD Al₂O₃ is also one of the most thoroughly studied and well-established ALD processes. The ALD Al₂O₃ growth is achieved using sequential, alternating exposures to trimethylaluminum (TMA) and H₂O. In the deposition process, TMA and H₂O are alternately injected via nitrogen carrier gas using computer-controlled pneumatic valves. The TMA and H₂O yield ALD Al₂O₃ according to the binary self-limiting reactions as shown in Figure 1.12.

![ALD Al₂O₃ growth diagram](image)

Figure 1. 12 ALD Al₂O₃ growth using sequential, alternating exposures to trimethylaluminum (TMA) and H₂O.
Figure 1.13 summarizes the barrier performance improvement of ALD Al$_2$O$_3$ barrier coatings over recent years, in which the red squares show the works associated with University of Colorado at Boulder.

![WVTR graph](image)

Figure 1.13 Summary of the development of barrier performance of ALD barrier coatings over recent years. (Note: the red squares are works associated with University of Colorado at Boulder and the value represented by the light blue square is overestimated)

Figure 1.13 shows the development of ALD barrier coatings has shifted from single layer coatings to multilayer/hybrid coatings and the barrier performance has been improved over years. Due to the saturation of ALD Al$_2$O$_3$ barrier performance with film thickness, Demenron et al developed Al$_2$O$_3$/SiO$_2$ multilayer structures by ALD [24]. However, they found the WVTR reached lowest value when used two Al$_2$O$_3$/SiO$_2$ bilayers and adding more bilayers decreased the
barrier performance. They explained that more bilayers increased the film thickness and made it brittle and easy to crack. To improve the cracking resistance of the barrier films, MLD organic layers were interposed in between the ALD Al₂O₃ layers [53]. However, it was found that the MLD Alucone layer was brittle itself and did not add improvement to the mechanical robustness. Meyer et al reported a lowest WVTR value or highest barrier performance by using ALD Al₂O₃/ZrO₂ nanolaminates [25], [26] (Note: this WVTR value is known to be overestimated and the real value is around 60X worse). They attributed the low WVTR value of the ALD nanolaminates to the suppression of void formation and formation of extended crystals as a result of the alternating multilayer structure. In addition, hybrid layer structures of ALD Al₂O₃/PECVD SiN [27], ALD Al₂O₃/Parylene [28] to improve the barrier performance have been demonstrated by Garcia et al. and Kim et al.

All these studies and many other studies [68], [69] focus on the applications of ALD barrier coatings for encapsulation of OLEDs, Organic Photovoltaics, and Organic Electronics. These studies mainly characterize the barrier performance (WVTR) of ALD barrier coating in film type using the techniques like Calcium test [23], [70] and HTO test [22], [71]. In Calcium test, ALD Al₂O₃ is coated onto Calcium and the barrier performance is characterized by measuring the change of optical transparency or electrical resistance in a humid environment. For HTO test, an ALD coated polymer film is clamped above tritium water and the tritium is collected on the other side and the WVTR is calculated according to the amount of tritium collected in a certain time. So far, there is no study on ALD barrier coating for cavity or packaging hermetic sealing, and test it for gas leak rate into the package. This project will study the ALD coating for hermetic sealing of polymer packages for MEMS packaging application and provide a good opportunity to extend the application of ALD barrier coatings.
Chapter 2 Defect Visualization Techniques

2.1 Introduction

ALD has been claimed as a pinhole-less thin film deposition process. However, there are always pinhole defects in ALD coatings that may associate with particle contamination or bad nucleation. ALD Al₂O₃ with thickness 25nm and above can be of high quality. Although the publicly reported OTR and WVTR values of ALD Al₂O₃ barrier coatings are excitingly low, the effective permeability of gas and water vapor is still orders of magnitude higher than fully dense crystalline alumina, suggesting the dominance of defects on gas/moisture permeation. To integrate the ALD with polymer package to achieve good hermetic sealing, these defects are crucial since they will become the leak sources for gas/moisture and will gradually degrade the vacuum inside the package and the performance of MEMS devices. We will discuss the requirement for defect densities in the ALD barrier coating for reaching the vacuum sealing targets in Chapter 7. In this chapter, we will focus on development of techniques to visualize defects in ALD coatings and demonstration of defects in ALD barrier coatings using these techniques.

2.2 Background

2.2.1 Defect Modeling

The transport process of gas/moisture through barrier films is called permeation. Many literatures studied the mechanism of defect dominant permeation [49], [51], [64], [66], [72-76]. Both analytical [49], [51], [64], [66] and numerical models [66], [75], [76] were developed to understand the effect of defects on permeation. Normally, it is assumed that the inorganic coating
is impermeable and gas and moisture can permeate the barrier film only through the defect area. The driven force is the gradient of chemical potential. During permeation, gas/moisture molecules first absorb and solve into the polymer film via the defect sites and form a concentration gradient of the permeant. Then, the molecules diffuse through the polymer driven by the concentration gradient. On the low concentration side of the film, the molecules are then desorbed into the gas phase. A steady-state of permeation can be reached after a certain period of time which depends on the diffusion coefficient and the film thickness. During the steady-state permeation, the concentration profile remains constant in time. The time required to reach steady-state permeation is called lag time. The permeability $P$ is a product of diffusivity $D$ and solubility $S$ as shown by Equation 2.1.

$$P = D \cdot S$$  \hspace{1cm} (2.1)

The transport process inside the polymer substrate can be described by using second Ficks’ law as shown by Equation 2.2

$$\frac{\partial C}{\partial t} = \nabla (D \cdot \nabla C) = D \left( \frac{\partial^2 C}{\partial X^2} + \frac{\partial^2 C}{\partial Y^2} + \frac{\partial^2 C}{\partial Z^2} \right)$$  \hspace{1cm} (2.2)

The concentration gradient $C$ can be obtained by Henry’s law as shown in Equation 2.2, where $\Delta p$ is partial pressure gradient of the permeant.

$$\Delta c = S \cdot \Delta p$$  \hspace{1cm} (2.3)

Solving the equation 2.2 with the assumption that the defect size $R$ is much smaller than the film thickness $L$ ($R \ll L$), the permeant quantity diffusing through one defect in a unit time can be simply expressed as the product of diffusivity $D$, upstream permeant concentration $C_0$, and defect size $R$ as shown by Equation 2.4 [66].

$$q = 4D \cdot C_0 \cdot R$$  \hspace{1cm} (2.4)
Based on modeling, several authors [51], [66], [75] drew conclusion that with a same total defect area, small defects with high defect densities yield a higher transmission rate than large defects with low defect densities. This indicates the importance of evaluating small defects in barrier coatings.

2.2.2 Defect Characterization

For barrier coating design, defect information such as number of density, size and spatial distribution locations in barrier coatings are in high demand to evaluate the quality of the coating and the corresponding barrier performance. For coating manufacturing, the defect information is critical to optimize the deposition process and material system. However, defect characterization in the nano-scale thin film coatings can be formidable if one tries to directly use common microscopic techniques, such as optical microscope, scanning electronic microscope, and atomic force microscope. This is especially true for ALD thin film coatings. The defects in ALD films could be as small as nanometer size. The ALD Al$_2$O$_3$ films can have ultrathin thicknesses of only few nanometers. The ALD Al$_2$O$_3$ films are also very homogeneous and transparent. Defect characterization is particularly challenging for multilayer structures, where the ALD layers are buried and thus not accessible to optical or electron probes. Before this project, no study had quantitatively evaluated the defect densities in ALD coatings and there was no effective approach developed to characterize defects in various ALD barrier films. Defect contrast enhancement techniques have been used in the past for defect visualization. Sobrinho et al. [51], [77] and Sonia et al. [61] used oxygen plasma etching to undercut the barrier films on polymer substrates. The etching renders the defects visible in transparent silicon-oxides and silicon-nitrides thin films deposited by physical vapor deposition (PVD) or chemical vapor deposition (CVD). No such defect contrast enhancement techniques have been reported to
characterize defects in ALD films. Usually, indirect measurements based on Calcium test [23], [70] and HTO [22], [71] have been used to characterize the barrier performance in terms of gas/moisture transmission rate of ALD Al₂O₃ thin films. However, these methods are time-consuming and do not yield information about the film defects, such as defect size, density and distribution.

2.3 Defect Estimation

From Equation 2.4, if we know the defect density $\rho$ and assume that $R$ is the average defect size, we then can estimate the species transmission rate as expressed by Equation 2.5. If we replace the $C_0$ using Equation 2.3 and combine Equation 2.1, we can obtain Equation 2.6, where the transmission rate is expressed as a product of permeability, pressure drop $p$, defect size $R$ and density $\rho$. Based on Equation 2.5 and 2.6, if we know gas/moisture transmission rates of the barrier coatings we can estimate the corresponding defect densities with an assumption of a nominal defect size.

$$Q = 4D \cdot C_0 \cdot R \cdot \rho$$ \hspace{1cm} \text{(2.5)}

$$Q = 4P \cdot p \cdot R \cdot \rho$$ \hspace{1cm} \text{(2.6)}

Table 2.1 compares the defect densities estimated for various barrier films. The defect densities are calculated based on the oxygen and water vapor transmission rate (OTR/WVTR) data reported in literatures [22], [23], [51]. Using the defect densities, the quality of the barrier coatings can be easily compared and evaluated. Comparing the calculated defect densities between ALD films and PECVD films, it is found that the defect densities of ALD films are around two orders of magnitude lower than PECVD films. This comparison demonstrates the superior film quality of ALD thin film coatings compared with PECVD coatings.
Table 2.1 Defect density estimation for various barrier films

<table>
<thead>
<tr>
<th>Film Materials</th>
<th>$\text{SiO}_2$/PET (PECVD) [51]</th>
<th>$\text{SiN}$/PET (PECVD) [51]</th>
<th>Alumina/Kapton (ALD) [22]</th>
<th>Alumina/PEN (ALD) [23]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test method</td>
<td>MOCON test</td>
<td>MOCON test</td>
<td>HTO test</td>
<td>Ca test</td>
</tr>
<tr>
<td>OTR (cc/cm²/day)</td>
<td>0.4</td>
<td>0.06</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>WVTR (g/m²/day)</td>
<td>-</td>
<td>-</td>
<td>$\sim 1 \times 10^{-3}$</td>
<td>$1.7 \times 10^{-5}$</td>
</tr>
<tr>
<td>Film/substrate thickness (um)</td>
<td>100nm/13um</td>
<td>100nm/13um</td>
<td>25nm/100um</td>
<td>25um/200um</td>
</tr>
<tr>
<td>Temp/RH</td>
<td>33°C</td>
<td>33°C</td>
<td>38°C &amp; 100%</td>
<td>38°C &amp; 85%</td>
</tr>
<tr>
<td>Substrate OTR(cc/cm²/day)/WVTR(g/m²/day)</td>
<td>-</td>
<td>-</td>
<td>WVTR: 2.4</td>
<td>WVTR: 1</td>
</tr>
<tr>
<td>Oxygen concentration (cm⁻²)</td>
<td>$1.7 \times 10^{-3}$</td>
<td>$1.7 \times 10^{-3}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Diffusivity (cm²/s)</td>
<td>$4.5 \times 10^{-3}$</td>
<td>$4.5 \times 10^{-3}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Defect density</td>
<td>0.6um 5400/cm²</td>
<td>0.6um 750/cm²</td>
<td>0.6um 170/cm²</td>
<td>0.6um 2/cm²</td>
</tr>
</tbody>
</table>

2.4 Defect Visualization Techniques and Experiment

It is important to characterize defects in ALD films for barrier coating applications. As film quality continues to improve, direct defect characterization has become increasingly challenging. TEM and AFM were used to characterize nanometer-scale film defect. However, small field/scanning size and low efficiency make the characterization of small defects with large spatial separation become time-consuming and torturous. To be worse, the characterization could hardly differentiate film defects with film surface morphology such as small depression that may be caused by substrate surface unevenness. Figure 2.1 shows the characteristics of ALD coatings and a SEM image of the surface condition for ALD $\text{Al}_2\text{O}_3$ coated on PEN substrate. When the coating layers are in buried structures the characterization would become especially challenging. We will discuss the non-destructive technique for inspection of ALD film in buried structures in Chapter 4. Instead of directly imaging defect using the common microscopic methods, in this chapter, we have developed two defect visualization techniques which can render pinhole defects visible in ALD $\text{Al}_2\text{O}_3$ barrier coatings grown on various substrates, allowing fast inspection of
defect densities and locations. Of the two techniques, electroplating decoration is used to visualize defects in ALD Al₂O₃ on conductive substrates while fluorescent tagging for ALD Al₂O₃ on polymer substrates. We will demonstrate these two techniques in the following sections.

2.4.1 Electroplating Decoration

Description

Copper electroplating was applied to visualize defects in the Al₂O₃ ALD thin films deposited on various metallic substrates. This method can be extended to other dielectric ALD films on conductive substrates including conductive polymers, and provide a good methodology to evaluate ALD film's quality for applications in diffusion barriers, surface modification and
protective coatings. Electroplating is commonly used to grow metal nanowires from porous alumina templates with diameter as small as 5 nm and length as long as hundreds of microns [78]. Electroplating is also known as a common way to grow metallic interconnects in electronics. For defect visualization, electroplating results in a copper bump grown at each defect site in the dielectric ALD Al₂O₃ film where electrolytic solution establishes contact with the substrate. A schematic of this visualization technique is shown in Figure 2.2. After the electroplating, the copper bumps can be easily observed using optical- and electron-microscopy. In related applications, electroplating has been used to decorate cleavage and slips steps on crystal surfaces [79], and pinholes in magnetic tunnel junctions [80–82].

![Schematics of Electroplating Decoration Mechanism](image)

**Electroplating decoration concept**

Figure 2.2 Schematics of electroplating decoration mechanism

**Experiment**

In a series of experiments, ALD Al₂O₃ thin films with a thickness of 25 nm were grown on substrates in a hot-wall ALD flow reactor at 120 °C using sequential, self-limiting exposures to trimethylaluminum (Aldrich) and water (Fisher HPLC-grade) [32]. Various metallic substrates such as copper, gold, and nickel have been used for ALD growth. The thickness of the Al₂O₃ ALD film was measured using ellipsometry (L2W16C.830, Gaertner Scientific Corp.) and X-ray photoelectron spectroscopy (XPS) (Phi5600, Physical Electronics Inc.) was used to characterize
the chemical composition of the films. Commercially available copper pads on a printed circuit board and physical vapor deposited copper on silicon wafers served as the copper substrate. The copper pads were polished using the sand paper with grit size of 1200 to remove the surface oxide and then cleaned using piranha and deionized water before ALD growth. Gold substrates were prepared by RF sputtering on glass substrates. The nickel substrates were prepared by physical evaporation of nickel on un-doped silicon wafers. On all the metal substrates, an area of ~2 cm² on the samples was masked against ALD Al₂O₃ deposition using Kapton tapes. This area was then used for electrode attachment for electroplating. Before electroplating, the Kapton tape was removed and an electrode was attached on the exposed metallic area using conductive epoxy.

Using a DC power supply (HP E3611A, Agilent), the electroplating current was controlled at 0.08 A and the electroplating voltage was 0.5 V. The electroplating solvent consisted of 1 mol/L H₂SO₄, 0.4 mol/L CuSO₄. The solvent was agitated in the tank and the electroplating temperature was controlled at 21 °C. After copper electroplating, the samples were inspected using a scanning electron microscope (SEM) (JSM-6480LV, Joel Limited) with operating voltage of 10 kV, and optical microscope (OM) (ECLIPSE LV150, Nikon) with a 20× objective. The chemical identity of the grown Cu bumps at the defect locations was identified using energy dispersive X-ray spectrometry (EDS). The EDS collection time was 30 s.

### 2.4.2 Fluorescent Tagging

**Description**

Fluorescent tags have been developed that can render nanometer-size defects visible in ultrathin transparent ALD Al₂O₃ films on polymer substrates. These fluorescent tags allow for rapid visualization of defect distribution and quality evaluation of thin film barriers. This
approach is non-destructive and fully compatible with the widely-used laser inspection microscopic systems. The fluorescent tags are specifically designed diaza-indacene fluorophores. The tag molecules are prepared by reaction of a dipyrrromethene precursor with boron trifluoride etherate in the presence of a tertiary amine. Dipyrrromethenes are prepared from a suitable pyrrole. Normally, one alpha-position in the employed pyrroles is substituted and the other is unsubstituted. Condensation of the pyrrole with an aromatic aldehyde in the presence of trifluoroacetic acid gives dipyrrromethane, which then is oxidized to dipyrrromethene using a quinone oxidant such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone or p-chloranil. A hydrophobic substituent is attached to the tag molecule. This hydrophobic substituent of the fluorescent tags preferentially binds to the hydrophobic polymer surface while avoiding the hydrophilic ALD Al₂O₃ film. This preferential bonding leads to the attachment of the fluorescent tag molecule only on the polymer surface.

Figure 2. 3 Function of the fluorescent tag, which binds solely to the polymer substrate, based on its greater hydrophobicity.
Figure 2.3 depicts the fluorescent tag molecules binding to a hydrophobic polyethylene naphthalate (PEN) polymer surface. The fluorescent tag molecule is preferentially bound to the polymer surface because of its hydrophobic moiety. The fluorescent tag molecules are small enough to access nanometer-scale regions of the polymer surface. The dimension of the tag molecule was calculated according to its chemical structure as given in Figure 2.3. When excited by light, the fluorescent moiety of the tag molecule emits a strong fluorescence signal. This fluorescence allows for direct identification of the defects in the Al2O3 ALD film.

**Experiment**

To demonstrate the usefulness of the fluorescent tags, ALD Al2O3 barrier films with a thickness of 25 nm were deposited onto polyethylene naphthalate (PEN) polymer substrates (Teonex Q65, Dupont Teijin, Inc) [32]. The ALD Al2O3 film growth is based on two sequential, self-limiting surface reactions. In the deposition process, TMA and H2O were alternately entrained in the N2 carrier flow using gas switching valves. The TMA and H2O yield ALD Al2O3 according to the follow two reactions:

(A) Al-OH* + Al(CH3)3 \(\rightarrow\) Al-O-Al(CH3)2* + CH4

(B) Al-CH3* + H2O \(\rightarrow\) Al-OH* + CH4

where the asterisks donate the surface species. By repeating the AB sequence, the film is grown to the required thickness. The ALD-coated polymers were then soaked in a fluorescent tag solution for 5 min. A solution containing 70% ethanol and 30% water was used to rinse off the excess fluorescent tag. The sample was subsequently dried using clean dry air and maintained in an ultraviolet-safe environment. A LSM 510 confocal microscope (Carl Zeiss, Inc.) was used for inspection of the fluorescence. An Argon ion laser at 488 nm was used to excite the fluorescent tag molecules. The fluorescent emission at a wavelength maximum of 515 nm was measured.
using a 505-530 nm band pass filter.

2.5 Results and Discussion

2.5.1 Defect Density in ALD Al₂O₃ on Ni Substrates

Figure 2.4 shows the electroplated copper bumps on the ALD Al₂O₃ thin films on copper, gold, and nickel substrates after 5 min of electroplating. EDS analysis indicated that the bump structures consisted of copper. As reported by Groner et al. [67], the quality of ALD Al₂O₃ grown on copper may suffer here because of the surface roughness of the substrate. The rough surface of the copper substrate is attributed to the polishing to remove the oxide. Groner et al. also reported ALD Al₂O₃ grown on gold substrate may suffer from nucleation problems due to the absence of hydroxyl groups [67]. In contrast to the copper and gold substrates, no copper bumps were observed on the ALD Al₂O₃ film grown on nickel after 5 min of electroplating as shown in Fig. 2.4 c. The good quality of ALD Al₂O₃ on nickel agrees well with previous electrical characterization results [67].

Figure 2.4 Defect decoration results for ALD Al₂O₃ film on (a) Cu, (b) Au and (c) Ni substrates.

To quantify the quality of ALD Al₂O₃ film, defect density was studied using the films grown on nickel substrates. To ensure a valid study, damage must not be caused by the
The electroplating process itself. Electrical breakdown cannot occur in the film during the electroplating and the film cannot be dissolved, deteriorated, or changed by the electroplating solvent. According to Groner et al. [67], the breakdown electric field strength of ALD Al₂O₃ films exceeds 5 MV/cm. For an ALD Al₂O₃ film thickness of 25 nm, the breakdown voltage is larger than 12.5 V. This film thickness is sufficiently thick to prevent tunneling behavior. The electroplating voltage of 0.5 V used in this study is expected to be safe for these Al₂O₃ films.

Aluminum oxide has been previously proven to be stable in electroplating [80-82]. In this study, ellipsometry and XPS were employed to prove that ALD Al₂O₃ film is stable in the H₂SO₄/CuSO₄ electroplating solvent during the exposure time. A sample with an ALD Al₂O₃ film with a thickness of 25 nm was partially immersed in the electroplating solvent for 120 min. The Al₂O₃ film thickness and surface chemical composition of the soaked and unsoaked regions were then compared using ellipsometry and XPS, respectively. No noticeable change was detected in either the thickness or the chemical composition.

![Figure 2.5](image_url)

Figure 2.5 Change of copper bump size and density with electroplating time for (a) 20 minutes and (b) 100 minutes.

Figures 2.5 a and b show the decoration results for the ALD Al₂O₃ film with a thickness of 25 nm on Ni substrate after 20 min and 100 min electroplating, respectively. Figure 2.5 reveals that the copper bump size and density increase with the electroplating time. Since each
copper bump corresponds to a defect site, the defect density can be obtained by counting the copper bump density. The change in the copper bump density was then monitored as a function of electroplating time to determine the defect density of ALD Al₂O₃ films on the Ni substrates.

The variation in copper bump density with time is shown in Figure 2.6. The copper bump densities increase gradually with the electroplating time and then become saturated after 60 min.

![Graph showing copper bump densities as a function of electroplating time for two samples.](image)

**Figure 2.6** Copper bump densities as a function of electroplating time for two samples.

The copper bump densities were counted using an optical microscope with a 20× objective. The theoretical resolution for the 20× objective is 0.55 μm. The theoretical threshold bump size for detection is also 0.55 μm. With longer electroplating times, more bumps grow bigger than the threshold size. The measured bump density becomes saturated after the copper bumps at all the
defect sites have grown to a sufficient size to be detected by the microscope. The final saturated bump density is the defect density of the ALD Al₂O₃ film. From Fig. 2.6, the defect densities are 59 /cm² and 38 /cm² for samples 1 and 2, respectively. Samples 1 and 2 were prepared using identical conditions. The defect densities characterized using this technique fall within the estimation values as shown in Table 2.1.

In comparison, Sobrinho et al. [51] have reported that the defect densities for plasma enhanced chemical vapor deposited (PECVD) SiO₂ and SiN films on polymer substrate were 8000 /cm² and 500 /cm², respectively, with a characteristic defect diameter of 0.6 μm as shown in Table 2.1. The defect density of the ALD Al₂O₃ films is about 2 orders of magnitude less than the PECVD films, which is consistent with the theoretical estimation. The lesser defect density can be confirmed by comparing their gas permeability data. The oxygen transmission rate (OTR) of the PECVD SiO₂ and SiN films were 0.4 cc/m²/day and 0.06 cc/m²/day, respectively, using the MOCON® test [22]. In contrast, the permeability of the ALD Al₂O₃ film was below the resolution of the MOCON® test, ∼5×10⁻³ cc/m²/day [22]. Water vapor transmission rates of 1 ×10⁻³ g/m²/day and 1.7×10⁻⁵ g/m²/day for 25 nm ALD Al₂O₃ coated polymer substrates have also been reported using the tritiated water test [22] and calcium test [23], respectively. The difference in the OTRs is consistent with the different defect densities.

2.5.2 Defect Size Characterization

As discussed in section 2.2, defect size is another important factor determining permeation. We tried different techniques to characterize the defect size in on ALD Al₂O₃ films. Figure 2.7 shows the copper bump size distribution of 100 min electroplated ALD Al₂O₃ on Ni (sample 1). The bump has a wide size range from 5.5μm to 450μm, suggesting the wide
distribution of defect size. To track the defect size, we first tried to remove the copper bump using microprobes and reveal its footprint and the defect site underneath. However, the removal process brought stress and in most cases tore the delicate film around the defect site. A large piece of film around the defect gone with the copper bump makes it difficult to track the real defect size. Figure 2.8 shows the removal process of the copper bump and an example of before and after removal the copper bump.

Figure 2.7 Copper bump size distribution of electroplated ALD Al₂O₃ on Ni for 100min.
To avoid the tear effect during the bump removal process, we used copper etchant Transene CE-200 to etch away the copper bump and expose the footprint for observation. The liquid etchant was applied on the bump by a syringe underneath a microscope. The change of the bump size in the etchant was captured by interferometer (Zygo) as shown in Figure 2.9. The bump was gradually resolved by the etchant and finally disappeared leaving a foot mark at the location. Further treatment of the sample caused undercut of the Ni substrate at the defect site as shown by the image of 4min treatment. After the etching, the footmark was imaged using SEM. Figure 2.10 shows the footmarks left by a copper bump with size of ~300 μm (a) and ~60 μm (b), respectively. This approach is good to track the defect underneath the copper bump. However, the possible erosion of the etchant to the Al₂O₃ film was not studied. Also, the bump location becomes dirty after the etching which influences the defect track. And, if the defect is too small,
it is difficult to track the defect in a comparatively large area left by the copper bump. Sometimes, the defect track using SEM just ended up with nothing.

Figure 2.9 Etching process of a copper bump in copper etchant followed by further undercutting of the Ni substrate.

Figure 2.10 SEM image of the footmark left by a copper bump with size of ~300 µm (a) and ~60 µm (b).

Focus ion beam (FIB) is another technique to track the defect and characterize the defect size. Figure 2.11 shows the mechanism of this technique for defect characterization. The copper
bump is milled gradually using ion beam while the cross section is observed using SEM. This technique can present rich information about the defect, such as defect size, defect source, by exposing the cross section of the defect site. Figure 2.12 shows an example of a milled copper bump (a) and the cross section of the defect site (b). From figure 2.12 (b), we can see the defect is associated with an imperfection in the Ni substrate. The defect diameter is around 200nm. The FIB technique is effective and can easily locate the copper bump and mill it to track the defect. Defects with size ranging from a few hundreds of nanometers to several microns were captured by cutting the copper bumps with different sizes. However, since it is secondary to this project no statistic study has been conducted on the defect size distribution.

![Mechanism to use FIB for defect characterization.](image1)

Figure 2.11 Mechanism to use FIB for defect characterization.

![A FIB milled copper bump (a) and the cross section of the corresponding defect site (b).](image2)

Figure 2.12 A FIB milled copper bump (a) and the cross section of the corresponding defect site (b).
2.5.3 Discussion on Causes for Defects

Particles and substrate surface roughness are two common reasons to cause defects in thin film coatings. To prevent particle contamination, the substrate needs to be cleaned thoroughly to remove particles before ALD coating. However, it is difficult to completely get rid of the fine particles. Another polymer cover-coat is normally applied on the substrate. This cover-coat can cover the particles on the substrate and smooth the surface, which prevent the negative effect in the following thin film coating process [16], [48].

During the defect characterization in this project, we also identified the causes for defects in ALD coatings. These causes include particles, surface contamination, micro-cracks, substrate roughness and imperfections, and scratches generated during sample handling. Figure 2.13 shows the SEM images of some examples of these causes.

![Figure 2.13 Examples of the causes for defects in ALD coatings.](image)

Figure 2.13 (a) exposed a particle at the defect site which was took after the copper bump was
etched by the etchant. Figure 2.13 (b) shows a defective area which was caused by an uncleanliness area of the substrate. Figure 2.13 (c) captures a scratch which might be generated during the sample handling while (d) is a micro-crack in the ALD coating which might be associated with the surface stress during deposition and cooling. Figure 2.12 (b) shows an example of substrate imperfection associated defect which was captured by FIB milling. The defects caused by particle and surface uncleanness stress the importance to clean the substrate and treat the sample in a clean environment. We compared the Ni substrates prepared in a normal environment and a 100 class clean-hood. The defect densities after ALD coating can have ten times difference. The substrate surface roughness also shows essence for defect formation. As shown in Figure 2.4, the ALD Al₂O₃ deposited on a rough Cu pad which was polished by a sand paper yielded a poor quality. In comparison, a low defect ALD Al₂O₃ film was obtained when we deposited it with a same thickness on a PVD copper film on a silicon wafer. The defect density has been reduced by more than 6000 times as shown in Figure 2.14. The mechanism of the formation of these defects is unknown. However, the results presented in this section provide interesting evidences for the future study. Further study is needed to investigate contributions of various factors and the mechanism for defect formation.

Figure 2. 14 Comparison of defect densities of ALD Al₂O₃ deposited on a rough copper pad and a PVD copper film coated on a silicon wafer.
2.5.4 Defect Visualization in ALD Al₂O₃ on Polymer Substrates

The previous sections discussed the defect characterization of ALD Al₂O₃ on metal substrates using electroplating decoration. This section discusses the defect visualization in ALD Al₂O₃ on polymer substrates using a fluorescent tagging technique.

The application of the fluorescent tag molecules was compared using: (a) a PEN substrate with no ALD Al₂O₃ film; (b) a PEN polymer substrate coated with a native ALD Al₂O₃ film; and (c) an ALD Al₂O₃-coated PEN substrate with scratches intentionally formed to produce defects in the ALD Al₂O₃ film. The fluorescent tag binds well to the uncoated PEN film and yields a uniform bright field across the entire polymer sample as shown in Figure 2.15 (a). In contrast, the fluorescent tag does not bind to the defect-free ALD Al₂O₃ film and an all dark field is observed in Fig. 2.15 (b). For the intentionally scratched Al₂O₃ film, the fluorescent tag only binds to the areas of the PEN polymer substrate that are exposed by the scratch defect.

![Fluorescence images showing: (a) PEN substrate with no ALD Al₂O₃ film; (b) PEN polymer substrate coated with a native ALD Al₂O₃ film; and (c) ALD Al₂O₃-coated PEN substrate with scratches intentionally formed to produce defects in ALD Al₂O₃ film.](image)

Figure 2.15 demonstrates that the fluorescent tag molecules attach selectively to the PEN polymer substrate and not to the ALD Al₂O₃ film. The fluorescent tag molecules were used
to image defects on other ALD Al₂O₃-coated polymer substrates. However, the fluorescent tag did not bind to a polyimide polymer substrate (Kapton HN, Dupont, Inc.) and could not identify defects in the ALD Al₂O₃ film on the polyimide surface. The water contact angles of PEN and Kapton substrates were measured as 90±5° and 70±5°, respectively. The less water contact angle of Kapton indicates that the Kapton is less hydrophobic than PEN substrate, which may explain that the fluorescent tag molecules bind to the PEN substrate but not to the Kapton substrate. Different fluorescent tag molecules may be required to image defects in ALD Al₂O₃ films on other polymer substrates.

Inorganic materials, such as ALD Al₂O₃ films, are brittle and prone to cracking on polymer substrates under mechanical or thermal-mechanical stressing. The evaluation of the critical strain for cracking is important because the cracking of the inorganic barrier films leads to device failure. The cracks resulting from mechanical strain have been observed previously to be up to several hundreds of microns long and only 10-30 nm wide [61], [83].

To demonstrate the use of the fluorescent tag to image cracking, an external tensile loading was applied to PEN substrates coated with 25 nm of ALD Al₂O₃. The fluorescent tags were then applied to these samples and a LSM 510 confocal microscope was used to observe the fluorescence. Cracking was clearly observed using a 20× objective. Figure 2.16 (a) shows channel cracks identified within the gage section of a sample that was subjected to a tensile strain of 5%. Cracks that form in a direction orthogonal to the applied tensile stain are common when the strain exceeds the critical strain for cracking [50], [52], [53], [55], [61], [62].
The cracks in Fig. 2.16 (a) may be compared with cracks at the edge of the samples shown in Fig. 2.16 (b). These cracks were generated during sample preparation when the ALD-coated polymer substrate was cut to size prior to testing. Fig. 2.16 (b) identifies the unique characteristics of these preparation-related cracks that arrest at the edge of the substrate. Excellent image contrast was obtained in all of the confocal microscope measurements. This contrast allows the cracks to be identified readily with minimal sample preparation. Using this crack visualization approach, the mechanical robustness of both single layer ALD Al₂O₃ films and multi-layer structures were characterized recently [53].

The fluorescent tags allow the cracks and defects to be located for subsequent analysis using field emission scanning electron microscopy (FESEM). The FESEM was performed using a JSM-7401F field emission scanning electron microscope (FESEM, JEOL Limited). The FESEM can determine the width of the cracks. Fig. 2.17 shows a crack width of ~20 nm that was observed close to the edge of the polymer substrate for the preparation-related cracks resulting from sample cutting.
Individual defects or pinholes are generally caused by particulate contamination or the surface roughness of the substrate and are believed to be the critical feature limiting the performance of gas diffusion barriers as we discussed. These defects must be controlled to assure high barrier quality and efficient barrier manufacturing. Figure 2.18 (a) shows a defect-rich region in an ALD Al₂O₃ film with a thickness of 25 nm deposited on a PEN polymer substrate. This image was obtained using the confocal microscope with a 20× objective. The white arrows in Figure 2.18 (a) show prescribed marker features that were used to locate defects for FESEM imaging. Sites #1 and #2 in Fig. 5a show the fluorescence signals from individual defects.
These individual defects at sites #1 and #2 were then evaluated using the FESEM. Defect diameters of ~200 nm and ~1.2 µm were determined for the defects imaged at sites #1 and #2 in Figure 2.18 (b) and (c), respectively. Figure 2.18 indicates that defect sizes between tens and hundreds of nanometers could be readily observed using the fluorescent tag. Smaller size of defects could be identified if the fluorescent tag molecules could access the defect region and accumulate to yield an observable bright spot. Considering the small dimension of the fluorescent tag molecule as illustrated in Figure 2.3, defects with size down to nanometer-scale could be accessed by the fluorescent tag and rendered visible.

We also note that these defects could be observed by FESEM without using the fluorescent tag. However, the location and density of defects cannot be determined at low magnification. FESEM imaging at high magnification with small field size is time-consuming. The fluorescent tag allows a large area to be probed and defects to be identified quickly at low magnification using optical microscopy. The FESEM images in Figure 2.18 (b) and (c) also provides information about the morphology of individual defects. Both FESEM images in Figure 2.18 (b) and (c) likely result from particle contamination on the PEN substrate. The particles are believed to mask the polymer substrate and prevent ALD Al₂O₃. The particles then move or are

Figure 2.18 (a) Confocal microscope image of prescribed markers and various defect sites close to markers. (b) FESEM image of defect at site #1. (c) FESEM image at site #2.
dislodged after the ALD Al₂O₃ coating process and leave an uncoated region of the polymer substrate. Understanding the morphology of defects is important to identify the origin of defects and to improve barrier quality.

2.6 Chapter summary

In this chapter, we discussed the importance to evaluate and characterize defects for barrier coatings. The defect densities of ALD Al₂O₃ coatings were theoretically estimated and experimentally characterized by developing two defect visualization techniques. Electroplating decoration is an effective and efficient technique to visualize defects in ALD Al₂O₃ on conductive substrates. The defect densities of ALD Al₂O₃ were quantitatively characterized and the corresponding defect size was successfully demonstrated. The defect density values were consistent with the theoretical estimation. The causes of defects in ALD Al₂O₃ were also demonstrated and discussed. Fluorescent tagging is another technique developed for defect visualization of ALD Al₂O₃ on polymer substrates. The fluorescent tag readily identified cracks and defects in ALD Al₂O₃ films on PEN substrates. The fluorescence emission allows the location and density of cracks and defects to be determined at low magnification using optical microscopy. The cracks and defects can then be examined at high magnification using FESEM. The fluorescent tag located cracks with widths as narrow as 20 nm and individual defects with diameters as small as 200 nm.
Chapter 3 Ultra-Thin ALD Films

3.1 Introduction

The development of defect visualization techniques in Chapter 2 enhances the capability to design barrier coatings for better performance. For example, it is well known that better mechanical robustness can be achieved with thinner thickness for thin film coatings [50], [53]. However, for barrier applications, thinner film thickness could mean worse barrier performance or higher defect densities. A critical thickness is generally required for a thin film coating to become continuous. The defect density of the film is further reduced with film thickness increase. Normally, there is a trade-off between film thickness and barrier performance in a certain thickness region. To guide the development of barrier coatings, we need to know the defect densities for different film thicknesses and the corresponding barrier performances.

In this chapter, we characterized the pinhole defect density of ultra-thin (10nm, 5nm, and 2nm) Al₂O₃ films grown by ALD using the copper electroplating based defect visualization technique as demonstrated in Chapter 2. A significant defect reduction was demonstrated for the 2nm-thick Al₂O₃ films by improving the Ni substrate with an ALD W layer. This W layer serves as a buffer layer which provides an excellent surface for the Al₂O₃ to grow and yield a low defect density. The chemical stability of the 2nm Al₂O₃ films and its effect on the defect characterization are analyzed, followed by discussions on the reasons for the defect reduction and the effect of the substrate on ALD Al₂O₃ film integrity. The results obtained in this study can be applied to an ALD dielectric layer grown on an ALD conducting layer. In addition, these results can be used to guide the development of a moisture barrier coating consisting of ALD inorganic and molecular layer deposition (MLD) organic layers [84], [85]. We cannot
characterize defects of an ALD Al₂O₃ film grown on a MLD layer. However, the ALD W buffer layer studied can represent an MLD organic layer since they follow the same self-limiting growth mechanism. The defect reduction enabled by the ALD W buffer layer demonstrated the feasibility to use 2nm-thick Al₂O₃ films for barrier applications. The MLD organic buffer layer is expected to reduce the defect densities of a 2nm thick ALD film.

3.2 Background

The aggressive shrinking of the device size drives the film thickness scaling down to the extremity, among which the most striking example is the gate dielectrics for modern transistors [86], [87]. Meanwhile, ultra-thin films are desired for many applications to achieve optimum performance or novel properties. To name a few, substantial mechanical robustness enhancement was demonstrated for ALD Al₂O₃ when its thickness was reduced from 125nm to 5nm [53]. Nanolaminates consisting of ultra-thin (few nanometers or less) ALD layers have demonstrated ultra-low moisture permeability [25], [26], ultra-low thermal conductivity [88], and ultra-high x-ray reflectivity [89]. Most recently, ultra-thin ALD Al₂O₃ has also been used to realize low optical power, low voltage, light-actuated digital microfluidic devices [90]. Continuous scaling down the film thickness often brings up a fundamental question about the continuity or integrity of the ultra-thin ALD films. The knowledge about the critical thickness at which the ALD film becomes continuous and the defect density as a function of the film thickness is important to many of the aforementioned applications as it is often directly associated with the film functionality and reliability. Al₂O₃ is one of the most attractive ALD materials because of its chemical and thermal stability, excellent dielectric properties, and good adhesion to many materials [67]. ALD Al₂O₃ is also one of the most thoroughly studied and well-established ALD processes. Despite the numerous studies and applications of ALD Al₂O₃ on various substrates,
the effect of different substrates on the growth of Al₂O₃ and film perfection is not well understood [67]. For ultra-thin ALD Al₂O₃ films (<10nm), the substrate plays an especially important role in determining the film growth and thereafter the film integrity. For ALD Al₂O₃ grown on hydrogen terminated Si substrates, it was reported to become continuous and smooth for thickness of around 2nm [91], [92]. However, there is no study to quantitatively evaluate ALD Al₂O₃ film integrity or defect densities of the film once it has been observed to be continuous.

The previous study reported that with 5nm-thick ALD Al₂O₃, the WVTR of Kapton film was reduced by one order of magnitude, and 10nm by three orders of magnitude, and the reduction became saturated with further increasing the thickness [22]. For single layer ALD coatings, 25nm Al₂O₃ is normally used for optimum barrier performance. To further improve the barrier performance, multilayer structures have been developed, in which the sub-layers can decouple the defects in the Al₂O₃ layers and make the diffusion path of the permeant become tortuous. A new development for ALD barrier coatings is to use ALD Al₂O₃ and molecular layer deposited (MLD) organic sub-layers to build up the nano-laminates [15], [53]. The interposed ductile organic sub-layers can also decouple the inorganic layers and potentially improve the mechanical robustness of the films.

3.3 Theoretical Analysis

A theoretical analysis can help us to understand the tolerable defect densities for different thicknesses. For multilayer barrier structures, higher number of barrier-layer/sub-layer (for here ALD/MLD) bilayers with lower defect densities in each barrier layer can create more tortuous or longer diffusion path [49]. In another words, the gas/moisture may take longer time to diffuse through the barrier structure. The time for the gas species to diffuse through the barrier
structure and become equilibrium is called lag time. For multilayer barrier structures, the lag time could be as long as several years so it is critical to determine the barrier performance of multilayer barrier films. According to ideal laminate theory, lag time can be expressed by Equation 3.1, where $K_j = S_j / S_{j+1}$. $S$ and $D$ are solubility and diffusivity of the organic sublayers, respectively. $l$ is the effective thickness of the organic layers which is determined by the defect spacing in the inorganic barrier layers as shown in Figure 3.1. This effective diffusion thickness results in a much longer diffusion path than the thickness of the organic layer. The detailed derivation of Equation 3.1 can refer to [49] and [93].

$$L = \frac{\sum_{i=1}^{n} \frac{l_i^2}{2D_i} \sum_{m=1}^{n} \frac{l_m}{D_m} \prod_{j=1}^{m} K_j - \frac{l_i^2}{3D_i^2} \prod_{j=1}^{i-1} K_j + \sum_{i=1}^{n} \frac{l_i}{D_i} \prod_{j=1}^{i-1} K_j \sum_{\beta=1}^{i} \frac{l_\beta}{\prod_{m=\beta}^{i} K_{m-\beta}} - \frac{l_{i+1}^2}{2D_{i+1}}}{\sum_{i=1}^{n} \frac{l_i}{D_i} \prod_{j=1}^{i} K_j}$$

(3.1)

Figure 3. 1 A schematic diagram of effective thickness $l$ which is determined by the defect spacing in the inorganic barrier layer (AlO$_x$) and results into a much longer diffusion path than the organic layer [49].

Figure 3.2 shows the lag time as a function of number of bilayers (Dyads) and its dependency on defect density. In order to yield longer lag time of better barrier performance, we need higher number of bilayers and low defect density which produces large defect spacing in
the inorganic barrier layers.

Figure 3. 2 Lag time as a function of number of bilayers (Dyads) and its dependency on defect density or defect spacing (from 100 microns to 5000 microns) [49].

Consider an ALD/MLD multilayer structure as shown in Figure 3. If we use ALD (25nm)/MLD (15nm) bilayer to build up a two bilayers structure, we have a total thickness of the barrier film of 80nm. If we keep the total thickness of 80nm but reduce both the thicknesses of ALD and MLD layers, for example ALD (2nm)/MLD (2nm) bilayer, the barrier film will consist of higher number 40 of ALD/MLD bilayers.
So, thinner layers will yield higher number of bilayers. However, thinner ALD layer may bear higher defect densities which may decrease the diffusion path and barrier performance. The effect of increase of defect densities counteract with the effect of increase of the number of bilayers by using thinner layers. In order not to reduce the barrier performance, there will be tolerable defect densities for different ALD thicknesses. These tolerable defect densities can be theoretically predicted from the effective thickness \( l \) using Equation 3.1 with a known lag time. The calculation can be conducted by any math software like Mathematica. For example, if we use ALD (25nm)/MLD (15nm) bilayer as a reference and assume the defect density in 25nm ALD \( \text{Al}_2\text{O}_3 \) is 35/cm\(^2\). This defect density value is close to the values we demonstrated in Chapter 2. Then two bilayers will produce a lag time of around 0.25 year. Using 0.25 year as the baseline and keeping the total thickness, Table 3.1 lists the calculated tolerable defect densities for different ALD/MLD thicknesses.

<table>
<thead>
<tr>
<th>ALD/MLD thickness</th>
<th>25 nm/15 nm</th>
<th>10 nm/10 nm</th>
<th>5 nm/5 nm</th>
<th>2 nm/2 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALD/MLD bilayers</td>
<td>2</td>
<td>4</td>
<td>8</td>
<td>20</td>
</tr>
<tr>
<td>Defect density</td>
<td>~35 / cm(^2)</td>
<td>?</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>Tolerable defect densities</td>
<td>-</td>
<td>200 / cm(^2)</td>
<td>800 / cm(^2)</td>
<td>5000 / cm(^2)</td>
</tr>
</tbody>
</table>

Figure 3.3 Use thinner layers to build up a higher number of ALD/MLD bilayers for multilayer barrier structure.
defect densities for different thicknesses of ALD Al₂O₃ layers. For example, if we want to use 2nm thick layer, the defect density should be less than 5000/cm² in order to produce a reasonably good barrier performance. And the use of a thinner thickness of ALD Al₂O₃ layer is attractive to obtain a better mechanical robustness which is important for many practical applications, such as flexible organic electronics encapsulation. In next sections, we will study the defect densities in ultra-thin ALD Al₂O₃ films.

3.4 Experiment

Nickel (Ni) substrates were prepared for the growth of the ultra-thin Al₂O₃ films with and without an ALD W buffer layer. The Ni substrates were provided by International Wafer Service, with 100nm-thick Ni deposited on 4 inches silicon wafers using physical vapor deposition. Before the ALD deposition, the wafers were cut into 2.5×2.5 cm² pieces. The substrates were cleaned using acetone followed by isopropanol and deionized water rinse. All the operation was conducted in a class 100 clean hood. The ALD Al₂O₃ growth is achieved using sequential, alternating exposures to trimethylaluminum (TMA) (97%, Sigma-Aldrich) and H₂O (HPLC-grade, Fisher). In the deposition process, TMA and H₂O are alternately injected via nitrogen carrier gas using computer-controlled pneumatic valves. The TMA and H₂O yield ALD Al₂O₃ according to the following binary self-limiting reactions [31]

(A) \( \text{Al-OH}^* + \text{Al(CH₃)}₃ \rightarrow \text{Al-O-Al(CH₃)}₂^* + \text{CH₄} \) (1)

(B) \( \text{Al-CH₃}^* + \text{H₂O} \rightarrow \text{Al-OH}^* + \text{CH₄} \) (2),

where asterisks represent the surface species. ALD Al₂O₃ films with thicknesses of 2, 5 and 10 nm were deposited respectively on the Ni substrates at 120 °C.

A thin ALD tungsten (W) layer was deposited on the Ni substrate as a buffer layer prior ALD Al₂O₃ deposition. ALD W is based on sequential, alternating exposures to WF₆ (99.9%,
Sigma-Aldrich) and Si$_2$H$_6$ (99.998%, Voltaix) which can be described as following reactions [94]

(A) \[ \text{WSiHFSiH}_3^* + 2\text{WF}_6 \rightarrow \text{WWWF}_4^* + 2\text{SiF}_4 + 1.5\text{H}_2 + \text{HF} \] (3)

(B1) \[ \text{WF}_4^* + \text{Si}_2\text{H}_6 \rightarrow \text{WSiH}_2\text{F}^* + \text{SiHF}_3 + 1.5\text{H}_2 \] (4)

(B2) \[ \text{WSiH}_2\text{F}^* + 0.5\text{Si}_2\text{H}_6 \rightarrow \text{WSiHFSiH}_3^* + 0.5\text{H}_2 \] (5)

The W layer with a thickness of 15nm was deposited onto the Ni substrate at 177 °C. Following the W deposition, in the same chamber, 2, 5 and 10nm Al$_2$O$_3$ films were then deposited respectively at 120 °C. The W deposition was fluorine terminated after the reaction (3) with WF$_6$.

For defect visualization, an electrochemical workstation (CH Instruments) was used to control the copper electroplating and 0.3V voltage was used for the electroplating process. The copper electroplating solution was provided by Technic Inc. which consists of CuSO$_4$·5H$_2$O (90g/L), H$_2$SO$_4$ (210g/L), Cu (23g/L), Chloride ion (50ppm), and Technic FB brightener (4mL/L). The original solution was diluted using de-ionized water for different CuSO$_4$·5H$_2$O and H$_2$SO$_4$ concentrations in the experiment. Before the electroplating, an electrode contact area of 0.5cm$^2$ near the sample edge was made by scratching the top Al$_2$O$_3$ layer lightly. An electrode was attached onto the sample via conductive epoxy. Copper electroplating was then conducted at room temperature. After the copper plating, the samples were inspected using an optical microscope (OM) (ECLIPSE LV150, Nikon) with a 20x objective and a scanning electron microscope (SEM) (JSM-6480LV, Joel Limited) with an operating voltage of 10 kV. The chemical identity of the grown Cu bumps at the defect locations was identified using energy dispersive X-ray spectrometry (EDS) and ImageJ image processing software was used to assist the defect density analysis.

X-ray photoelectron spectroscopy (XPS) and X-ray reflectivity (XRR) were used to
analyze the deterioration of the Al₂O₃ film in the electroplating solution. XPS spectra were acquired using a Perkin-Elmer 5600 photoelectron spectrometer with a monochromatic Kα source (12.5 mA, 12 kV) using a 1.1 μm diameter spot size and operating at a base pressure of 2 × 10⁻¹⁰ Torr. Survey spectra were acquired using pass energy of 187 eV. High resolution spectra of the Al 2s and W 4d regions were collected with pass energy of 23 eV. All of the peaks were fit using Gaussian–Lorentzian line function and a linear background when necessary.

XRR was performed using a high resolution Bede D1 diffractometer from Bede Scientific Inc. The diffractometer was equipped with a Cu Kα X-ray tube with a 1.54 Å wavelength. A filament current of 40 mA and a voltage of 40 kV were used for the measurements. For each sample, a ω-2θ scan was performed using 5s acquisition and a 10 arcsec step size. The data were fit using the REFS fitting software from Bede Scientific Inc. to independently extract the thickness, density, and surface roughness of the thin films.

3.5 Results and Discussion

3.5.1 Defect Densities in Ultra-Thin ALD

Figure 3.4 compares the defect density for 2nm, 5nm, and 10nm Al₂O₃ films deposited on the Ni substrates and on the Ni with a 15nm ALD W buffer layer respectively. The defect density values were obtained by monitoring the copper structures or copper bumps grown at defect sites in the ALD Al₂O₃ films and then evaluating the number of densities of the copper bumps for the corresponding defect densities. It should be noted that the defect density values were characterized on the Al₂O₃ layer only. The defect densities for 5nm and 10nm Al₂O₃ on both the Ni substrate and the Ni with a 15nm ALD W buffer layer are well below the tolerable defect densities as listed in Table 3.1. However, for 2nm Al₂O₃ on the Ni substrate, huge defect
densities were obtained after the copper electroplating visualization. In comparison, a significant defect density reduction is demonstrated for the 2nm Al₂O₃ deposited on the ALD W layer. This defect reduction is thickness-dependent and it becomes less with thicker ALD Al₂O₃. More than three orders of magnitude defect density reduction from $\sim 1.2 \times 10^5$/cm² to $\sim 90$/cm² is obtained for the 2nm Al₂O₃ while the defect densities are almost same for the 10nm Al₂O₃. Figure 3.5 compares the SEM images of the electroplated samples of the 2nm Al₂O₃ deposited on the Ni substrate (a) and on the Ni substrate with a W layer (b). The insets are the bare Ni substrate and the bare W electroplated with the same plating condition. The insets illustrate that the two substrates without the 2nm ALD Al₂O₃ are exactly the same after electroplating. As a result, Figure 3.5 presents the significant quality difference of the 2nm Al₂O₃ on the two different substrates.

Figure 3. 4 Comparison of the defect densities of Al₂O₃ deposited on Ni substrates and Ni substrates with a 15nm ALD W buffer layer as a function of Al₂O₃ thickness. The copper electroplating solution was 0.03mol/L CuSO₄·5H₂O and 0.03mol/L H₂SO₄ with a 30 minute plating time for all samples. Note the breaks in the vertical scale in the figure.
Comparison between the SEM images of 2nm-thick Al₂O₃ ALD deposited on the Ni substrate (a) and the Ni substrate with a 15nm-thick tungsten ALD seed layer (b). The insets are the bare Ni substrate and the bare W electroplated with the same plating condition. Energy Dispersive X-ray analysis showed that the light-color structure mainly consist of copper while the dark areas in between are free of copper.

3.5.2 Effect of Electroplating Conditions on Defect Density Characterization

The quantitative characterization of the defects using the copper electroplating based visualization technique could be dependent on the electroplating conditions, i.e. electrolyte concentration (EC) and electroplating time (ET). In addition, such thin Al₂O₃ films could be vulnerable to the aqueous electrolytic solution, even though the copper plating solution was diluted around 30 times to 0.03mol/L CuSO₄·5H₂O and 0.03mol/L H₂SO₄ to mitigate the potential detrimental effect of the electrolytes. Possible deterioration could yield a significant amount of artificial defects in the Al₂O₃ films which might skew the results. To justify the defect density values and to evaluate the dependence of the density characterization on the electroplating conditions, we then characterized the copper bump densities in a wide range of electroplating conditions using the 2nm Al₂O₃ films deposited on the W buffer layer as an example. The deterioration of the Al₂O₃ films in the electrolytic solution was analyzed using XPS and XRR.
The change of the copper bump density as a function of electrolyte concentration (EC: CuSO4 and H2SO4) (a) and electroplating time (ET) (b). The copper bump densities were evaluated for 2nm Al2O3 samples deposited on nickel substrate with a 15nm tungsten ALD seed layer. The dash lines correspond to the mean value of the bump densities and three times standard deviation from the mean value for EC varying from 0.01 to 0.2mol/L (a) and ET varying from 5 to 30 minutes (b). The ET was 30 minutes for (a) and EC was 0.03mol/L (CuSO4 and H2SO4) for (b). Note the breaks in the vertical scale of (b).

The dependence of the copper bump density values on the electrolyte concentration EC was evaluated as shown in Figure 3.6 (a). In Figure 3.6 (a), we varied EC (CuSO4 and H2SO4) but kept the ET at 30 minutes for all the samples. As shown in the figure, when EC varied from 0.01mol/L to 0.2mol/L, the copper bump density values of the electroplated 2nm Al2O3 samples distributed randomly in a certain density range, which is within three times the standard deviation (17 cm⁻²) from the mean value (94 cm⁻²). There is no noticeable dependence of the copper bump densities on EC for a 30 minutes plating. However, when EC continued to increase to 0.5mol/L, the copper bump densities had a significant increase and fell well outside this range as shown in the figure. This shows that high ECs have a significant effect on the electroplated bump densities. Considering the copper bump densities had no dependence on EC in a wide range of low ECs, we suspect that the 2nm Al2O3 film was rapidly deteriorated in the high EC solution, which created a considerable number of artificial defects and caused the obvious
increase of the copper bump densities. Per this fact, even in a low EC solution we expect a significant increase of the bump densities after a long enough plating time due to the \( \text{Al}_2\text{O}_3 \) film deterioration. Before significant degradation to the \( \text{Al}_2\text{O}_3 \) film has occurred, though, we anticipate that the copper bump density be representative of the intrinsic defect densities for the ALD film. Figure 3.6 b shows the dependence of the copper bump density values on electroplating time ET with an EC value of 0.03mol/L. As expected, the bump densities distributed within an almost same density range \((89 \text{ cm}^{-2} \pm 3*18 \text{ cm}^{-2}.\) when the ET varied from 5 to 30 minutes. The two mean values and standard deviations were calculated independently using the data points in the corresponding low EC and EC ranges. The densities then increased about three orders of magnitude when the samples were plated for 60 minutes.

Figure 3. 7 SEM images of typical electroplated 2nm Al2O3 samples after (a) 5 minutes, (b) 10 min, (c) 30min, and (d) 60 min plating. The electrolyte concentration was 0.03mol/L for both CuSO4 and H2SO4.
The SEM images of the electroplated 2nm Al₂O₃ samples in Figure 3.7 reveals that from 5 minutes (a) to 30 minutes (c) the size of the copper bumps increases with time but there is no apparent change of the bump density. Figure 3.7 (d), however, shows that a larger number of copper bumps with a uniform size appear to have formed in the area between the large bumps after 60 minutes electroplating. The uniform size and distribution of the small bumps could be associated with electrical tunneling of the thinned Al₂O₃ film or weak points exposed due to the deterioration.

To verify the deterioration of the ALD Al₂O₃ films in the electrolytic solution, XPS and XRR analysis was conducted for samples exposed in the solution for different times with no voltage applied. Chemical composition analysis by XPS was conducted for the samples of 2nm Al₂O₃ on nickel substrate with a 15nm W layer. Three samples which underwent exposure in the 0.03mol/L electrolytic solution for 0, 30 and 60 minutes respectively were compared for characteristic Al 2s and W 4d peaks as shown in Figure 3.8 (a). The spectra of all the three samples showed both Al 2s and W 4d peaks at the corresponding binding energies, which indicated the existence of the Al₂O₃ film on top of the W layer even after a long time exposure. By comparing the peak areas of the Al 2s and W 4d peaks, Al₂O₃ film thinning in the electrolytic solution was identified by the decreasing Al/W ratio with the exposure time. To confirm this thinning effect, three Al₂O₃ film samples with original thicknesses of 31nm, 31nm, and 21nm were exposed in the solution for 30, 60 and 180 minutes respectively and the thickness changes were measured using XRR. A linear relation between the exposure time and the thickness reduction was obtained as shown in Figure 3.8 (b). From Figure 3.8 (b), the film thinning rate or the deterioration rate is about 0.12Å/minute. Although this deterioration rate is rather small for a short time exposure, long time exposure would considerably change the film thickness. For 60
minutes exposure, the Al$_2$O$_3$ film thickness reduction is about 7.2 Å, which is considered to be significant for the 2nm film.

Figure 3. 8 (a) XPS intensities of characteristic Al 2s and W 4d peaks of three samples of 2nm Al$_2$O$_3$ on 15nm W which underwent exposure in the 0.03mol/L electrolytic solution for 0, 30 and 60 minutes respectively; (b) XRR results for Al$_2$O$_3$ film thickness reduction as a function of exposure time in the 0.03mol/L electrolytic solution.

To summarize the above discussion, the defect density values of the 2nm Al$_2$O$_3$ characterized using the electroplating visualization technique were justified in a wide range of electroplating conditions, i.e. EC (0.01 to 0.2mol/L) and ET (5 to 30 minutes). In this range of conditions, the copper bump densities were independent of the electroplating conditions and represented the intrinsic defect densities in the Al$_2$O$_3$ films. High concentration of electrolyte (> 0.2 mol/L) and a long time of electroplating (> 30 minutes) can lead to a significant amount of artificial defects and defect density increase due to the deterioration of the Al$_2$O$_3$.

3.5.3 Effect of Substrate Surface Conditions on Defect Reduction

Now that the issues of film degradation due to the electroplating technique have been discussed, the effect of the substrate surface on defect of the ultra-thin ALD Al$_2$O$_3$ films will be examined. As shown in Figure 3.3, the W ALD buffer layer enhances the quality of the ultra-thin
ALD Al₂O₃ and lowers the defect density for the 2nm Al₂O₃ films by about three orders of magnitude. For such thin ALD films, the substrate surface is the most important factor determining the ALD nucleation and growth. ALD growth is determined by two processes: surface adsorption and surface diffusion [95]. The arriving reactant is first adsorbed on the surface in a weakly bound state through a process called physisorption. Surface diffusion process then allows the adsorbed species to find the most reactive sites and form a chemical bond with the surface. A facile nucleation of Al₂O₃ on W has been observed using Auger and quartz crystal microbalance [96, 97, 98]. A much higher mass gain of the first ALD Al₂O₃ cycle on the W surface was found than during the steady state growth. This facile nucleation was attributed to TMA dissociation on the W ALD surface. The dissociative species readily adsorbed on the surface and formed a chemical bond with the surface for nucleation. In addition, comparing with the Ni substrate the fluorine terminated ALD W may serve as an excellent surface with highly concentrated reactive surface sites for the ALD Al₂O₃ layer to nucleate and grow. The facile nucleation of Al₂O₃ on ALD W enhances a uniform layer-by-layer film growth at the initial stage and helps to form a continuous film and eliminate defects rapidly. A less efficient nucleation may need more AB cycles for randomly nucleated sites to grow together. For Al₂O₃ grown on the Ni substrates, a larger thickness of about 5nm is needed to obtain a film without a significant amount of defects as indicated in Figure 3.4. The defect densities finally become almost same for 10nm Al₂O₃ grown on both W and Ni substrates.

To further understand the cause of the defects associated with the thickness change, we applied focus ion beam (FIB) to cross section the copper bumps of the samples used for Figure 3.4 and exposed the location where it grew up from for analysis. Figure 3.9 (a) shows the typical cross section of the milled copper bumps grown on 2nm Al₂O₃ on the Ni substrate. The image
reveals that the bump growth is associated with a centric point defect. A close-up view of the centric defect in Figure 3.9 (b) clearly shows that the copper bump roots from an incomplete Al₂O₃ site with a diameter of around 200nm. This provides evidence explaining the significant amount of defects existing in the 2nm Al₂O₃ on the Ni substrate. At the same time, by analyzing the cross section of the bumps grown on 2nm Al₂O₃ on the 15nm ALD W layer, we found that the roots of the bumps always involve a particle at the substrate as shown in Figure 3.9 (c). This indicates 2nm is already thick enough to eliminate the pinhole defects for Al₂O₃ deposited on the 15nm ALD W layer because of efficient nucleation. Any remaining defects were shown to mainly be due to the substrate surface physical imperfections. Because of the less efficient nucleation of ALD Al₂O₃ on the Ni substrate, thicker films were needed to eliminate the aforementioned pinhole defects. When the film thickness increases to 10nm, the pinhole defects are all eliminated for both Al₂O₃ grown on the W layer and Ni substrate. The remaining defects are only related to the surface physical imperfections such as particle contamination. Defect densities then become statistically similar between the two substrate conditions since the substrates were cleaned in a same condition.

Figure 3.9 (a) A typical cross section image of the focus ion beam milled copper bumps grown on 2nm Al₂O₃ on the Ni substrate; (b) Close-up view of (a) at the location where the copper bump grew up from revealing an incomplete coverage site in the Al₂O₃ film due to less efficient nucleation; (c) Close-up view of a typical cross section image of the copper bumps grown on 2nm Al₂O₃ on the 15nm ALD W revealing particle contamination on the substrate.
According to the above discussion, there are both chemical and physical factors determining the perfection of the ALD films. At the initial growth stage, the defects in the film are mainly related to the substrate surface chemistry which determines the film nucleation and growth. The present results illustrate that the ultra-thin ALD quality is quite sensitive to the substrate material and the initial surface status. For these ultra-thin films, orders of magnitude reduction in the pinhole defect density can be achieved by appropriate substrate preparation. Once the film becomes continuous, though, the major film defects are associated with the physical conditions like particle contamination. Further growth may completely cover the particles, but the particles could be displaced later and still yield defects. In order to achieve superior ultra-thin ALD films without defects, we need to consider both the substrate surface material selection and its physical condition preparation. The substrate material and surface should promote the film nucleation. The surface should also be thoroughly cleaned and well-treated to eliminate particulate contamination.

3.5.4 Barrier Structure Consists of Ultra-Thin ALD Layers

From the above discussion, the ALD W buffer layer achieves > 1000X reduction of defect density for 2nm thick ALD Al₂O₃ and yields a reasonably low defect density. The ALD W buffer layer can represent an MLD organic layer since they follow the same self-limiting growth mechanism. The defect reduction enabled by the ALD W buffer layer demonstrated the feasibility to use 2nm-thick ALD Al₂O₃ films for barrier applications. For real application, a MLD layer would be used as the buffer layer to achieve low defect of the extremely thin ALD Al₂O₃ layers grown on it. Figure 3.10 shows this concept.
Based on the defect densities values shown in Figure 3.4, we can now predict the corresponding barrier performances in terms of lag time for the multilayer structure consisting of ALD/MLD layers with different thicknesses. Plug these values into Equation 3.1, we can obtain the lag times for different thicknesses as listed in Table 3.2. As shown in Table 3.2, using thinner ALD Al₂O₃ layers to formulate the multilayer structure can yield better barrier performance. Particularly, if we use 2nm thick layers, the barrier performance can be improved by about 7 times in comparison with 25nm ALD Al₂O₃. In addition, thinner thickness of the barrier layer will be beneficial for improvement of mechanical robustness. The mechanical robustness of ALD films will be studied and discussed in Chapter 4.
Table 3. 2 Barrier performance prediction for different ALD/MLD thicknesses

<table>
<thead>
<tr>
<th>ALD/MLD thickness</th>
<th>25 nm/15 nm</th>
<th>10 nm/10 nm</th>
<th>5 nm/5 nm</th>
<th>2 nm/2 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALD/MLD bilayers</td>
<td>4</td>
<td>8</td>
<td>16</td>
<td>40</td>
</tr>
<tr>
<td>Defect density / cm²</td>
<td>~35</td>
<td>~35</td>
<td>~57</td>
<td>~115</td>
</tr>
<tr>
<td>Lag time / yrs</td>
<td>0.25</td>
<td>0.52</td>
<td>0.89</td>
<td>1.80</td>
</tr>
<tr>
<td>Barrier performance improvement</td>
<td>-</td>
<td>2X</td>
<td>4X</td>
<td>7X</td>
</tr>
</tbody>
</table>

3.6 Chapter Summary

In this Chapter, we explored the possibility to use ultra-thin ALD Al₂O₃ barrier films and MLD organic sub-layers to formulate multilayer structured barrier films and improve the barrier performance. A theoretically analysis gave the tolerable defect densities for different thicknesses of ALD Al₂O₃ layers in order not to decrease the barrier performance. We then quantitatively characterized the defect densities of ultra-thin ALD Al₂O₃ films deposited on Ni substrates with and without an ALD W buffer layer using the electroplating defect visualization technique. The defect densities for 5nm and 10nm Al₂O₃ on both the Ni substrate and the Ni with a 15nm ALD W buffer layer are well below the tolerable defect densities. However, for 2nm Al₂O₃ on the Ni substrate, huge defect densities were obtained. In comparison, an ultra-low defect density around 90/cm² has been demonstrated for 2nm-thick Al₂O₃ grown on a 15nm ALD W buffer layer. This is more than three orders of magnitude defect density reduction when compared to the same thickness Al₂O₃ grown on the Ni substrates directly. The ALD W buffer layer can represent an MLD organic layer since they follow the same self-limiting growth mechanism. The defect reduction enabled by the ALD W buffer layer demonstrated the feasibility to use 2nm-thick ALD Al₂O₃ films for barrier applications. The corresponding barrier performance in terms of lag time for 2nm ALD/MLD formulated multilayer structure can be
improved by 7 times in comparison with the counterpart formulated by using 25nm ALD and 15nm MLD layers. The mechanical robustness can also be improved for thinner layers as we will demonstrate in next Chapter.
Chapter 4 ALD Film Mechanical Robustness and Real-Time Cracking Inspection

4.1 Introduction

Thin ALD Al$_2$O$_3$ films are brittle ceramic layers and prone to cracking under mechanical and environmental stress [53]. The mechanical robustness associated with film cracking of brittle inorganic layers is a major concern for barriers since the barrier protection is either significantly reduced or lost if the integrity of the film is broken, especially for flexible applications where the devices are designed to be used under bending, flexing, or rolling. Thus, there are significant interests in studying the mechanical failure, such as cracking, of the inorganic barrier films on polymer substrates. However, the film cracking characterization is not trivial on these nanoscale, transparent, and conformal thin films. The thickness of ALD Al$_2$O$_3$ films is only few nanometers to several tens of nanometers and the width of the crack opening could range from a few tens nanometers to less than 10nm depending on the film thickness [53], [83]. In addition, the crack could be in a “close” state which becomes difficult to detect, due to elastic recovery of the substrate after the sample is unloaded for ex-situ characterization [50], [61]. In-situ tests, where the material is maintained under stress, are needed to avoid inaccurate measurement of the crack onset strain [50]. The detection can become even more difficult when the barrier films are buried by protective layers or other functional layers. The use of a multilayer structure with organic/inorganic alternating layers also gives significant challenges in crack detection. In this Chapter, we developed a technique for in-situ inspection of cracking in barrier films, which is based on laser scanning confocal microscopy (LSCM) and can readily inspect film cracking either on surface or in buried structures. For the demonstration, we use ALD Al$_2$O$_3$ thin films on
the polyethylene naphthalate (PEN) substrate as a model system. A deflection-bending apparatus is conducted to strain the film for LSCM inspection of film cracking in real time. This LSCM-based technique is non-destructive and does not require sample pretreatment. It also enables rapid and large-area inspections.

4.2 Background

Thin inorganic films deposited on plastic substrates are used in a wide range of applications. The composite configuration, which combines the flexibility of plastic materials with the functionalities of the inorganic films, offers a number of advantages over the pure bulk materials, such as light-weight, tailored optical and/or mechanical properties, design freedom, and cost-effectiveness [50]. One important example is gas/moisture diffusion barriers. Depositing thin oxide or nitride films onto plastics leads to a significantly reduced gas/moisture permeability while maintaining a light-weight and flexible substrate. Typical thin film barriers on polymers are single layer films of oxides and nitrides, such as SiOx, SiNx, AlOx, that are deposited using thermal or electron beam evaporation, sputtering and reactive magnetron sputtering, chemical vapor deposition and plasma enhanced chemical vapor deposition [15-17], [50]. Recently, atomic layer deposition (ALD) has been proposed as an alternative approach to produce extremely thin barrier films due to its low defect density and low temperature process [19-23], [29-32]. Due to the saturation of barrier performance with film thickness for single layer ALD Al2O3, ALD Al2O3/SiO2 multilayer structures were developed to improve the barrier performance [24]. However, it is found that WVTR reached lowest value when used two Al2O3/SiO2 bilayers and adding more bilayers decreased the barrier performance, which lead to the concern for ALD film cracking.
Figure 4.1 An example of cracking of ALD Al₂O₃/SiO₂ multilayers encapsulated thermal ground plane test vehicle under 100°C.

To improve the cracking resistance of the ALD films, molecular layer deposition (MLD) has been used to create polymer-like films to be interposed between ALD inorganic layers. The polymer-like films may mechanically decouple the inorganic layers, thereby increasing the critical strain associated with film cracking. However, the recent study demonstrates that the “Alucone” based MLD films themselves are brittle and the critical strain increase is either limited or reversed [53]. New MLD materials with better cracking resistance are under development. To understand the mechanical robustness of ALD and MLD films, tensile test has been used to characterize this thin film materials system. Usually, a special sample treatment step, such as oxygen plasma undercutting [51], [61] and fluorescent tagging (as we demonstrated in Chapter 2), is utilized to highlight the cracks for microscopy observation. As an example, Figure 4.1 shows the cracking, highlighted by plasma undercutting, of Al₂O₃/SiO₂ multilayers
encapsulated thermal ground plane test vehicle under 100 °C. However, those techniques are either destructive, like plasma undercutting, or limited by the material properties of the film/substrate, like fluorescent tagging. More importantly, they are difficult to be applied for in-situ characterization of the film cracking in buried layer structures. Other considerations such as rapid and large-area crack inspection are also desired for various characterization needs.

4.3 Methods

4.3.1 LSCM-Based Inspection

Figure 4.2 shows schematically the principle of the LSCM-based crack inspection. As shown in the figure, the sample is configured as a thin film coated on polymer substrates with or without a polymer-based cover-coat on top. Coherent laser light passes through a pinhole and is focused to form a scanning point on the sample. The reflected light from the sample is re-focused to a pinhole aperture in front of the photo detector. The photo detector which is behind the pinhole aperture measures the intensity of the light passing through the pinhole. Each time, only the light coming from a slice of layer in the sample which is positioned at the focal plane of the objective is confocal with the pinhole aperture and can pass the pinhole to form the image. The light reflected from the points above and below the focal plane is not confocal with the pinhole aperture and most of the intensity is blocked by the pinhole. Therefore, at each Z position only a slice of layer in the sample is imaged by the scanning. The thickness of the slice is controlled by the size of the pinhole aperture. Now, if the thin film layer is positioned at the focal plane and cracks are generated in this layer, the incident light will be scattered by the geometric change of the crack sites when the laser probe reaches the cracks. Since the scattered light has different phase from the reflected light from the surrounding area, it will be blocked by the pinhole and
form an intensity dip at the detector. When the intensity dip exceeds a preset threshold, it is imaged as a crack. In Figure 4.2, as an example, three images are taken at the layer of the cover-coat, the thin film, and the substrate, respectively. The film cracks are captured in the thin film layer as marked with arrows in image 2, in which each arrow corresponds to a channel crack in the field. Figure 4.3 shows an example of the intensity dip triggered by a crack.

Figure 4. 2 Schematics of the crack inspection principle using laser scanning confocal microscopy.

LSCM allows continuous inspection through moving the stage continuously in x-y plane. The efficiency of the inspection is determined by the objective and the scanning parameters. Table 4.1 gives the available objectives and the corresponding scanning parameters. The
objective with higher numerical aperture (NA) possesses higher resolving power but smaller field size in each scan. Scan speed up to 5 frames per second can be achieved with the default image setting of 512×512 pixel. The zoom for full resolving power is a software-controlled setting to avoid loss of information during the scanning based on Nyquist theorem [95]. In this study, Carl Zeiss LSM 510 equipped with a HeNe laser source (λ:458nm) is used and a 63x objective with oil immersion and numerical aperture (NA) of 1.4 is chosen for the inspection. The objective has a field size of 0.14mm × 0.14mm for each scan.

Figure 4. 3 Example of the intensity dip triggered by a crack.

<table>
<thead>
<tr>
<th>Table 4. 1 LSCM objectives and scanning parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Objective</strong></td>
</tr>
<tr>
<td>NA</td>
</tr>
<tr>
<td>Field size(mm) per scan</td>
</tr>
<tr>
<td>Scan speed (512 x 512 pixel)</td>
</tr>
<tr>
<td>Zoom for full resolving power (512 x 512 pixel)</td>
</tr>
</tbody>
</table>
4.3.2 Deflection Bending

To enable in-situ LSCM inspection of film cracking, a deflection bending apparatus has been developed in this study for straining the thin film coated on flexible substrates. To simulate the cracking of the thin films in real applications under such mechanical stress as bending, flexing, or rolling, the most direct and appropriate evaluation is bending the sample to a given radius of curvature $R$ [47], [60-62]. In-situ inspection of the film cracking is conducted using LSCM while the sample is under bending.

![Deflection bending apparatus and crack measurement locations](image)

Figure 4.4 Deflection bending apparatus and crack measurement locations for in-situ inspection of film cracking.

As shown in Figure 4.4, a fixture with two parallel plates is designed to clamp the sample. The distance between the two plates is controlled and adjusted by a screw bolt. By reducing the distance between the two plates, axial displacement of the sample can be induced.
The axial displacement causes the sample to deflect with a continuous change of radius. The sample reaches the maximum strain in the middle of the two plates at the convex side. The crack generation is inspected at the maximum strain across the width of the sample at three different locations as shown in Figure 4.4. For each location, the crack density is counted within the 0.14mm × 0.14mm field size. Figure 4.5 shows an example of cracking at the three locations of 40nm ALD Al₂O₃ film on PEN strained to 2.5%.

Figure 4.5 Example of cracking at three locations across the width of the sample strained to 2.5%

An analytical solution can be derived to describe this deflection bending [62], [99]. If the sample is mounted in relax and flat status onto the plates with an original distance of L. The axial displacement of the sample δa, induced film deflection δd, and radius of curvature R can be calculated using the equations below

\[
\delta_d = \frac{\eta \cdot L}{K(\eta)} \tag{4.1}
\]

\[
\delta_a = 2L[1 - \frac{E(\eta)}{K(\eta)}] \tag{4.2}
\]

\[
R = \frac{L}{8\eta \cdot K(\eta)} \tag{4.3}
\]
in which $K(\eta)$ and $E(\eta)$ are the first and second kind complete elliptic integrals [99]. The axial displacement $\delta a$ shown above is a parameter which is under control and adjustment while the other parameters can be calculated accordingly.

![Figure 4.6](image)

**Figure 4.6** Comparison between the analytical solution and the measurement of the deflection as a function of the displacement for a PEN strip.

Before the test, we verified the accuracy of the analytical solution with the experiment data in order to evaluate the possible calculation errors which could cause the errors in the film property characterization. We compare the values of the analytic solution and the experiment measurement of $\delta d$ as a function of $\delta a$ for a 200µm-thick PEN strip with $L$ of 40mm and a width of 10mm when they are under bending. As shown in Figure 4.6, the error between the
analytical solution and the measurement data is below 6% even for a large displacement.

4.3.3 ALD Sample Preparation

$\text{Al}_2\text{O}_3$ thin films with a thickness of 5, 12.5, 20 and 40 nm are deposited on 200μm PEN substrates (Teonex Q65, Dupont Teijin, Inc) using atomic-layer-deposition. The ALD $\text{Al}_2\text{O}_3$ is achieved using sequential, alternating exposures to trimethylaluminum (TMA) (97%, Sigma-Aldrich) and H2O (HPLC-grade, Fisher). In the deposition process, TMA and H2O are alternately injected via nitrogen carrier gas using computer-controlled pneumatic valves. The TMA and H2O yield ALD $\text{Al}_2\text{O}_3$ according to the following binary self-limiting reactions [31]

(A)  $\text{Al-OH}^* + \text{Al(CH}_3\text{)}_3 \rightarrow \text{Al-O-Al(CH}_3\text{)}_2^* + \text{CH}_4$  \hspace{1cm} (1)

(B)  $\text{Al-CH}_3^* + \text{H}_2\text{O} \rightarrow \text{Al-OH}^* + \text{CH}_4$  \hspace{1cm} (2)

where asterisks represent the surface species. The dose time of 1 and 0.2 s are used for TMA and H2O respectively at the injection pressure of 300 mTorr. Dosing is followed by purging with ultrahigh purity N2 at the injection pressure of 300 mTorr for 75 s. The growth temperature of 155 °C and baseline chamber pressure of 650 mTorr are used for all the depositions. After the ALD deposition, the film samples are cut into 45mm×10mm strips (with the effective distance L of 40mm) using paper cutter for deflection bending and in-situ inspection.

4.4 In-Situ Inspection of ALD Cracking

4.4.1 Channel Cracking of Single Layer Films

Figure 4.7 shows the results of the crack density as a function of the bending radius R (a) and bending strain (b) of the ALD $\text{Al}_2\text{O}_3$ films on PEN with thickness of 5, 12.5, 20 and 40nm, respectively. The data points are connected with lines for each thickness to guide the reading.
Figure 4.7 Crack densities as a function of the bending radius of curvature (a) and bending strain (b) of ALD Al$_2$O$_3$ films coated on PEN substrate.

In Fig. 4.7 (a), the crack density increases with reducing $R$ for all the thicknesses. The crack density should then gradually become saturated with further reducing $R$ [53]. For thinner films, the cracking onset radius $R_c$ shifts to a smaller value but final crack density becomes higher. We note that due to the limit of our deflection bending apparatus, the test stops at $R=4$ mm in this study. Further reducing the bending radius could lead to the contact of the two sides of the curved sample. According to Ref. [53], the crack density of ALD Al$_2$O$_3$ films should vary with strain depending on the distribution of defects in the film rather than the interaction between closely separated cracks, since the crack saturation spacing is significantly greater than the film thickness. This may explain that a higher saturated crack density is found in thinner films, which is consistent with a higher defect density as we discussed in Chapter 3. The cracking onset radius $R_c$, however, depends only on the intrinsic properties of the material system and the film thickness.

To better understand the mechanical robustness of ALD films, we transform the radius of curvature to strain as shown in Figure 4.7 (b). For thin film coated a polymer substrate, the film strain under bending can be determined from the radius of curvature $R$ using Eq. (4.4) [100]
where \( t_f \) and \( t_s \) are the thickness of the film and the substrate, respectively. The ALD film thickness is negligible comparing to the substrate. Figure 4.7 (b) shows a substantial increase of crack onset strain \( \varepsilon_c \) when decreasing ALD thickness. The \( \varepsilon_c \) increases by three times from 0.5% to 1.47% when the thickness decreases from 40nm to 5nm. More importantly, the crack onset strain measured using this in-situ technique is much lower than the previous reported values using ex-situ fluorescent tagging technique [53]. The measurement using fluorescent tagging shows the crack onset strain of 5nm ALD is \(~5\%\). This significant difference tells that one of the techniques could be inappropriate and yield invalid results. For the ex-situ fluorescent tagging technique, the sample is first stretched to a certain strain value and then released, followed by fluorescent tagging treatment, and then crack visualization using fluorescent microscope. Since the treatment and crack detection are carried out under a strain-released state, any cracks initiated could “close” to a state that is not detectable due to the elastic recovery of the substrate. Therefore, the crack onset strain could be overestimated in the ex-situ fluorescent tagging characterization.

4.4.2 Cyclic Loading Test and Sensitivity of the Inspection

A cyclic loading test can show the process of the crack opening change and the sensitivity of the LSCM for crack inspection. Figure 4.8 shows the cyclic loading test of 5nm and 20nm ALD Al\(_2\)O\(_3\) on PEN substrate. The sample with 20nm ALD film on PEN substrate is bent first to a strain at 1.14%, which is slightly above the crack onset strain and is then unloaded. The crack density increases with loading, when unloading the crack density keeps unchanged at first and then decreases to zero at the fully released state. The decrease of the crack densities
during the unloading process indicates the “close-up” process of the crack openings due to the elastic recovery of the substrate. Consequently, these cracks become undetectable in a “close” state. However, only a slight decrease of the crack density is observed instead of dropping to zero when unloading the 20nm ALD film that is strained to 1.56%. It indicates that after releasing, most of the cracks keep a detectable state for the LSCM inspection, though some “close” to below the detectable size.

Figure 4. 8 Crack density change during cyclic loading test of ALD Al₂O₃ film on PEN. The insets are the width of the crack opening measured using SEM at a strain of 0.88% and 0%, respectively, when unloading 5nm ALD Al₂O₃ films on PEN.

We use SEM to track the width change of the crack opening during the releasing. The insets show the crack opening width measured at a strain at 0.88% and 0% respectively using SEM.
The width measured at the fully released state indicates that the crack opening as small as ~10nm can be inspected using this LCSM based technique. The cracks completely disappear for the 5nm ALD sample released from a same strained level, which can be partly attributed to the worse contrast of the cracks in 5nm ALD for the inspection. In addition, according to Ref. [53], the displacement of the crack opening is thickness dependent. Under the same conditions, the smaller thickness yields smaller displacement of the crack opening. This explains why the crack density of 5nm ALD drops to zero but not for 20nm ALD after completely releasing the load.

![Figure 4.9](image)

Figure 4. 9 (a) Intensity dips and the corresponding detection contrast values produced by the cracks on 5nm ALD Al₂O₃ films at different strain levels; (b) Detection contrast of cracks for ALD Al₂O₃ films with different thicknesses at different strain levels.

Figure 4.9 shows the detection contrast of cracks on 5nm ALD films when released from a bending strain at 2.5%. The detection contrast of the crack is taken to be the absolute value of the difference between the maximum intensity tip produced by the crack and the average background signal, normalized by the average background signal, or \( C = |I_{\text{crack}} - I_{\text{background}}| / I_{\text{background}} \). Fig. 4.9 (a) shows the intensity dips produced by the cracks at a strain of 2.5%, 1.67%, 0.71%, and 0%, respectively, and the corresponding contrast values marked beside the tips. The intensity
data points are directly read from the pixels across the crack images while the lines are Gaussian fit of the data points for each strain. The sample surface noise level is around 3% as marked by the dot line. When the sample is completely released, the crack contrast of 2.5% is below the surface noise level 3% and the cracks cannot be inspected facilely.

Figure 4.9 (b) shows the dependence of the detection contrast of cracks on ALD film thickness. Clearly, the detection contrast of cracks is dependent on thickness and it becomes worse for thinner films. A worse contrast will pose challenge for crack inspection of ultra-thin ALD films. Contrast enhancement technique can potentially be applied to mitigate this problem, for example, by depositing a high reflective coating such as Au on top of the ALD films, which is out of the scope of this study though. We also note that the extra coating could change the property of the thin ALD films and add complexity to the analysis of the composite films.

4.4.3 Channel Cracking of Buried ALD Films

In practical applications, thin inorganic barrier layers are often coated by some polymer based hard-coat or protective layer to prevent mechanical damage and improve barrier performance. In addition, multilayer films with organic/inorganic alternating layers have been used to achieve ultra-high barrier performance for OLED application. To test the usefulness of the technique described in this paper for the in-situ inspection of ALD layer cracking in buried structures, epoxy-based SU8 is spin-coated onto the 40nm ALD Al₂O₃ films, which is on a 125 μm PEN substrate. Three different thicknesses of 20, 90, 140μm of the SU8 layers are used. The cured samples are inspected as they are bent continuously to reduced radii. Figure 4.10 shows the crack density as a function of the bending radius of the uncoated and coated ALD films. The data show that the crack onset occurs at a smaller radius for thicker SU8 layer. Particularly, the crack onset radius shifts from 14.1mm to 8.8mm, 6.4mm, and even less than
4mm, when the ALD film is coated with SU8 for a thickness of 20, 90, and 140µm, respectively. The SU8 layer breaks at the radius of 4mm for the 140µm SU8 layer coated case, while the buried ALD film remains intact.

![Crack densities as a function of the bending radius for 40nm ALD Al₂O₃ film and the films coated by SU8 layers.](image)

Figure 4. 10 Crack densities as a function of the bending radius for 40nm ALD Al₂O₃ film and the films coated by SU8 layers.

It has been reported that a polymer cover-coat can improve the mechanical ruggedness of the brittle inorganic layer by passivating its mechanical flaws [16,61]. More effectively, the SU8 cover-coat can, in principle, shift the so-called neutral plane where the strain equals zero closer to the ALD film, therefore decreasing the strain experienced by the ALD film in bending
[100]. As shown in Figure 4.11, when the cover-coat layer and the substrate satisfy Equation (4.5) [100],

\[ E_c \cdot t_c^2 = E_s \cdot t_s^2 \]  

(4.5)

the ALD film comes to lie in the neutral plane. Where Ec, Es, tc, ts are the modulus and thickness of the cover coat and the substrate respectively. In this case, the bending does not add any strain to the ALD film and therefore the bending radius of curvature is not limited by the critical strain. Theoretically, a flexible barrier which can be bent to extremely small radii can be achieved by choice of appropriate cover-coat material with right thickness.

![Diagram showing tensile and compressive strain](image)

**Zero strain at the film when:**

\[ E_s t_s^2 = E_c t_c^2 \]  

Suo et al., 1999

Figure 4.11 Schematics of the principle using cover-coat to shift the neutral plane where the strain equals zero to the ALD film.

4.5 Merits of the LSCM Based Optical Inspection

4.5.1 Versatility

This LSCM-based optical inspection technique is versatile, which can be used for a
variety of films and substrates, since the crack imaging is based on the signal intensity change caused by the geometric change at the crack sites and not determined by the film/substrate materials type. We have also utilized this technique for ALD Al2O3 deposited on Kapton and molecular layer deposited alucone organic layers on PEN and the film cracking has been readily inspected for different material systems. However, the signal intensity can be influenced by the optical properties, such as the refractive index, of the film/substrate materials. The cover-coat layers have to be transparent or semi-transparent to the laser probe for inspection of buried thin film structures. The contrast of the crack image can be enhanced by sputtering a thin layer of Au coating on top of the ALD Al2O3 films due to the enhanced reflectivity of the laser beam on the neighboring area of the cracks.

4.5.2 In-situ Characteristics

Comparing with the previously reported ex-situ characterization techniques, the LSCM-based in-situ inspection technique captures the film cracking process with the sample strained continuously and avoids the inaccurate measurement of the crack onset strain associated with the crack “close-up” phenomenon. The efficiency of this in-situ technique is also much higher since no sample treatment required and the mechanical deformation and the crack detection are conducted simultaneously. In addition, the technique needs only one sample to cover a wide range of strain values while the ex-situ destructive characterization often uses many samples for different strain values.

4.5.3 Resolution

Here we consider the resolution for the LSCM-based optical inspection in both lateral and axial directions. The lateral resolution is the same as the normal wide-field optical
microscopy and the axial resolution describes how small the slice thickness in the Z axial
direction can be differentiated. The resolutions in both directions depend on the pinhole aperture
setting of the microscopy, the laser probe wavelength, NA of the objectives, and the refractive
index of the immersion liquid. For confocal microscopy, the best resolution is ~180nm for lateral
and ~500nm for axial direction [95]. We also note the difference between the resolution and the
detection sensitivity. In section 4.4.2, we demonstrate that the crack opening width as small as
~10nm can be inspected by the LSCM technique. This only means this technique would have
~10nm size crack sensitivity. But, the size of the crack could still correspond to hundreds of
nanometers in the image coordinate system.

The axial resolution is an important consideration for inspection of multilayer thin film
barrier structures. Different cracking modes could happen in one individual inorganic layer, or, in
two or more layers simultaneously depending on the materials properties and layer thickness [52].
Using this technique we could detect the cracking modes and cracking onset in the multilayer
structures. However, in order to differentiate the cracking happened at different inorganic layers,
the two neighboring layers have to be separated by the organic layer with a thickness larger than
the axial resolution (~500nm). To further improve the axial resolution is a forefront of the optical
microscopy development for various applications. There are several techniques have been
developed to achieve this goal. For example, the axial resolution can be improved to roughly
100nm by 4Pi and I^5M microscopy [101]. Further improvement to 50~60 nm has been reported
by using stochastic optical reconstruction microscopy [102], and to 20~50 nm using stimulated
emission depletion microscopy [103], [104]. Although these topics are out of the scope of the
current study, they could be the future considerations for performance improvement of the
inspection for multilayer structures.
4.6 Chapter Summary

In this chapter, an optical inspection technique using laser scanning confocal microscopy has been developed for the inspection of mechanical cracking in thin films on flexible substrates. This study demonstrates the in-situ inspection of cracking in atomic-layer-deposition thin films both on surface and in buried layer structures. To achieve in-situ inspection, a deflection-bending test apparatus is conducted to strain the sample continuously while the film cracking is inspected in real-time by the LSCM. This in-situ inspection avoids the inaccurate measurement of the crack onset strain associated with the crack “close-up” phenomenon as demonstrated in this study. SU8 cover-coat is applied to form a buried ALD layer structure and the in-situ inspection demonstrates the ALD film cracking in real-time underneath the cover-coat. This technique is nondestructive and versatile for a variety of film/substrate material systems. It allows rapid and large-area inspection without any special requirement for sample pretreatment. This technique is expected to be important for mechanical evaluation and design of reliable barrier films and other functional films used in macro-electronics.

Using this LSCM-based inspection technique, we demonstrated the critical strains of ALD Al₂O₃ as a function of thicknesses under bending. We also demonstrated to use cover-coat to improve the mechanical reliability of ALD Al₂O₃ for flexible encapsulation applications. Table 4.2 summarizes the approaches to improve the mechanical reliability of ALD barrier films under bending. These approaches can be categorized into internal type and external type. The internal type is to improve the mechanical robustness of the films while external type reduces the stress/strain at the film under bending. The first two approaches are internal type. By reducing the film thickness we demonstrated that, for example from 40nm to 5nm, the critical strain can
be improved by ~3×. Using ALD/MLD multilayer structure, the improvement is about 1.5× by theoretical analysis. The approaches using protective coat or cover coat and changing the substrate properties belong to external type. Using cover-coat we demonstrated more than 3.5× reduction of radius curvature without cracking the ALD films. And, the selection of thinner substrate with higher modulus can further reduce the stress/strain at the film when it is under bending. To develop robust ALD barrier coatings, we need to consider all these approaches to achieve optimum mechanical performance in addition to the barrier performance as discussed in Chapter 3.

Table 4.2 Approaches to improve the mechanical reliability of ALD barrier films under bending

<table>
<thead>
<tr>
<th>Approach</th>
<th>Type</th>
<th>Improvement</th>
<th>Demonstration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness Reduction</td>
<td>Internal</td>
<td>~3X Critical Strain (40nm to 5nm)</td>
<td>Experiment</td>
</tr>
<tr>
<td>ALD/MLD Multilayer Structure a</td>
<td>Internal</td>
<td>~1.5X critical strain</td>
<td>Theoretical analysis</td>
</tr>
<tr>
<td>Protective coat</td>
<td>External</td>
<td>&gt;3.5X radius curvature (40nm ALD)</td>
<td>Experiment</td>
</tr>
<tr>
<td>Substrate</td>
<td>External</td>
<td>Thinner substrate with higher modulus reduces the stress/strain at the film</td>
<td>Theoretical analysis</td>
</tr>
</tbody>
</table>

* David Miller et al, 2009
Chapter 5 Design and Fabrication of Sensors for MEMS Packaging Study

5.1 Introduction

In this Chapter, we will design and fabricate a MEMS sensor for the study of critical issues for MEMS packaging. The fundamental problems and development of MEMS packaging were already reviewed in Chapter 1. Using ALD thin film barriers to provide hermetic sealing is a potential solution for polymer packaging of MEMS. However, there are no standards to test hermeticity of a MEMS package with extremely small cavity volume. A typical test is to integrate a MEMS sensor or device inside the package and monitor the device performance. The commonly used sensors include inertial sensors and resonators, humidity/dew point sensors, and pirani gauges. In this project, we use a pirani gauge to study the feasibility of ALD enabled hermetic polymer packaging. The pirani gauge’s thermal conductance is very sensitive to the vacuum level. A major wafer level polymer packaging process is developed to integrate this pirani gauge into a vacuum package. This Chapter will focus on the design, fabrication, and test of the pirani gauge. Next Chapter will discuss the development of wafer level polymer packaging process and the test results for ALD-sealed polymer packages.

5.2 Background

A standard approach for hermetic test of electronic packages is to use helium gas for leak test. This approach is described in detail by the military-standard-883 [105]. Here, we give a brief introduction. This test consists of perfluorinated gross leak and helium fine leak. For helium fine leak, the package samples are placed in a pressure chamber and subjected to Helium for a period of time. After the conditioning time has elapsed, the samples are removed from the chamber and tested on a Helium leak detector. The leak detector is basically a mass spectrometer
tuned for helium that will measure the helium leak rate of the samples. All samples are tested within 1 hour after its removal from the pressure chamber. The operational range for helium fine leak is $10^{-6}$ to $10^{-10}$ atm-cc/sec. For perfluorinated gross leak, after the samples have finished fine leak testing, the samples are placed in a beaker and subjected to gross leak. The beaker is placed in a pressure chamber with an intro tube in the beaker. The tube leads from a valve on the outside of the chamber. A vacuum is drawn on the chamber for 5 hours. After the vacuum time has elapsed, a perfluorinated fluid with a boiling point of approx. 85°C is introduced to the internal beaker through the intro valve without breaking the vacuum. The fluid covers the samples in the internal beaker. The beaker is then is subjected to nitrogen gas for a certain duration. After the pressurization time has elapsed, the beaker is removed from the chamber keeping the samples submerged in the fluid. Each sample is placed in a tank of a different perfluorinated fluid with a boiling point of approximately 155°C. The tank temp is regulated at 125°C for these samples. Each sample is held in the hot fluid for a minimum of 30 seconds. Bubbles emanating from the seal area are considered failures. No bubbles are considered passing. The theory is if you have an ingress pathway to the internal cavity, the low boiling point fluid will be forced in during the conditioning phase of the test. When these samples are submerged in the hot tank, the low boiling point fluid will boil and the bubble stream will indicate the leak site. The operational range for perfluorinated gross leak is $10^{-1}$ to $10^{-5}$ atm-cc/sec. This helium leak based test approach is limited by the resolution of the helium gas measurement using mass spectroscopy and the package volume. The resolution of the helium measurement is $10^{-12}$ atm-cc/sec or worse. The package volume limit is $10^{-3}$ cc and most MEMS package is below this volume limit. So helium test does not apply for MEMS packages with small volumes and extremely low leak rate.

There are many approaches developed for a hermetic test of MEMS packages, some
notable ones including optical deflection test [11], [106], residue gas analysis [107], and enclosed sensor in-situ test [3-6], [9], [12-14]. In the optical deflection test, the package sample is placed in a pressurized test chamber with pressure control. The pressure difference between the environment and inside the package causes the deflection of the package lid. And the deflection can be captured by using an interferometer or an optical profilometer with nanometer resolution. Combining the pressure measurements, the lid stiffness and deflection change, the leak rate of the package can be calculated. Residue gas analysis involves crushing the package sample in a vacuum chamber and sampling the residue gas using a residue gas analyzer. This approach does not directly measure the leak rate of the package. It measures the residue gas inside the package and the initial gas pressure and a capability of sampling of 30 nano liter interval volume was reported.

To enclose a MEMS sensor inside the package and monitor the pressure or humidity change is the most direct way for an in-situ leak test. The Q factors of many MEMS devices such as inertial sensors and resonators are very sensitive to pressure change [3], [4], [6]. Humidity sensors and dew point sensors are used to monitor the humidity change inside a package by measuring capacitance change of the sensors [108]. Pirani gauges are another type of sensors which responds to pressure change with varying thermal conductance or fractional resistance [109-111]. Pirani gauges are easy to calibrate and test and generally have higher sensitivity for pressure as compared with inertial sensors and resonators [109]. In this project, we choose the pirani gauge to develop the test vehicle for hermetic performance test of ALD-sealed polymer packages.
5.3 Pirani Gauge Design and Fabrication

5.3.1 Design and Analysis

Figure 5.1 shows the design of the pirani gauge in this project, which is a suspended poly-silicon micro-ladder structure. The basic idea for the pirani gauge to sense pressure change is that the gauge thermal conductance changes with the pressure. Passing a current I through this structure leads to a temperature increase and the corresponding increased resistance. The heat generated gets dissipated through both the anchors of the poly-silicon structure and the air gap between the structure and the substrate. The portion of heat dissipated through the air gap decreases with reducing air pressure and results in a higher temperature of the pirani gauge. This temperature rise can be tested by measuring the resistance increase of the sensor. With a calibration curve correlating the resistance and vacuum level, the pressure change is monitored.

There are three different pressure regions to which the pirani gauge responds. At a relatively high pressure, the mean free path of air molecules is much smaller than the gap between the suspended structure and the substrate. When the pressure changes, there is a very small change of the heat getting dissipated through the air gap and therefore small change of the thermal conductance of the sensor as measured by the resistance change. In this pressure range, a small air gap would increase the sensor’s sensitivity.

At an intermediate pressure range, the mean free path is comparable to the air gap, the heat transferred by the air molecules is proportional to the molecule density; a high sensitivity of the sensor is demonstrated. When the pressure becomes very low, the mean free path is much larger than the air gap. The pressure change in this region does not apparently change the thermal conductance of the sensor, and most of the heat is dissipated through the anchors of the sensor to the substrate. Like the first region, the sensitivity is reduced. To increase the sensitivity in this
pressure range, a longer beam length with a slender structure having a larger surface is required to increase the interaction area between the air molecules and the sensor surface. A detailed description of the principle of pirani gauges is presented in [109-111].

Figure 5.1 Design of pirani gauge for fabrication using polymumps process

The pirani gauge design is a micro ladder structure suspended above the substrate. The dimension of the structure is shown in Figure 5.1. This design is based on a standard PolyMumps process and consists of a two-layer polysilicon structure. The suspended structure is created by releasing the sacrificial oxide right below the poly1 layer. The gap between the poly1 structure and the substrate is 2.5 µm defined by the thickness of the sacrificial oxide layer. The fabrication process will be described in Section 5.3.2. For different sensing ranges, two beam lengths of 250 µm and 500 µm are designed. An analytic model [109], [112] is used to understand the operation and the sensing ranges of the designs. In this model, the temperature distribution along the suspended beam can be predicted according to the steady-state heat transfer Equation 5.1

\[
\delta = \frac{\partial^2 T}{\partial x^2} - \varepsilon T
\]

, where \(\delta\) is the ohmic power generation; \(\varepsilon\) is the heat loss; \(T\) is the temperature along the beam;
and x is the position from 0 to L. It was assumed that the temperature at the anchors, i.e. x = 0 and L equals to the room temperature $T_0$. This is an accurate assumption if the heat is sunk efficiently from the beam to the substrate. With this boundary condition, the resistance $R_p$ as a function of ambient pressure $P$ can be solved and expressed by Equation 5.2

$$R_p = R_0[1 + \frac{\delta \varepsilon}{\varepsilon}(1 - \frac{\tanh(\sqrt{\varepsilon} \frac{L}{2})}{\sqrt{\varepsilon} \frac{L}{2}})]$$

(5.2)

, where

$$\delta = \frac{I^2 R_0}{k_b w l t}$$

(5.3)

$$\varepsilon = (\frac{\eta k_g(P)}{k_b g t} - \delta \xi)$$

(5.4)

, where w, l, t are the width, length, and thickness of the beam and in this case, the values are 5 $\mu$m, 250 $\mu$m (or 500 $\mu$m), and 2 $\mu$m, respectively. $g$ is the air gap between the beam and the substrate which is 2.5 $\mu$m in this case. $\eta$ is a correction factor considering the fringing heat flux through the gap. $\zeta$ is the thermal coefficient of resistance (TCR) of the beam. $k_b$ and $k_g$ are the thermal conductivities of the beam and the ambient gas. For highly phosphorous-doped polysilicon, the $k_b$ was measured to be 14.2 W·m$^{-1}$·K$^{-1}$[109]. $k_g$ is pressure dependent and can be calculated using Equation 5.5 [112]. A complete explanation of the theory and derivation of the expressions can be referred to [112].

$$k_g(P) = \frac{0.0249 P}{99.5 + P}$$

(5.5)

Figure 5.2 shows the modeling results for the operational curves of the two beam designs with a 4mA probe current. The fractional resistance change is the resistance change divided by the resistance at atmospheric pressure, which is proportional to the average
temperature change of the beam as expressed by Equation 5.6.

\[ FRC = \frac{R_p - R_a}{R_a} = \xi \Delta T \]  

(5.6)

The 500 μm beam has higher pressure sensitivity due to its length. The 250 μm beam has a sensing range from ~0.1 Torr to atmospheric pressure while the 500 μm beam covers a range from ~0.03 Torr to atmospheric pressure according to the modeling. In this project, the requirement for sensing range of vacuum packaging is from 1 Torr to atmospheric pressure. This requirement is defined by the 1 Torr pressure in a typical ALD reactor. The polymer package will be evacuated in a vacuum chamber to around 1 Torr and then sealed with ALD alumina coating for leak test. The packaging process will be discussed in the next Chapter.

Figure 5.2 Modeling results of the operational curves of two beam designs
5.3.2 Designs for Different Packaging Schemes

CoventorWare is used to design the sensors. As shown in Figure 5.3, two wafer-level polymer packaging schemes will be developed and studied in this project. For the packaging scheme I, an extra poly-cap with release holes will be fabricated to enclose the sensor during the sensor fabrication. After release of the sensor, a polymer encapsulant such as BCB cyclotene will be spin coated to encapsulate the whole structure and seal the release and feed-through holes. Due to the high viscosity of the encapsulant, it will not wick into the package through the release holes. After curing the encapsulant, ALD coating is applied to hermetically sealing the package. The scheme II is based on PerMX3000, an epoxy based permanent dry film provided by Du Pont. The dry film is photo-definable and can be applied onto the device wafer by lamination. A polymer package will be fabricated using the dry film to enclose the pirani gauge sensor. The package will then be hermetically sealed by ALD. The packaging processing for the two schemes will be discussed in next Chapter.

![Diagram showing two packaging schemes for pirani gauge sensors.](image)

Figure 5.3 Two packaging schemes for pirani gauge
5.3.3 Fabrication

The pirani gauge sensors are fabricated using Multi-User MEMS Processes (MUMPs), which is provided by MEMSCAP and widely used to fabricate MEMS devices. There are three standard processes of MUMPs: PolyMUMPs, MetalMUMPs, and SOIMUMPs. PolyMUMPs is the one to be used in this project. As shown in Figure 5.4, PolyMUMPs is a three-layer polysilicon micromachining process consisting of 7 physical layers and 8 lithography levels. After the fabrication, the wafer is diced into 2mm × 2mm small chips, each chip having one pirani sensor on it. The sensor is released by dipping into 48% HF for 2 min to remove the sacrificial oxide. The sensor is then soaked in methanol before transferring it to critical point dryer (CPD). CPD uses liquid CO\(_2\) to flush out methanol and the remained CO\(_2\) keeps in liquid state at low temperature in a pressurized chamber. The liquid then vaporizes completely into gas at a raised temperature. The low surface tension CO\(_2\) liquid can prevent the beam from pulling down and sticking to the substrate. Figure 5.5 shows the SEM images of the released sensors for scheme I and scheme II.

Figure 5.4 PolyMUMPs
Figure 5.5 SEM images of the released sensors for scheme I (left) and scheme II (right).

5.4 Pirani Gauge Calibration

5.4.1 Test Setup

Figure 5.6 shows the test setup for the pirani gauge sensor. Before the test, the sensor chip is wire-bonded to a dual in-line package. Four-point test is conducted to measure the resistance change of the sensor under different pressures. Four contact pads are designed on the chip and connected to each side of the sensor through the poly1 leads. During the test, a probe current $I_p$ passes through two leads while the voltage drop across the sensor being measured through another two leads as shown in Figure 5.6. The resistance of the beam $R_p$ is measured by $V/I_p$ and it is independent of the resistance of the leads running to the sensor beam and the electrical contacts. For calibration, the sensor is put in a vacuum chamber with a vacuum control and an electrical feedthrough. Inficon pilot plus vacuum gauge is used as a reference to calibrate the sensor. Keithley 2400 source meter is used for the current supply and the voltage drop is measured using Keithley 2000 multi-meter. The resistance can also be measured directly by Keithley 2400 in a four wire mode.
5.4.2 Test Methods

Two methods are used to test the sensors. The first method is to test the fractional resistance change of the sensor as a function of vacuum level. For this method, we pass a probe current with a certain value to the sensor while measuring the resistance change. To avoid the heat-up of the substrate, only pulse current is used. The second method is to vary the input power and measure the thermal impedance of the sensor as a function of vacuum level. Figure 5.7 shows the test results of the sensor with 250 µm beam using the first test method. Four different input currents were used. Low input current such as 0.5mA does not yield a good response of the sensor. And the measurement is limited by the noise which may be caused by the environment temperature fluctuation and the piezoresistive effect. Increasing the input current improves the sensitivity of the sensor, for example, the FRC from atmospheric pressure to 0.1 Torr raises from
around 1% to 6% when the input current is increased from 2mA to 4mA. However, too high input current will cause the heat-up of the substrate and influence the accuracy of the measurement.

Figure 5. 7 FRCs of pirani gauge with 250 µm beam as function of vacuum level with different current inputs.

Figure 5.8 shows the test results of the sensor with 250 µm beam using the second test method. For this method, the average temperature of the sensor is measured as a function of input power at different pressures. The input power is determined by $I_p \cdot V$ that varies by varying input currents. The average temperature is a function of the sensor’s resistance and can be determined by Equation 5.6. The TCR of the sensor can be measured by putting the sensor in an
oven and measuring the resistance of the sensor at different temperatures. A linear curve fit is applied to the temperature versus power and the thermal impedance data is extracted as the slope of the linear fit. As shown in the left of Figure 5.8, the slope increases with the pressure decreasing. The right figure shows the thermal impedance values extracted as a function of the pressure. We can see this is a similar curve as the curve generated by the first method.

![Figure 5.8](image)

Figure 5.8 Measurement of thermal impedance as a function of vacuum level of pirani gauge with 250 µm beam.

Figure 5.9 shows the repeatability of the pirani gauge at 10 Torr for 7 days using the 500 µm beam as an example. Both test methods were used to obtain the repeatability. The mean value was the average of the 7 days results. Uncertainty was determined by three times of the standard deviation value. The uncertainties obtained by both methods are smaller than 10% demonstrating a good repeatability of the pirani gauge sensor. The test method using thermal impedance always yielded a smaller uncertainty compared with the method using FRC. However, FRC test gives satisfactory test results and is relatively simple and involves less data processing compared with thermal impedance test. For all the hermetic tests in this project, FRC test is utilized.
5.4.3 Test Results

Figure 5.9 shows the comparison between the modeling and the typical experiment calibration data for both 250 µm and 500 µm beams. The input probe current is 4mA for the test. The sensing range of 250 µm beam covers pressure range from ~0.1 Torr to Atm. The 500 µm beam covers a pressure range from ~0.03 Torr to Atm. The sensing ranges of both beams meet the requirement for monitoring a vacuum level between 1 Torr and atmospheric pressure. Compared with the 250 µm beam, the 500 µm beam demonstrates higher sensitivity on pressure change. Its sensing range for the low pressure region is wide due to a longer beam length that increases the interaction area between the air molecules and the sensor surface. On the other hand, although the sensor with longer beam reaches higher sensitivity to lower pressure, it is not stiff from buckling failure. This concern is important during the release process or operation.
under vibration or shock conditions. We use the 250 µm beam pirani gauge for all the package tests in this project due to its satisfactory sensing range and stiff beam.

Figure 5.10 shows the experimental calibration curves for the 250 µm beam gauges with a probe current of 4mA. The gauges are randomly chosen from 30 chips and one curve corresponds to one individual gauge. The gauges with and without poly-cap are compared in the figure. The pressure measurement variations of both types of gauges are checked at 1, 10, and 100 Torr, respectively. The gauges without poly-cap have approximate variation ranges of <0.1~2.4 Torr, 7.6~13.4 Torr, 71.7~151.38 Torr, at 1, 10, and 100 Torr, respectively. That means,
for example, if we would like to measure 10 Torr using different gauges from the batch, the variation would be 7.6 to 13.4 Torr. The gauges with poly-cap have approximate variation ranges of <0.1~2.3 Torr, 7.7~12.7 Torr, 79.7~165.9 Torr at 1, 10, and 100 Torr, respectively. For pressure characterization inside a package cavity, since the exact pressure is not as important as the pressure change over time, these variation ranges are acceptable. For pressure < 0.1 Torr, it is necessary to calibrate each individual gauge in order to reasonably predict the actual pressure inside the package cavity. Also, we can notice that the gauges with poly-cap have higher FRC comparing the gauges without poly-cap at the same pressure, demonstrating higher sensitivity on pressure change. The reason could be attributed to that the poly-cap creates an extra air gap between the beam and the cap.

Figure 5. 11 Experiment calibration curves for the 250 µm beam gauges with/out poly-cap.
In order to measure the pressure inside a package cavity at different temperatures and get a reasonable estimation of the gauge’s temperature sensitivity, we need to test the resistance temperature dependency of these gauges. Figure 5.12 left shows an example of the resistance change of the 250 µm beam gauge as a function of temperature. Resistance change rate of 0.274 Ohm / °C is obtained from the linear fit of the data points. The corresponding TCR is 0.0012 / °C with respect to the resistance of 227.73 Ohm at 23 °C. Using the model presented in 5.3.1, approximate drift in pressure of 0.35, 1, and 24 Torr is predicted for the pressure measurement at 1, 10, and 100 Torr, respectively, with per 1°C temperature change. An environmental chamber with control tolerance of ±0.3 °C is used in this study to test the packages at a setting temperature. Figure 5.12 right shows the calibration curves of a 250 µm beam with poly-cap at 23, 60, and 100 °C, respectively. We can see that the gauge has larger FRC at elevated temperature. In order to test a package at elevated temperature, the calibration at corresponding temperature is conducted.

Figure 5. 12 Experiment calibration curves for the 250 µm beam gauges with/out poly-cap.

5.5 Chapter Summary

In this chapter, we demonstrated a pirani gauge with a micro-ladder structure which can
be designed for sensing different pressure ranges. Two beam lengths of 250 µm and 500 µm were designed and PolyMUMPs was used to fabricate the sensors. An analytic model was applied to simulate the sensor’s responses to pressure changes. The sensors were tested using two test methods and the test results showed repeatability of <10% at 10 Torr. The sensing range of 250 µm beam covered the pressure range from ~0.1 Torr to atmospheric pressure and the 500 µm beam covers the pressure range from ~0.03 Torr to atmospheric pressure. The experimental test results showed a good match with the modeling results. The sensing ranges of both beams meet the requirement of this project for monitoring vacuum level from 1 Torr to atmospheric pressure.
Chapter 6 Critical Issues for ALD-Enabled Polymer MEMS Packaging

6.1 Introduction

It is the final Chapter that will integrate knowledge and techniques accumulated in previous chapters to study critical issues for wafer-level packaging for MEMS. ALD is applied to provide vacuum sealing for the polymer packages. About 100 times reduction of leak rate is demonstrated by coating ALD on the polymer packages. A model with consideration of temperature effect is developed to predict the pressure change inside the ALD sealed polymer package cavity at different temperatures based on the defect density in the coating. Five critical issues are identified for the ALD enabled polymer MEMS packaging. To achieve good hermetic or vacuum sealing for polymer MEMS packages, it is important to understand these critical issues. We will discuss these critical issues and corresponding solutions in the following sections.

6.2 Background

There are usually two types of MEMS devices that require vacuum for optimal performance [5]. The first type includes resonators and resonant sensors, which normally require a vacuum ambient to reduce damping and achieve reasonable oscillation amplitudes. These micro-resonators are used for high accuracy clocks, filters and mixers in a wide range of RF applications. The second type includes primarily transducers that require a significant amount of thermal isolation, such as micro-bolometer for infrared imaging (<10 mTorr). In addition, a much wider range of devices simply requires hermeticity or even protection from the environment, such as pressure sensors and microphones. Table 6.1 lists the desired vacuum levels for
packaging a number of MEMS devices and their market size summarized by Mitchell et al.[5].

Table 6. 1 Desired vacuum level for packaging a number of MEMS devices and their market size [5]

<table>
<thead>
<tr>
<th>Applications</th>
<th>Desired Vacuum Packaging Level</th>
<th>2011 Market Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF MEMS (Resonators and Switches)</td>
<td>1 mTorr to 760 Torr</td>
<td>$820M</td>
</tr>
<tr>
<td>Accelerometer (Resonant/Piezoelectric/Capacitive)</td>
<td>100 mTorr to 760 Torr</td>
<td>$1,400M</td>
</tr>
<tr>
<td>Gyroscope</td>
<td>1-10 mTorr</td>
<td>$920M</td>
</tr>
<tr>
<td>IR MEMS</td>
<td>1-10 mTorr</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6. 2 Comparison of the major concepts in literatures for the aspects for wafer level packaging of MEMS

<table>
<thead>
<tr>
<th>Publications, Year</th>
<th>Packaging concept</th>
<th>Capping wafer</th>
<th>Bonding</th>
<th>Feedthrough seal</th>
<th>Package thickness</th>
<th>Process temperature</th>
<th>Hermeticity Demonstrated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cheng et al., 2002 [6]</td>
<td>Glass capping</td>
<td>Yes</td>
<td>Aluminum/Silicon-to-Glass Bonding</td>
<td>No</td>
<td>760 um</td>
<td>Up to 800 C</td>
<td>25 mTorr (Long term)</td>
</tr>
<tr>
<td>Stark et al., 2004 [10]</td>
<td>Electroplated Ni capping</td>
<td>No</td>
<td>No</td>
<td>Solder</td>
<td>40 um</td>
<td>Up to 250 C</td>
<td>1.5 Torr (Short term)</td>
</tr>
<tr>
<td>Heck et al., 2007 [11]</td>
<td>Electroplated Au capping</td>
<td>No</td>
<td>No</td>
<td>Stamp wafer</td>
<td>No data</td>
<td>Up to 350 C</td>
<td>No</td>
</tr>
<tr>
<td>Kim et al., 2009 [4], Kim et al., 2008 [3], Candler et al., 2006 [12]</td>
<td>Poly-Si &quot;epi-seal&quot; encapsulation</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>20-50 um</td>
<td>Up to 1000 C</td>
<td>&lt; 7.5 mTorr (Long term)</td>
</tr>
<tr>
<td>Joseph et al., 2007 [14]</td>
<td>Polymer package</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>4-20 um</td>
<td>Up to 280 C</td>
<td>No</td>
</tr>
</tbody>
</table>

Table 6.2 lists the major concepts for wafer level packaging of MEMS presented in literature. We compare several aspects for wafer level packaging of MEMS. The polymer packaging can simplify the packaging process, reduce process temperature, and reduce the
package size, which would substantially reduce the packaging cost for commercialization. In addition to the example listed in the table, other polymer materials and techniques have been demonstrated for MEMS packaging [40-44]. The polymer materials include epoxy based materials, such as SU 8[44], BCB cyclotene [43], and LCP [40-42]. However, so far no hermeticity and associated tests have been demonstrated for polymer packaging of MEMS.

6.3 Polymer Packaging Based on Encapsulant

To simplify the packaging process, an extra poly-cap with release holes is fabricated above the gauge by taking advantage of the standard MUMPs process. After release of the gauge, a polymer encapsulant such as BCB cyclotene is spin-coated to encapsulate the whole structure and seal the release and feed-through holes. Due to the high viscosity of the BCB encapsulant, it does not wick into the package through the release feed-through holes. Also, the BCB encapsulant is known for low outgassing during the curing process. After curing the encapsulant, ALD coating is applied to hermetically sealing the package. In this study, BCB cyclotene 4026-46 and polyimide PI-2574 are used. This packaging process is not successfully developed though.

We find out that the polymer encapsulant curing deforms the poly-cap structure and damages the device inside as shown in Figure 6.1. This is the first critical issue identified for polymer MEMS packaging. This failure is the result of shrinkage and residue stresses of the polymer encapsulant during curing. The gap between the poly-cap and the device is very small; it is associated with the thickness of the sacrificial oxide layer defined in the standard MUMPs process. As shown in Figure 6.1 top left, the gap is around 0.7 µm. This small gap can be easily compromised during the encapsulant curing process. When the deformed poly-cap structure touches the device inside, the device is dead. Figure 6.1 top right shows the comparison before
the BCB encapsulation and after the BCB encapsulation and curing. We can see the poly-cap deflects into the cavity for about 2 µm distance which is approximately the gap between the device and the substrate. After curing the encapsulant, the gauge loses the response to the change of pressure. In addition, the thermal impedance of the gauge changes considerably before the encapsulation and after encapsulation and curing.

Figure 6.1 Critical issue I: device damage during polymer curing.

In order to increase the stiffness of the poly-cap structure, posts are designed to support the cap structure as shown in Figure 6.2. This improved design increases the structure stiffness, but it is not good strong enough to avoid the device damage caused by the polymer curing. The residue stresses after curing could reach 28 MPa for BCB and 36 MPa for polyimide, according to the product data sheets. The thickness of the cap structure is limited by the thickness of the poly 2 layer which is only 1.5 µm based on the MUMPs process. For the improved design, the distance of the suspended cap structure between two posts is about 10 µm and the width of the
posted cap structure is around 100 µm. However, the structure still collapses after polymer encapsulation and curing.

Figure 6. 2 Cross section of pirani gauge with poly-cap structure: initial design (left) and improved design (right) with posts.

### 6.4 Polymer Packaging Based on Dry Film Adhesive

To avoid the aforementioned device damage caused by polymer curing, a polymer package can be fabricated with enough space between the device and the package. The normal polymer materials are not photo-definable and therefore not suitable for micro-fabrication. The polymer-based photo-definable materials are usually liquid type resin, like SU 8 and BCB cyclotene. In addition to many other considerations, liquid type resin increases the complexity of the packaging process since we have to avoid the contact of the packaging material with the device once it is released. To simplify the packaging process, we decide to study the use of dry film type polymer material.

#### 6.4.1 Material for Packaging

PerMX3000 is a dry film type polymer adhesive developed by Du Pont for wafer level
packaging and permanent structure application. It is epoxy-based and photo-definable like normal photoresist. This dry film can be applied on the device wafer by hot roll lamination. Table 6.3 lists the physical properties of this film.

Table 6.3 Physical properties of PerMX3000 (after cured at 150°C, 30 min)

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>PerMX 3000</th>
<th>Measuring Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tg, max tagδ / Tg, TMA inflection</td>
<td>120 °C / 105 °C</td>
<td>DMA / TMA</td>
</tr>
<tr>
<td>5% weight loss temp.</td>
<td>346 °C</td>
<td>TGA</td>
</tr>
<tr>
<td>Decomposition onset temp.</td>
<td>416 °C</td>
<td>TGA</td>
</tr>
<tr>
<td>CTE ζ₁/ζ₂, ppm</td>
<td>72 / 73</td>
<td>TGA</td>
</tr>
<tr>
<td>Shrinkage, X, Y, Z %</td>
<td>&lt; 1%</td>
<td>CD, FT loss</td>
</tr>
<tr>
<td>Young’s modulus</td>
<td>2.0 GPa</td>
<td></td>
</tr>
<tr>
<td>Residue stress, MPa</td>
<td>3.3</td>
<td>Wafer Bow</td>
</tr>
<tr>
<td>Bend radius, cured 50 μm film</td>
<td>&lt; 1 mm</td>
<td>Spindle</td>
</tr>
<tr>
<td>Adhesion, MPa</td>
<td>(a. 40 μm post; b. 20 μm post)</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>71ᵃ, 42ᵇ</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>69ᵃ, 40ᵇ</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>68ᵃ, 39ᵇ</td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>30ᵇ</td>
<td></td>
</tr>
<tr>
<td>Glass, borosilicate</td>
<td>44ᵇ</td>
<td></td>
</tr>
</tbody>
</table>

The PerMX3000 is provided with thicknesses of 15, 20, and 50 μm. For larger thickness application, multilayer layer lamination can be used. Figure 6.3 shows the film structure and the diagram for the lamination process. The film is sandwiched by a polyester cover sheet layer and a polyolefin separator sheet. Before lamination, the separator layer is released and the polymer film is laid on the wafer. A laminator with a hot roll is used to help laminate the film and avoid air encapsulation. The cover sheet will be then released before or after the UV exposure.
Figure 6.3 PerMX 3000 dry film structure and the diagram for lamination process

Figure 6.4 shows a PerMX 3000 dry film enclosed pirani gauge. The package structure is made with a 50 µm film. The sensor has a beam length of 250 µm.

Figure 6.4 PerMX 3000 dry film enclosed pirani gauge sensor
For vacuum packaging, the pressure difference inside and outside the package will cause a deflection of the package lid. A large deflection is not allow since it may damage the sensor packaged inside and create other reliability problems. Figure 6.5 shows the deflection of 50 µm film above a 400 µm (W) × 600 µm (L) × 50 µm (H) cavity caused by one atmospheric pressure difference. This deflection is simulated using CoventorWare. The deflection is less than 1 µm in comparison with 50 µm air gap; it illustrates good mechanical stiffness of PerMX 3000 dry film for MEMS packaging applications.

![Deflection simulation](image)

Figure 6. 5 Deflection of 50 µm dry film above a package cavity caused by one atmospheric pressure difference

### 6.4.2 Packaging Process

Figure 6.6 shows the major steps for the dry film-based packaging process for MEMS.
The ten steps start with a MEMS device wafer without HF release. Before the dry film packaging processes, the sacrificial oxide surrounding the device has to be removed by wet etching in the second step. It should be noted that the device is not released in this step. The surrounding area will be used for dry film package adhesion with the substrate. The reason to remove the sacrificial oxide in this area is to prevent a lift-off of the dry film package structure during the HF release of the device. In the third step, the first dry film is laminated on the wafer following by photolithography patterning of the film to form a package ring surrounding the device as shown in the fifth step. Afterwards, the MEMS device is released by HF and dried by CPD in the sixth step. In the seventh step, the second dry film lamination encloses the device in a cavity formed with the package ring. The second lamination is the most critical step for the packaging process since this step encloses the package without affecting the device. The dry film is not absolutely “dry” at a raised temperature. It gradually becomes viscous fluid with increasing temperatures and this viscous fluid can flow into the cavity under lamination pressure and damage the device. The normal lamination temperature is around 65~85 °C depending on different requirements and process conditions. To prevent viscous fluid from flowing into the cavity, the lamination temperature has to be lower than 60 °C. However, low temperature process can lead to poor bonding between the second film and the packaging ring, which will generate major leakage for vacuum. In this study, we use the temperatures between 50 and 60 °C for the second lamination. After patterning the second film, the polymer package is cured at a temperature of 150 to 200 °C for half hour. To avoid outgassing later, we increase the cure temperature and time. We cure the package at a temperature of 200 to 250 °C for at least one hour within an inertial gas ambient.
Before ALD coating, the package is baked in a vacuum chamber with pressure of $< 30$ mTorr for overnight at a temperature of $200^\circ$C in step nine. The purpose of the vacuum bake is to degas the air from the polymer package. We will discuss the degassing process and leak test of the polymer package later. After degassing, the package is quickly transferred into the ALD chamber with a pressure around 1 Torr for $\text{Al}_2\text{O}_3$ coating. In this study, we demonstrate this process to package the aforementioned pirani gauge sensor. The pirani gauge is afterwards used as the sensor to monitor the pressure change inside the ALD sealed polymer package and test the hermetic sealing performance. Figure 6.7 shows a dry film package we fabricated on a $2\text{mm} \times 2\text{mm}$ chip with a pirani gauge sensor inside. The volume of the package is only around $10\text{ nL}$. 
6.4.3 Test of the Polymer Package

Before ALD hermetic sealing, the polymer package has to be tested for vacuum degassing in a vacuum chamber. The degassed package is then placed in an atmospheric environment and tested for leak rate of air to the package. The test will be compared with the leak rate of ALD sealed package in order to evaluate ALD sealing performance. In this study, natural air is used as the leak medium and all the leak rates tested in this study are the effective leak rate of air. For accurate gas leak rate, a pure gas such as nitrogen can be used for the future...
study. Figure 6.8 shows the test setup for polymer packages. Basically, the package is placed in a vacuum chamber for degassing at a controlled temperature. The pressure in the chamber is vacuumed to less than 30 mTorr. The pressure decrease inside the package is monitored by the pirani gauge using four-point test. After degassing, the vacuum in the chamber is released to the atmosphere pressure and the package is transferred into an environmental chamber with a temperature control of ±0.3 °C and tested for the leak of air into the package by monitoring the pressure increase inside the package. It should be noted that the atmosphere pressure in Boulder, Colorado is around 625 Torr instead of 760 Torr due to high altitude.

![Test setup for polymer package](image)

Figure 6.8 Test setup for polymer package

Figure 6.9 shows the test results on pressure change as a function of time of the PerMX 3000 dry film package at room temperature. The package has a cavity dimension of 400 μm (W) × 600 μm (L) × 50 μm (H) and the second enclosure film thickness of 50 μm. In the figure, the
light green region is the vacuum region in which the package is degassed in the vacuum chamber. The light blue region is the release region where the package is tested under an atmosphere pressure. The black points are the in-situ monitoring results of the pirani gauge inside the package. The red dots are theoretical calculations based on the package dimension using Kapton HN film (50 µm) as a reference. Total surface area of the polymer package is used for the calculation. The experiment data show much faster degassing and leak rate than the theoretical calculation indicating the existence of major leak paths. Based on the leak rate in the release region, the leak path diameter is estimated to be around 60 µm. With such large openings, ALD coating will not be able to hermetically seal the package.

Figure 6.9 Test results on pressure change as a function of time of the PerMX 3000 dry film package

For theoretical calculation, the pressure change inside the package for the vacuum
region and release region can be expressed as Equation 6.1 and 6.2, respectively [113]

\[
\frac{dp}{dt} = -\frac{F \cdot (p - p_m)}{V} \tag{6.1}
\]

\[
\frac{dp}{dt} = \frac{F \cdot (p_{en} - p)}{V} \tag{6.2}
\]

where the \( p \) and \( p_{en} \) is the pressure inside the package and the environmental pressure, respectively, \( t \) is time, \( F \) is the conductance of air leak through the polymer package at a particular temperature, and \( V \) is the volume of the package cavity. \( F \) equals \( R/p \), where \( R \) is the leak rate of the package and \( p \) is the pressure gradient. When the pressure gradient is 1 atm, the corresponding leak rate is called true leak rate (\( L \)) and we have \( R/p \) equals \( L/p_0 \) (\( p_0 \): 1atm). For simplicity, we use the true leak rate \( L \) to describe the vacuum sealing performance of packages in this study. The volume of the package is \( 1.2 \times 10^{-5} \) cc which can be calculated according to the dimension of the package cavity, \( 400 \mu m \) (W) \( \times \) \( 600 \mu m \) (L) \( \times \) \( 50 \mu m \) (H). Solving the equations 6.1 and 6.2, we can obtain the pressure change as a function of time for the vacuum region and release region as shown by Equation 6.3 and 6.4, respectively, where \( P_i \) is the initial pressure inside the package, \( P_0 \) is 1 atm pressure.

\[
P = P_i \cdot e^{\frac{Lt}{Vp_0}} \tag{6.3}
\]

\[
P = P_{en} - (P_{en} - P_i) \cdot e^{\frac{Lt}{Vp_0}} \tag{6.4}
\]

For the calculation, the oxygen and nitrogen transmission rates (TR) of Kapton HN film are used as a reference to estimate the effective air leak rate through the dry film polymer package. The true leak rate \( L \) equals the transmission rate times the package effective diffusion area. The package effective diffusion area is calculated to be \( 2.4 \times 10^{-3} \) cm\(^2\) according to the package dimension. The reference air transmission rate is \( 7.75 \times 10^{-3} \) cc/cm\(^2\) day. So the estimated true
leak rate is $1.86 \times 10^{-5}$ cc/day. Also, we have to note that the transmission rate and leak rate are polymer film thickness dependent. The leak path size can be estimated by Equation 6.5 [113]

$$F = \frac{0.182 D^4 P_{\text{ave}}}{l}$$  \hspace{1cm} (6.5)

where $F$ is the viscous conductance of a cylinder in liters/second, and the constant 0.182 is a coefficient of air at room temperature. $P_{\text{ave}}$ is the average pressure drop in microns of mercury. $D$ is the inside diameter of the leak cylinder and $l$ is the path length in cm. For the calculation, $F$ equals $L/1\text{atm}$ and can be obtained from the experiment data according to Eq. 6.4. $l$ is the package thickness.

![LSCM Image](image1.png)

**Figure 6.10 Critical issue II: cracking of the dry film package**

To check the leak path of the dry film package, we use LSCM to inspect the surface of the package. Cracking of the dry film is captured by LSCM after fabrication as shown in Figure 6.10. The cracking of the dry film package is the second critical issue identified in this study. With this polymer package structure cracking, ALD coating will not achieve a hermetic sealing due to the existence of the major leak paths. In order to figure out the reason for the cracking, we
conduct a comparison study on the possible causes. Basically, we treat a dummy dry film package structure with different solvent rinses and thermal treatment which are used in the packaging process and compare the consequent cracking condition using LSCM. Solvent (acetone + isopropanol) rinse is proved to be the reason leading to the dry film cracking. This is one type of environment induced cracking, which may be associated with the absorption of the solvent into the polymer which induces the cracking with the existence of residue stress. Figure 6.11 shows the dry film structure with and without acetone rinse. In addition, we find the dry film cracking can consolidate at a temperature above $T_g$.

![Comparison of cracking of the dry film structure with and without acetone rinse](image)

Knowing how to avoid dry film cracking, we fabricate the package with a revised process. Figure 6.12 left shows the test results on the dry film package with an improved process at room temperature. In this study, the measured leak rates are smaller than the theoretical calculation indicating that major leak paths are eliminated. LSCM inspection does not find cracks in the new package. The test is repeated in the vacuum region and release region and similar test results are demonstrated as shown in the figure. Since we are only interested in air
leak into the package in the release region, we select the release region in the marked square area to study the leak rate of the package. The air leak rates in the release region are compared for the packages with cracks as the major leak paths as shown in Figure 6.12 right. In Figure 6.12 right, the leak region start time is reset to zero for both the cases of the packages with and without cracks for comparison.

![Figure 6.12 Test results on pressure change as a function of time of the dry film package with elimination of cracks (left) and comparison on air leak rate in the release region for the packages without and with cracks (right)](image)

Figure 6.13 shows the test results of the dry film package at different temperatures in the release region. The package has double lamination of the second enclosure layer with total thickness of 100 µm. Figure 6.13 provide us with rich information. First of all, the temperature shows a significant effect on the leak rate. When the test temperature raises from 23.8 °C to 79.3 °C, the leak rate is increased by about 17 times. Again, the leak rate measured here is the effective leak rate of air. This significant temperature effect on leak rate will become a critical issue for polymer packages when they are used or tested at elevated temperatures. Second, for each leak curve in Figure 6.13, two distinctive stages can be identified: transient and steady-state.
At the transient stage, the pressure increases in a slow rate. The transient stage can be attributed to the solution of air into polymer material and diffusion through the polymer package. The gas molecules then desorb from the other side of the polymer package into the vacuum ambient inside the package. This process takes a period of time to reach steady-state. From the figure, the lag is around 50 min for the 100 µm-thick package tested at room temperature. With increasing temperatures, the lag time becomes short and the leak reaches steady-state quickly at elevated temperatures. The transient and steady-state stages are characteristic of polymer materials for gas permeation. From the steady-state stage, we can calculate the corresponding true leak rate according to Equation 6.6. Eq. 6.6 is a transformation of Eq. 6.4. The corresponding effective air transmission rate through the dry film can be calculated by $L/A$. The true leak rate and transmission rate are calculated to be $3.74 \times 10^{-6}$ cc/day and 15 cc/day·m$^2$ in at room temperature.

$$L = \frac{-V \cdot P_i \cdot \ln\left(\frac{P_{en} - P}{P_{en} - P_i}\right)}{t}$$

(6.6)

![Graph](image)

Figure 6.13 Critical issue III: temperature effect on leak rate of the dry film polymer package
As a reference, Table 6.4 lists the oxygen transmission rate of various polymer films at room temperature with a normalized thickness of 100 µm from literature [16]. Since the transmission rate obtained in this study for dry film is the effective air transmission rate, the oxygen transmission rate values are only used as a reference to justify that the experimental value is reasonable. The effective air transmission rate of dry film measured in this study is close to the OTR reported for PET and Kapton films as shown in Table 6.4.

Table 6.4 OTR of various polymer films [16]

<table>
<thead>
<tr>
<th>Polymer</th>
<th>PP</th>
<th>Dry Film (this study)</th>
<th>PET</th>
<th>PEN</th>
<th>Kapton</th>
</tr>
</thead>
<tbody>
<tr>
<td>OTR(a) (cc/day/m²)</td>
<td>90-300</td>
<td>~15 (air)</td>
<td>1.8-7.7</td>
<td>3.0</td>
<td>0.04-17</td>
</tr>
</tbody>
</table>

\(a\): 20-23°C / 100 µm

According to Arrhenius equation, the temperature effect on true leak rate can be expressed as Equation 6.7

\[
L = L_0 e^{-\frac{E_a}{RT}}
\]

(6.7)

where \(L_0\) is a constant, \(E_a\) is the activated energy, \(R\) is gas constant, and \(T\) is the temperature in K. From Eq. 6.7, we can derive the relationship of the leak rate between two arbitrary temperatures as Equation 6.8

\[
L_2 = L_1 e^{\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)}
\]

(6.8)

The activated energy \(E_a\) can be obtained from the product of the gas constant and the slope of the linear fit of the ln (L) rates as a function of 1/K as shown in the Figure 6.14. The activated energy of 43 kJ / mole is obtained for the dry film.
Figure 6. 14 Linear fit of ln (L) as a function of $1/\theta K$ to derive the activation energy for air leak through the dry film package

Again, as a reference, Table 6.5 lists the $E_a$ of various polymer films for OTR [114]. The $E_a$ of dry film for effective air transmission rate is close to those reported for LDPE and Nylon 6.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>HDPE</th>
<th>LDPE</th>
<th>Nylon 6</th>
<th>PET</th>
<th>PVC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_a$ (KJ/mole)</td>
<td>35</td>
<td>42.6</td>
<td>43.5</td>
<td>32.3</td>
<td>55.6</td>
</tr>
</tbody>
</table>

6.4.4 Modeling on ALD-Coated Polymer Package

Based on the test results of the dry film polymer package, we can formulate a model to predict the pressure change inside the ALD sealed polymer package as a function of time. To formulate the model, we first assume that the ALD Al$_2$O$_3$ coating is impermeable to air and air leak is only through the defect sites in the coating. Since air is a mixture of different gases,
as an approximation we only consider a single effective permeant gas. In addition, to simplify the problem we assume the package is represented by a flat film. The leak is only dependent on the total surface of the package and independent of the package geometry. We can then start with the formula to express the gas quantity diffusing through one defect in a unit time as shown in Equation 6.9, with an assumption that the defect size is much smaller than the polymer substrate.

\[ q = 4D \cdot C_0 \cdot R \]  
(6.9)

where, D is effective diffusivity of the polymer, \( C_0 \) the gas concentration at the outer surface of the package, and \( R \) the defect diameter. The details of the derivation can be referred to [66]. If we know the defect density \( \rho \), the corresponding air transmission rate can be expressed by Equation 6.10

\[ Q = 4D \cdot C_0 \cdot R \cdot \rho \]  
(6.10)

Since \( C_0 \) is not a convenient quantity for use, we can use Henry’s law to replace \( C_0 \) by \( S \cdot p \), where \( S \) is the effective solubility of air in the polymer and \( p \) is the pressure gradient inside and outside the package. Since \( S \cdot D \) can be replaced by permeability \( P \), Equation 6.10 is then converted to 6.11.

\[ Q = 4P \cdot p \cdot R \cdot \rho \]  
(6.11)

Figure 6.15 Air leak through the defects in the ALD Al₂O₃ coated polymer package
Now, if we have a polymer package with a total surface area of $A$ coated with ALD $\text{Al}_2\text{O}_3$ coating as shown by Figure 6.15, the true leak rate can then be expressed as Equation 6.12.

$$L_s = Q \cdot A = 4P \cdot p_0 \cdot R \cdot \rho \cdot A \quad (6.12)$$

where $p_0$ means the pressure gradient inside and outside the package ($p_{en} - p_i$) equals 1 atm. The permeability $P$ of the polymer can be replaced by Equation 6.13

$$P = \frac{L \cdot d}{A \cdot p_0} \quad (6.13)$$

$L$ is the true leak rate of polymer package without ALD coating, which can be experimentally obtained according to Equation 6.5. $d$ is the polymer package thickness. Then the true leak rate of the ALD sealed package become Equation 6.14

$$L_s = 4d \cdot R \cdot \rho \cdot L \quad (6.14)$$

Considering the temperature effect by integrating the Arrhenius equation, the temperature dependent true leak rate of ALD sealed package is expressed by Equation 6.15

$$L_s = 4d \cdot R \cdot \rho \cdot L_0 \cdot e^{\frac{E_a(T-T_0)}{RT_0^2}} \quad (6.15)$$

where $L_0$ is the true leak rate of polymer package at room temperature, $T$ and $T_0$ are an arbitrary temperature and room temperature, respectively, $E_a$ is the activation energy for leak obtained by testing the polymer package at different temperatures as discussed above. Plugging Equation 6.15 into Equation 6.4, we can predict the pressure change inside the ALD sealed package with time as expressed by Equation 6.16

$$p_t = p_{en} - (p_{en} - p_i) \cdot e^{\frac{E_a(T-T_0)}{4d \cdot R \cdot \rho \cdot L_0 \cdot e^{\frac{E_a(T-T_0)}{RT_0^2}} \cdot t}} \quad (6.16)$$

where $P_{en}$ is the environment pressure, $P_i$ is the initial pressure inside the ALD sealed package.
In Equation 6.16, d and V are the geometric constants of the polymer package, \( L_0 \) and \( E_a \) are characteristics of the polymer materials which can be obtained by testing the polymer package without ALD coating, R and \( \rho \) are the quality factors of the ALD coating, \( p_i \) equals to the pressure inside the package after degassing and \( P_{en} \) equals atmosphere pressure if the package is placed in an atmospheric environment. For the package studied, d is 100 \( \mu \)m and V is \( 1.2 \times 10^{-5} \)cc for the dry film package, \( L_0 \) is \( 3.7 \times 10^{-6} \)cc/day and \( E_a \) 43kJ/mole. Assume the ALD defect density is 50/cm\(^2\) with average defect size of 0.6 \( \mu \)m, the initial pressure inside the package is 0.01 Torr and the atmosphere pressure is 625 Torr at Boulder, Colorado. Figure 6.16 shows the modeling results on the pressure change as a function of time for the ALD-coated dry film polymer package at room temperature and 100\( ^0 \)C, respectively.

![Graph showing pressure change over time for ALD-coated dry film polymer package](image)

**Figure 6.16** Modeling results on the pressure change as a function of time for the ALD-coated dry film polymer package at room temperature and 100\( ^0 \)C.
The pressure change as a function of time for dry film package without ALD coating at room temperature is used as a reference for comparison in the figure. With the ALD coating, the leak rate can be reduced by ~ 10000 times. The corresponding gas transmission rate is reduced from 15 cc/m\(^2\)·day to 1.7×10\(^{-3}\) cc/m\(^2\)·day at room temperature. As a reference, the OTR for 25nm ALD Al\(_2\)O\(_3\) coated on Kapton and PEN film is measured less than the MOCON limit 5×10\(^{-3}\)cc/m\(^2\)·day and the WVTR is measured around 1×10\(^{-3}\)g/m\(^2\)·day [22].

For the ALD-sealed package, the pressure increases from 0.01 Torr to 0.16 Torr after one week at room temperature. The the pressure increase is significant for 100 \(^0\)C to 5.09 Torr as shown in the figure. For this modeling results, we only consider the leak through the defect sites in the ALD coatings and do not consider the outgassing of the polymer material, and also assume that the polymer package is perfect and completely sealed by the ALD coating. To reduce the leak rate and hermetic sealing performance, we can either improve the coating’s quality by reduction of the defect density or use multilayer barrier structure as we discussed in previous Chapters. Table 6.6 lists the ranges of pressure change at room temperature inside the ALD coated polymer package for different years of use based on two different coating defect densities. This is an estimation based on the model without consideration of outgassing and other possible leak sources. For the estimation, the nominal defect size is 0.6 \(\mu\)m and the initial pressure is 1 mTorr. The estimated performance for both the defect densities could meet the requirements for vacuum packaging of RF MEMS and accelerometers as listed in Table 6.1. For better performance, multilayer ALD coatings could be used. However, in reality, we may have to address many other issues, such as outgassing and fine leak paths in the polymer package.
Table 6.6 Ranges of the pressure change inside the ALD coated polymer package for different years of use

<table>
<thead>
<tr>
<th>Years of Use</th>
<th>Single Layer ALD (Defect density: 50/cm²)</th>
<th>Single Layer ALD (Defect density: 1/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1mTorr to 7.56 Torr</td>
<td>1mTorr to 0.15 Torr</td>
</tr>
<tr>
<td>2</td>
<td>1mTorr to 15.03 Torr</td>
<td>1mTorr to 0.31 Torr</td>
</tr>
<tr>
<td>5</td>
<td>1mTorr to 36.89 Torr</td>
<td>1mTorr to 0.76 Torr</td>
</tr>
</tbody>
</table>

6.4.5 Test on ALD-Coated Polymer Package

Figure 6.17 shows the test results of the dry film package before and after 25nm ALD Al₂O₃ coated. The ALD coating is conducted at 115 °C. Before ALD coating, the pressure inside the package is vacuum baked to < 1 Torr at 150 °C. From the figure we can see the pressure inside the cavity increases to around 12 Torr right after ALD coating. This pressure increase can be attributed to the transition between the vacuum chamber and ALD chamber and the H₂O and TMA absorption during the ALD deposition. The pressure change inside the package cavity is then monitored with time. A lag of around 500 min is shown before the pressure starts to increase. During the lag time, the pressure almost does not change. Then, the pressure increases with a steady-state leak rate of 3.1×10⁻⁷ cc/day. This leak rate is about of 10× reduction compared with the leak rate of the polymer package before ALD coating, 3.7×10⁻⁶ cc/day. We also noticed the lag time is also around 10× increase compared with the polymer package. This study demonstrates a very good improvement for polymer package sealed by ALD coating. However, if the coating has good integrity we can expect better performance as discussed above.
Using LSCM to check the integrity of the ALD sealed package, we find the ALD coating cracks on the dry film package as shown by Figure 6.18. Before the LSCM inspection, the packaged is treated by oxygen plasma (80W) by one hour. This process etch polymer under the ALD cracks and expose the cracks clearly. We can see the strips of the undercutting area at the crack site. The cracking results from the large mismatch of coefficient of thermal expansion (CTE) between the dry film (72 ppm) and the ALD Al₂O₃ (4ppm) [58]. This CTE mismatch can cause high compressive stress when the sample cools from the deposition temperature to room temperature. This compressive stress induced cracking is also reported when ALD Al₂O₃ is coated on teflon substrates [115] and PET substrate [116]. The ALD cracking due to CTE
mistmatch is the fourth critical issue identified in this study. It is essential to address this cracking issue when ALD is deposited to provide hermetic sealing for polymer packages.

Figure 6. 18 Critical issue IV: ALD Al₂O₃ cracking on dry film package due to CTE mismatch.

6.4.6 Buffer Layer to Address ALD Cracking

To reduce the stresses in ALD induced by the CTE mismatch, we consider the use of a buffer layer between the ALD coating and the dry film. ALD is reported to reduce the WVTR of polyimide (PI) by 1000 times. PI is also a common dielectric and stress/passivation used for electronics. In this study, we use PI as an example to reduce the compressive stress. We try two types of PI from Du Pont for the buffer, PI 2574 and PI 2611. Table 6.7 lists the CTE and Young’s modulii of ALD Al₂O₃, dry film substrate, and PI buffer layers. The CTE of PI 2574 is in between the Al₂O₃ and dry film, and the CTE of PI 2611 is close to Al₂O₃. The high modulus of PI 2611 is also desirable to overcome the contraction effect from the dry film substrate.
Table 6. 7 CTEs and Young’s moduli of ALD Al₂O₃, dry film substrate, and PI buffer layers

<table>
<thead>
<tr>
<th>Material</th>
<th>CTE</th>
<th>Modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALD</td>
<td>4.2 ppm</td>
<td>180 GPa</td>
</tr>
<tr>
<td>PerMX3000</td>
<td>72 ppm</td>
<td>2 GPa</td>
</tr>
<tr>
<td>PI 2574</td>
<td>50 ppm</td>
<td>2.5 GPa</td>
</tr>
<tr>
<td>PI 2611</td>
<td>3 ppm</td>
<td>8.5 GPa</td>
</tr>
</tbody>
</table>

To understand the effect of stress reduction of the buffer layer, we employ a thermal mechanical model [117] to estimate the stress generated at the ALD coating during cooling from 115°C to room temperature. If the ALD Al₂O₃ coated polymer substrate has a total thickness of 2c. The stress can be estimated using Equation 6.17

\[
\sigma_{\text{res}}(y) = E(y)[\alpha(y) - \frac{A_1}{E_1} - \frac{(A_2 - \frac{A_1}{E_1}E_2)(yE_1 - E_2)}{E_1E_3 - E_2^2}]\Delta T
\]  

(6.17)

where \( y \) is the coordinate derivative in the thickness direction of the ALD coated polymer substrate from one side (-c) to other side (c), \( \sigma_{\text{res}}(y) \) is the residue stress at \( y \) position, \( E(y) \) is the Young’s modulus at \( y \) position, \( \alpha(y) \) is the CTE value at \( y \) position, \( \Delta T \) is the temperature drop.

In Equation 6.17, \( A_1, A_2, E_1, E_2, E_3 \) can be expressed as below

\[
A_1 = \int_{-c}^{c} E(y)\alpha(y)dy
\]  

(6.18)

\[
A_2 = \int_{-c}^{c} E(y)\alpha(y)ydy
\]  

(6.19)

\[
E_1 = \int_{-c}^{c} E(y)dy
\]  

(6.20)

\[
E_2 = \int_{-c}^{c} E(y)ydy
\]  

(6.21)
The modeling results are shown in Figure 6.19.

![Stress generated at ALD with/out buffer layer when it cools down from 115°C to room temperature.](image)

Figure 6.19 Stress generated at ALD with/out buffer layer when it cools down from 115°C to room temperature.

The stresses are substrate thickness dependent. For the case of the 100 µm-thick substrate, the maximum compressive stresses generated in ALD coating are 1GPa, 0.8GPa, and 0.06GPa for the cases without buffer layer, with 20 µm PI 2574 encapsulated, and with 20 µm PI 2611 encapsulated, respectively. For the case with 20 µm PI 2611 encapsulated, the maximum stress is almost negligeable. To examine the modeling results and the corresponding ALD cracking, dummy dry film packages are fabricated. 25nm ALD Al$_2$O$_3$ is coated at 115°C on the packages with and without PI buffer layers. ALD cracking is checked using LSCM after O$_2$ plasma (120W)
treatment for 120 min. ALD cracking is again found on the dry film package without buffer layer, but for both the PI buffered dry film packages no ALD cracks are inspected on the package surface as shown by the insets of Figure 6.19. This experimental result demonstrates the effectiveness of the use of the buffer layers to reduce the compressive stresses in ALD induced by CTE mismatch. Such a reduction can avoid ALD cracking.

Using PI 2611 as an example, Figure 6.20 shows the test results of 25nm ALD coated on the PI encapsulated dry film package. The ALD coating is conducted at 115 °C. Due to the low permeability of PI 2611, the leak rate is reduced by 7 times after the PI encapsulation. Total reduction of 14 times is achieved for the steady-state leak rate after the ALD coating. The lag time, however, is demonstrated to be increased considerably after the ALD coating. From Figure 6.20, we can see the lag time is increased from around 30 min to around 1100 min. This increase is about 40 times. The inspection using LSCM does not find ALD cracking on the local surface of the package. However, breaches are found using optical microscope at the PI buffer layer around the side of the chip substrate as shown in Figure 6.21. These breaches formation can be attributed to the encapsulation and curing process of PI. This PI is viscous and has comparatively high modulus and low elongation. These breaches then become openings for the air leak but it may take a long time before the gas diffuses into the package cavity as indicated in Figure 6.21. The long diffusion distance yields the long lag time. It also indicates that the ALD coating provides a good sealing locally of the package. But, the breaches can not be sealed by ALD coatings. The long lag time after ALD coating can become a critical issue for test of the ALD sealed package. In Figure 6.20, for example, if the test time is less than 1100 min a misleading conclusion could be drawn since the pressure keeps almost no change during the lag period.
Figure 6. 20 Critical issue V for package test: a long lag time after the ALD coating.

Figure 6. 21 Breaches found at the PI buffer layer surround the chip substrate, which become the openings for air leak and yield a long lag time due to long diffusion distance to the package cavity.
To improve the encapsulation quality of the buffer layer, new type of materials have to be selected which should satisfy the CTE requirement and possess good process and mechanical properties. PI 2545 is another type of PI resin which is developed specifically for stress buffer and passivation layer application and provides comprehensive thermal-mechanical properties for the use in this study. Table 6.8 compared the properties of different types of PI. The CTE of PI 2545 is lower than PI 2574. The large elongation of PI 2545 provides a good cracking resistance. Figure 6.22 is the optical microscope images which show the encapsulation quality of PI 2545 on a dummy dry film package. No breaches, cracks, and bubbles are found in the PI 2545 encapsulation after curing. Unfortunately, we do not have MEMS devices available for a test using such PI as the stress buffer for ALD coating. We will conduct another run of the test in the future.

<table>
<thead>
<tr>
<th>PI</th>
<th>CTE</th>
<th>Elongation</th>
<th>Modulus</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>2574</td>
<td>50 ppm</td>
<td>55%</td>
<td>2.5 GPa</td>
<td>Interlayer dielectric</td>
</tr>
<tr>
<td>2611</td>
<td>3 ppm</td>
<td>35%</td>
<td>8.5 GPa</td>
<td>Interlayer dielectric</td>
</tr>
<tr>
<td>2545</td>
<td>30 ppm</td>
<td>120%</td>
<td>2.1 GPa</td>
<td>Stress buffer/passivation</td>
</tr>
</tbody>
</table>

Figure 6.22 Optical microscope images show the encapsulation quality of PI 2545 on a dummy dry film package.
ELC-2500 UV cure epoxy is another choice for the buffer layer, which has CTE of 33 ppm and also provides a good encapsulation quality. Du Pont reported the use of this epoxy as an encapsulation layer to bond ALD coated polymer on Calcium for water vapor transmission rate test [23]. Since the PerMX 3000 dry film is also epoxy-based, ELC-2500 should compatible with the dry film package and yield a good adhesion. We also fabricate a dummy dry film package to test this epoxy-based buffer layer. Figure 6.23 shows the LSCM images of the ALD coated dummy dry film package buffered by ELC-2500 after O₂ plasma (120W) treatment for 120 min. No ALD cracking is found on the epoxy buffer layer surface.

![LSCM images of an ALD coated dummy dry film package buffered by ELC-2500.](image)

Figure 6.24 shows the test results on 25nm ALD coated on the epoxy encapsulated dry film package. The ALD coating is conducted at 115 °C. Again, we can see that right after ALD coating the pressure inside the package cavity increases to around 25 Torr from < 1 Torr before the ALD coating. This large increase of pressure is attributed to the high moisture absorption property reported for the ELC-2500 epoxy material. Also, the ELC-2500 encapsulated package shows comparatively higher leak rate which is due to the comparatively high permeability of the
epoxy material and the thinner thickness of the dry film package (50 µm). The ALD deposition process alternately injects vaporized H₂O and TMA. The vaporized H₂O is then absorbed and diffuse into the package cavity, and therefore increases the cavity pressure. We can also note that the pressure decreases at the early stage of the test. This pressure decrease can be attributed to the condensation process of the water vapor inside the package cavity. The pressure starts to increase after about 2000 min test. The test is conducted for 4361 min. The corresponding leak rate for the ALD coated package is 6.9×10⁻⁸cc/day in comparison of 7×10⁻⁵cc/day before the ALD coating. This is around 100× reduction of the leak rate by sealing the package with ALD Al₂O₃ coating. While longer test time is desired, a significant improvement of the hermetic sealing is demonstrated.

Figure 6. Test results on 25nm ALD coated on ELC-2500 epoxy encapsulated dry film package.
Many issues remain to be studied: selection of appropriate encapsulation buffer materials with low moisture uptake for test, leak test using pure gas such as nitrogen, elevated temperature test, and minimum vacuum level possible with a consideration of outgassing. Nevertheless, this study demonstrates the feasibility of ALD-enabled wafer level polymer packaging for MEMS applications and identifies several critical issues.

6.5 Chapter Summary

In this chapter, we have successfully developed a wafer level polymer packaging process for MEMS, based on a photodefinable dry film adhesive. This packaging process was demonstrated to successfully package a MEMS-based pirani gauge sensor with a cavity volume of 10nL. The pirani gauge sensor was then used to test the vacuum sealing of the polymer package. Vacuum sealing was achieved by coating the dry film package with ALD Al₂O₃. A model with a consideration of the temperature effect was developed to predict the pressure change inside the ALD-sealed polymer package at different temperatures. Five critical issues have been identified for the ALD-enabled polymer MEMS packaging. These critical issues include: 1) device damage caused by polymer curing; 2) cracking of the polymer package structure; 3) significant increase of leak rate at elevated temperatures; 4) ALD cracking on polymer package due to CTE mismatch; and 5) long lag-time for leak after ALD coating. To achieve an appropriate vacuum sealing performance of the polymer MEMS packages, it is essential to understand these critical issues. Around 10X reduction of leak rate was demonstrated for the ALD-sealed dry film package. However, ALD cracking on the dry film package resulting from CTE mismatch limited the sealing performance. The ALD cracking problem was solved by using a stress buffer layer; and we have demonstrated about 100X leak rate reduction achieved by the ALD-sealed polymer package.
Chapter 7 Summary and Future Work

7.1 Summary

In this thesis work, we study the feasibility of using ALD Al₂O₃ barrier coatings to hermetically seal wafer level polymer packages for MEMS. This work primarily focuses on two topics: quality of ALD thin film coatings and critical issues for ALD-enabled polymer packaging. For the quality of ALD coatings, we address the issues associated with defects and cracks. The results are reported in Chapters 2, 3, and 4. For ALD-enabled packaging, we address the design and fabrication of the test vehicle and the process development and identification of critical issues for packaging. The results are reported in Chapters 5 and 6.

In Chapter 2, we characterize the pinhole defects and their densities in ALD Al₂O₃ by developing several visualization techniques. Using electroplating decoration technique we can visualize defects in ALD Al₂O₃ on conductive substrates. The defect density values measured are consistent with the theoretical estimation using moisture transmission rates as the reference. The defect size is characterized by other approaches, and the causes for defects are discussed. Fluorescent tagging is another visualization technique to characterize ALD Al₂O₃ on polymer substrates such as cracks and defects in ALD Al₂O₃ films on PEN substrates. Using this technique, we can visualize mechanical cracks as small as 20nm in width and pinhole defects in diameter of ~200nm in ALD Al₂O₃ on PEN substrates.

In Chapter 3, we explore the possibility in using ultra-thin ALD Al₂O₃ barrier films. A theoretical analysis determines acceptable defect densities for ALD Al₂O₃ layers with respect to different thicknesses. The defect densities in ultra-thin ALD coatings (2nm ~ 10nm) are quantitatively characterized using the electroplating decoration technique developed in Chapter 2.
More than three orders of magnitude defect density reduction is achieved for a 2nm thick ALD Al$_2$O$_3$ film by using an ALD W buffer layer. The ALD W buffer layer represents a Molecular Layer Deposition (MLD) organic layer to be developed for real applications in the future. The defect density reduced 2nm-thick ALD Al$_2$O$_3$ films will be critical to formulate multilayer barrier structure with substantially improved barrier performance and mechanical robustness.

In Chapter 4, the mechanical robustness in terms of film cracking of ALD coatings on flexible polymer substrates is studied. The first real-time and non-destructive inspection technique based on LSCM is developed for the characterization of ALD films coated on a surface or buried in a multilayer structure. Using this inspection technique, we can measure accurate critical strains of ALD Al$_2$O$_3$ as a function of thicknesses under bending. This in-situ inspection technique avoids the errors resulting from the crack “close-up” phenomenon as demonstrated in this study. We also demonstrate the effective use of a cover-coat to substantially improve the mechanical toughness of ALD Al$_2$O$_3$ for flexible hermetic sealing applications. Specifically, we apply LSCM to inspect the ALD film cracking underneath the cover-coat in real-time. This technique is nondestructive and versatile for a variety of film/substrate material systems. It allows rapid and large-area inspection without any special requirements for sample pretreatment. This technique is expected to be important to evaluate and design reliable barrier films and other functional films used in macro-electronics.

In Chapter 5, we design and fabricate pirani gauge sensors to be integrated into the polymer packages. The sensors enclosed in the packages for in-situ monitoring of vacuum pressure inside the package. This sensor is designed for sensing different pressure ranges with different beam lengths. The pirani gauges designed can cover a range from 0.03 Torr to atmospheric pressure. This pirani gauge sensor is a good device to evaluate ALD sealed polymer
packages.

In Chapter 6, a wafer level polymer packaging process is successfully developed for MEMS. It is based on a photodefinable dry film adhesive. The pirani gauge sensor developed in Chapter 5 is packaged in the dry film package with a volume of only 10 nL. The air leak rates of the dry film polymer packages and the ALD-sealed polymer packages are measured and compared using the pirani gauge sensor. The sensor monitors the pressure changes inside the package cavity. A model is developed to predict the time-dependent pressure variation inside the ALD sealed polymer package at different temperatures. Using this test vehicle, we identify and solve the critical issues for ALD-enable MEMS packaging. Vacuum sealing is achieved by coating the dry film package with ALD Al$_2$O$_3$. A 10X reduction of the leak rate is demonstrated for the ALD sealed package. For enhanced vacuum sealing performance, we have to eliminate the cracking of ALD on the dry film package resulting from CTE mismatch. Using a buffer layer, we successfully reduce the compressive stress in the ALD coating and avoid the cracking of ALD. The leak rate is reduced by 100X with the buffered ALD sealed polymer package.

7.2 Future Work

This research explores and demonstrates the feasibility to apply ALD barrier coatings for wafer level polymer packaging for MEMS. Based on the this study, we have identified new issues to be considered in future studies. The recommendations for these studies are summarized as follows.

7.2.1 Inspection on ALD Thin Film Coating

The techniques for non-destructive defect inspection of ALD Al$_2$O$_3$ on polymer substrates will be an important but challenging aspect for future study. There is a strong interest
in non-destructive pinhole defect inspection that is important to the design and manufacturing of thin film coatings. In this study we develop various key techniques to characterize ALD thin film coatings. For example, we develop LSCM based real-time and non-destructive technique for inspecting ALD cracking on polymer substrates. This technique is very effective for crack inspection. However, it is challenging to apply it for non-destructive pinhole defect inspection. Zero-dimensional pinhole defects have much less contrast on such a thin coating and it is difficult to differentiate the defects with surface features and particles. Although we demonstrate that fluorescent tagging can render the pinhole defect visible, there are many other problems remained to be solved. For example, the fluorescent tagging technique is based on different hydrophilic/hydrophobic properties of the ALD coating and the substrate. Its attachment on fine particles on the film can create false defect identification. We are able to characterize and inspect the cracks of the ALD coating buried in multilayer structures. However, the vertical resolution of the current approach is around 500 nm. A substantial improvement is needed if we want to inspect each layer in an ALD/MLD-based, nano-scaled multilayer. Different cracking modes may occur in one individual inorganic layer, or, in two or several layers simultaneously depending on the materials properties and layer thicknesses. Using this technique we may detect the cracking modes and cracking onset in the multilayer structures. All these issues remain to be studied in the future.

LSCM technique is demonstrated for ALD Al₂O₃ coating on a planar surface. The capability for 3D surface inspection would be challenging. A hermetically sealed package has 3D surface covered by ALD coating. It is important to inspect the sealing quality of such 3D coatings. We need to address how to rotate the sample to accommodate the field of view of the optical lens. For high resolution power, we usually use oil immersion so the lens has to zoom in
to a small distance with the sample surface. For 3D geometry, we may not be able to move the lens close to the sample surface.

### 7.2.2 ALD-Enabled Polymer MEMS Packaging

For packaging, first of all, this study only investigates a low vacuum range from 1 Torr to atmosphere pressure. This vacuum level may not be enough for many MEMS devices as listed in Table 6.1. To achieve high vacuum level sealing using polymer materials, we have to consider two aspects. First is to improve the quality of ALD Al₂O₃ barrier coatings and suppress defects. For enhanced vacuum sealing performance, ALD coatings with very low defect densities or with multilayer structures have to be developed. ALD Al₂O₃ with low defect densities could be developed by reducing particle contamination or using a buffer layer to improve ALD nucleation on polymer substrate. The second consideration is about outgassing from the polymer materials. The outgassing species could be gas/moisture or small molecules which are absorbed or resolved in the materials; these species can be desorbed and released after sealing. Outgassing can be reduced by baking and using getters. Another possible approach is to reduce outgassing from the polymer package by coating the polymer surface with ALD Al₂O₃.

As mentioned in Chapter 6, cracking of ALD Al₂O₃ resulting from a CTE mismatch is a critical issue. The stress buffer layer can solve the problem. It is necessary to conduct a more extensive study considering buffer layer’s CTE, adhesion with the substrate, cracking resistance, moisture uptake, permeability, and processing properties. The PI and low CTE epoxy studies can be good candidates. Parylene C might be another good candidate which has low CTE, low moisture uptake and permeability, and good cracking resistance. In addition, parylene C can be conformally deposited on ALD coating with excellent encapsulation property.

One fundamental solution to solve the ALD Al₂O₃ cracking problem is to use very thin
coatings. Based on the studies reported in Chapters 3 and 4, we know that thin Al₂O₃ layer has higher mechanical robustness. And we have demonstrated that extremely thin 2nm ALD coating can have reasonably low defect densities. It will be very exciting to study how to apply 2nm ALD Al₂O₃ to seal the polymer packages. The model developed in this study can be used to predict the defect density required for excellent sealing performance. The measured leak rate can be compared with the defect density characterized in the coating.

To evaluate leak rates, we have to apply different pure gases instead of natural air. A good sealing against nitrogen may not be a good one against helium. In addition, temperature and humidity effects on hermetic/vacuum sealing have to be studied.

The coating can be damaged by mechanical scratch or abraction. A well designed protective layer should place the hermetic coating on the neutral plane of the structure which will provide extra protection from cracking as demonstrated in Chapter 4. Materials such as parylene C might be a good candidate for the protective layer, which has low moisture absorption, excellent gas barrier performance, and good mechanical properties.

Last but not least, the test vehicle developed in this thesis work can be used as a new approach to evaluate performance of thin film barriers used for organic electronics. It is very challenging to measure ultra low permeability. The standard Mocon test does not have the sensitivity to characterize gas transmission rates through ALD coatings. Using the test vehicle developed in this work, extremely low transmission rate can be measured, especially when it is tested at elevated temperatures as illustrated in Figure 6.15. The sensitivity and sensing range of the pirani gauge sensor can be designed to meet different requirements. However, we have to consider the potential outgassing problem that may affect the measurement.
Bibliography


