Assessment of Normal force testing to measure adhesion at organic-inorganic interfaces in organic optoelectronic devices
ASSESSMENT OF NORMAL FORCE TESTING TO MEASURE ADHESION AT ORGANIC-INORGANIC INTERFACES IN ORGANIC OPTOELECTRONIC DEVICES

By

HRISHIKESH DAS GUPTA, B.Sc.

A Thesis

Submitted to the School of Graduate Studies in Partial Fulfillment of the Requirements for the Degree Master of Applied Science

McMaster University

©Copyright by Hrishikesh Das Gupta, September 2014
M.A.Sc Thesis - Hrishikesh Das Gupta; McMaster University - Engineering Physics

McMaster University
Hamilton, Ontario, Canada

MASTER OF APPLIED SCIENCE (2014)

Department of Engineering Physics

TITLE: Assessment of Normal force testing to measure adhesion at organic-inorganic interfaces in organic optoelectronic devices

AUTHOR: Hrishikesh Das Gupta, B. Sc., Chittagong University of Engineering and Technology (CUET)

SUPERVISOR: Dr. Ayse Turak, Assistant Professor

PAGES: xvi, 123
Abstract

Organic photovoltaic (OPV) devices are emerging as a reliable source of energy due to their combination of unique features. Though desired for their flexibility, low cost, light weight, large area fabrication compatibility and eco-friendly nature, these devices face numerous challenges in achieving high performance and stability. The organic-electrode interface specifically plays a key role in controlling device stability. Recent studies have revealed that the stability is heavily affected by the adhesion of the organic-electrode interface. Measurement of adhesion at these interfaces, however, is a challenging task. In this study, Normal Force Adhesion testing was assessed to determine its suitability for organic devices. In this approach, force is applied perpendicular to the substrate, over the entire surface area of one device (9 mm$^2$) until delamination occurs. In addition to the extracted force-distance curves, images of the interfaces before and after each experiment and a real-time, in-situ video taken from a lateral perspective were examined. All three of these critical pieces of information are necessary to obtain a complete picture of the success of a Normal test. A statistical assessment has been made of the testing apparatus, using many samples (> 50) of one metal - organic combination, Al-Alq$_3$ - an archetypal combination for organic electronics. In addition, five other metal-organic combinations widely used in organic electronic devices, have been chosen to assess the Normal force approach. Due to the ease of testing a large number of samples, Normal force testing does appear to be a viable approach to examining interfacial adhesion, though care must be taken in the experimental design to avoid common experimental failures. Based on the results, a few recommendations have been made to improve the utility of the adhesion testing system for rapid quality testing of organic devices.
Acknowledgements

First of all, the author is thankful to the Lord Almighty for His everlasting grace for the success of the thesis work. The author would like to express his sincere gratitude and profound gratefulness to his supervisor Dr. Ayse Turak for her constant supervision, steady support and continuous encouragement at each and every stage of the master’s study. She will always be an inspiration to the author.

The author would like to acknowledge Jim Garrett for his valuable suggestions in the experiments. The author is greatly indebted to Bo Mi Lee for her significant contribution to making the samples for analysis.

Special gratitude to Dr. Marleen Kamperman and Juan Yang for their continuous support and assistance during this work.

The author would also like to extend his appreciation to his colleagues for their generous support throughout the thesis. He would also like to thank all the members of the Department of Engineering Physics for shaping him up for such important research.

The author also wishes to thank Dr. Jonathan Hare for providing general information about materials. A special thanks to the committee members for their technical suggestions.

The author acknowledges financial support from 436100-2013 RGPIN and 384889-2010 CREAT.

At last but not the least, the author remains deeply grateful to his mother Mamata Das Gupta and sisters, Shampa Das Gupta and Munmun Das Gupta for their love, patience and continuous motivation throughout his study in Canada.
Contents

1 Introduction and Motivation 1
   1.1 Introduction ......................................................... 1
   1.2 Possibility and challenges of organic photovoltaic devices ............ 2
   1.3 Objectives of the Thesis ........................................... 3
   1.4 Organization of the Thesis ......................................... 3

2 Adhesion Theory 4
   2.1 Introduction ......................................................... 4
   2.2 Intrinsic fracture resistance ....................................... 6
   2.3 Adhesion modeling for elastic contacts ............................ 7
   2.4 Factors that influence adhesion .................................... 10
   2.5 Adhesion Testing Methods .......................................... 12
      2.5.1 Four point bending (FPB) test ................................. 13
      2.5.2 Double cantilever beam (DCB) test .......................... 14
      2.5.3 Adhesion tape test ........................................... 14
      2.5.4 Atomic Force Microscopy (AFM) .............................. 14
      2.5.5 Normal force test ............................................ 15
   2.6 Detailed description of the Normal testing method ...................... 15
### 2.7 Measurement of adhesion in organic electronics

### 3 Material systems examined in Normal testing system

3.1 Inorganic materials

3.1.1 Aluminum (Al)  

3.1.2 Gold (Au)  

3.2 Organic materials

3.2.1 Alq3  

3.2.2 BCP  

3.2.3 C60  

3.3 Summary of physical properties of organic and inorganic materials of interest

### 4 Experimental Procedure

4.1 Sample preparation

4.1.1 Sample preparation for Normal Test I  

4.1.2 Sample preparation for Normal Test II  

4.1.3 Experimental parameters

4.2 Normal Testing Systems

4.2.1 Description of Normal Test I

4.2.1.1 Data conversion

4.2.2 Description of Normal Test II

4.2.2.1 Data conversion

4.3 Comparison between two Normal testing systems

4.4 Tape test

4.4.1 Setup of Tape test

4.5 Statistical tests

### 5 Results and Analysis

5.1 Classification of tests

5.1.1 Identification of “Experimental errors”  

5.1.1.1 Failure I: Incomplete experiment  

5.1.1.2 Failure II: Tape adhesion
5.1.1.3 Failure II: Misalignment ................................. 53
5.1.1.4 Failure II: Sample delamination ........................ 55
5.1.1.5 Failure II: Dust on the sample surface ............... 55
5.1.2 Uncategorized tests from NT ............................... 56
5.1.3 Standards for “Good tests” ................................. 56
5.2 Implications of adhesive strength in Normal testing ....... 58
5.2.1 Observations from the tape test ........................... 59
5.2.2 Statistical assessment for the tape test .................. 60
5.2.3 Microscopic image and AFM study ......................... 61
5.2.4 Selection of suitable tape ................................. 64
5.2.5 Implementation of ideal tape in a Normal testing system 65
5.3 Reproducibility of data for one material system .......... 66
5.3.1 Statistical evaluation for Normal Test II .................. 66
5.3.2 Implications of including “Bad test” in the statistical analysis 69
5.3.3 Implications of including uncategorized results in the statistical analysis 71
5.4 Physical interpretations of differences between different material systems .......... 72
5.4.1 Suitability of Normal testing to distinguish between different metal-organic interfaces ................................. 72
5.4.2 Chemical reaction .................................. 73
5.4.3 Van der Waals interaction between surfaces ............ 74
5.4.4 Intrinsic fracture resistance (IFR) ........................ 75
5.4.5 Metal diffusion ..................................... 76
5.4.6 Summary ........................................... 77
5.5 Suitability for comparing different material systems ....... 80
5.5.1 Comparison of different material systems in NT I .......... 81
6 Conclusion and Recommendations ................................. 82
6.1 Summary ........................................ 82
6.2 Recommendations for future experiments with Normal testing ..................... 83
6.3 Proposal for the extension of the present work .............. 84

Bibliography ........................................ 86
Appendix A  Estimation of cut-off distance  
Appendix B  Summary of adhesion test analysis by various research groups  
Appendix C  Vacuum chamber setup at McMaster University  
  C.1 Vacuum chamber setup  
  C.1.1 Vacuum chamber  
  C.1.2 Port A [High temperature source]  
  C.1.3 Port B [View port]  
  C.1.4 Port C [Ion gauge source]  
  C.1.5 Port D [Sample input port]  
  C.1.6 Port E [Sample manipulation port]  
  C.1.7 Port F [Vacuum Port]  
  C.1.8 Port G [Low temperature source]  
  C.2 Electrical Setup  
  C.2.1 DC power supply and temperature controller for High temperature source  
  C.2.2 Ion gauge controller  
  C.2.3 Quartz crystal thickness monitor  
  C.2.4 Turbo pump  
  C.2.5 DC power supply and temperature controller for low temperature source  
  C.3 Experimental problems and solutions  
  C.3.1 Table design  
  C.3.2 Sample holder  
  C.3.3 Cooling water supply for high temperature source  
  C.3.4 Low temperature source  
Appendix D  Complete force-distance curve from NT II
List of Figures

1.1 Schematic representation of organic devices [(a) organic solar cell and (b) organic light emitting diode]. In these devices, the donor (hole transport layer) and acceptor (electron transport layer) are two organic layers sandwiched between two electrodes. 2

2.1 Macroscopic and molecular adhesion ranges in logarithmic scale (modified from [38]). 4

2.2 Schematics of (a) two building blocks adhering to each other in a mortise and tenon joint, b) complete adhesion at the macro level, c) pre-mature adhesion observed at the nanometer level (modified from [38]). 5

2.3 Adhesion between a) rough contact surface; b) smooth and rough contact surface (modified from [38]). Arrows indicate the strength of the applied force to separate the surfaces. 10

2.4 Influence of applied load on the adhesion test: a) light load gives an elastic asperity deformation; b) heavy load gives plastic flow (highlighted in the red box) (modified from [38]). 11

2.5 a) Roughness leaves capillary gaps in the surface; b) water condensation can occur in the gaps (modified from [38]). 11

2.6 Flowchart showing different types of adhesion tests based on the applied force. 12

2.7 Schematics of different types of adhesion testing systems: a) four point bending test, b) double cantilever beam test, c) adhesion tape test, d) atomic force microscopy. 13

2.8 Schematic of a Normal testing method. 15
2.9 Schematic showing various steps of Normal test with the movement of actuator: (a) before contact between tape and contact; (b) initial contact between tape and sample; and loading of tape towards the sample, (c) start of unloading and (d) continuation of unloading until delamination. .................................................. 16

2.10 Graphical representation of the force-distance curve with in situ video observation where each significant stage: a) approach, b) contact, c) loading, d) unloading, e) pull off point, f) snap out point, have been identified from the video. ............................. 17

2.11 Adhesion failure in a) PEDOT:PSS/P3HT:PCBM and cohesion failure in b) P3HT:PCBM interface [37]. ................................................................. 20

2.12 Schematic representation of a BP junction formed between a gold-coated AFM cantilever and a gold substrate. Au, C, H and N atoms are shown in yellow, grey, white and blue, respectively [60]. .............................................. 21

2.13 Simulation measurement of conductance and force for a) Au, b) BP and c) BPE. The figure is divided into two regions. The upper region is showing the change in conductance of the junction. The lower region is showing the force-distance curve at the interference. The force-distance curve is showing the fluctuation of forces. Stability of force is an indication of elastic stretching and when the force drops it undergoes structural arrangement of bond lengths. From the investigation, the researchers concluded that, before complete delamination the pyridine molecules make a structural re-arrangement by themselves to prevent de-bonding (modified from [60]). ....... 22

3.1 Chemical structure of organic materials: a) Alq3 [80], b) BCP [81] and c) C60 [82]. 26

3.2 Density of states for (a) BCP on Al and (b) BCP on Au using density functional theory (DFT) [81]. ............................................................. 27

4.1 Schematic of a sample showing all the layers. ........................................... 30

4.2 Top view of the UHV system consisting of a loading chamber and a deposition chamber that are separated from each other by valves and connected to with each other by transfer bars (modified from [102]). ................................................... 31

4.3 Nine samples of a metal-organic material system mounted on a substrate holder. .... 31

4.4 (a) Inside view of the evaporation chamber, (b) schematic of the basic components inside [103] and (c) sample holder with active layer mask at the Niagara College. . . 33
4.5 Twenty five Al - Alq$_3$ samples attached to a glass slide prepared in the Niagara college facility. 33

4.6 Schematic of the Normal testing system I (modified from [105]). The inset on the top (green box) shows the side view and inset on the bottom (light blue box) shows the bottom view of the sample by the optical microscope. 35

4.7 Schematic of the sample arrangement for Normal testing system I. Here the force is applied to the sample from a perpendicular direction. 36

4.8 Setup of Normal testing system I [105]. 36

4.9 Schematic of the Normal testing system II. The inset on the top (light blue box) shows the side view of the sample by the optical microscope. 38

4.10 Schematic of the sample arrangement for Normal testing system II. Here the force is applied to the sample from a perpendicular direction. 38

4.11 Setup of Normal testing system II at Wageningen University, Holland; the highlighted portion is shown in figure 4.10. 39

4.12 Raw data obtained from the adhesion tester in Holland showing all the resultant curves from the experiment. 39

4.13 Schematic of Normal testing system developed in (a) Germany and (b) Holland; the features of these two devices have been described in detail in section 4.3. 41

4.14 Schematic of the tape testing system. 43

4.15 Schematic of the sample arrangement tape testing setup. 44

5.1 Snapshots of the video observation during tape adhesion in NT II: a) before contact between tape and sample; b) contact between sample and tape; c) contact between the two tapes (in the highlighted section) observed during loading where sample was not visible; d) tape necking (in the highlighted section) observed during unloading. 49

5.2 Force-distance curve from a material system which deviates from the ideal behavior. 50

5.3 Snapshots of the video observation during tape adhesion in NT I: a) initial position of tape and sample; b) tape and sample in contact during loading; c) observation of tape adhesion (in the highlighted section) while unloading; d) tape and sample after unloading. 51
5.4 Snapshots of the video observation during tape adhesion from the bottom view in NT I: a) tape and sample before delamination; b) tape and sample after delamination. The video from the bottom view was not very useful to extract any information about the experiment. .................................................. 51

5.5 Optical micrograph of the sample after delamination showing that the tape is not strong enough to delaminate the metal interface completely. .................. 52

5.6 Force-distance curve of Al - Alq₃ material system for misalignment. ........... 53

5.7 Misalignment between sample and tape causes incomplete delamination. ........ 53

5.8 Snapshots of the video observation showing misalignment: a) improper alignment; b) not an instant contact; c) contact; d) not an instant delamination; e) tape necking; f) close up of tape necking (in the highlighted section). .................. 54

5.9 Snapshots of the video observation showing sample delamination: (a) sample position before contact; (b) sample position while unloading. The highlighted portions are showing the change of position of the sample while unloading. .................. 55

5.10 Observation of dust particles in the highlighted portion on a sample in the (a) image and (b) video. ................................................................. 56

5.11 Typical “good” force-distance curve from Normal testing system for a metal-organic material system. ......................................................... 57

5.12 Optical micrograph of (a) organic and (b) metal surface after complete sample delamination from a typical test in a Normal testing system. .................. 57

5.13 Snapshots of each significant stage (a-b) observed from a successful “good test” from the in-situ video: a) approach, b) loading, c) unloading, d) instant delamination. ... 58

5.14 Box plot is showing the percentage of delamination for several tapes. ........... 60

5.15 Optical micrographs of a typical region on the organic surface after delamination using several tapes: a) 0.5 N/mm, b) 0.7 N/mm, c) 0.8 N/mm and d) 1.09 N/mm; All the images have same length scale (~0.025 mm). .......................... 62

5.16 Optical micrographs of a typical region on the metal surface after delamination using several tapes: a) 0.5 N/mm, b) 0.7 N/mm, c) 0.8 N/mm and d) 1.09 N/mm; All the images have same length scale (~0.025 mm). .......................... 63
5.17 AFM analysis: a) Surface image of organic interface after using tape 0.8 N/mm; b) Profile of organic interface after using tape 0.8 N/mm; c) Surface image of organic interface after using tape 1.09 N/mm; d) Profile of organic interface after using tape 1.09 N/mm.

5.18 (a) Pull off force and (b) preload normalized values of Al-Alq3 samples for flexible tape (boxplot) and stiff tape (red dots).

5.19 Boxplot and histogram of pull off force for all good tests.

5.20 Boxplot and histogram of preload normalized pull off force for all good tests.

5.21 Boxplot and histogram of work of adhesion (W) for all good tests using pull off force value.

5.22 Boxplot and histogram of work of adhesion (w) for all good tests using preload normalized pull off force value.

5.23 Statistical evaluation of all good tests with the bad tests of NT II.

5.24 Pull off force and preload normalized pull off force of 16 good tests merged with the uncategorized data (red dot).

5.25 Boxplot of pull off force for six metal-organic material system.

5.26 Comparison of organic-metal ratio for intrinsic fracture resistance / length of the interface parameter: (a) Al-organic material system and for (b) Au-organic material system.

5.27 Preload normalized pull off force for six metal-organic material systems.

5.28 Dot plot of preload normalized pull off force for metal-organic material systems.

C.1 Flowchart for the complete setup of the vacuum chamber.

C.2 Experimental setup of the vacuum system.

C.3 (A) Front view of the vacuum chamber; (B) Isometric view of the vacuum chamber.

C.4 Port A - High temperature source.

C.5 Overview of high temperature source(Port A): (A) Isometric view and (B) Bottom view.

C.6 A) Port B - View port; B) Port C - Ion gauge source; C) Port D - Sample input port.

C.7 A) Port E - Growth deposition port; B) Schematic of Port E representing all the positions; C) Port F - Vacuum source.

C.8 Port G - Low temperature source.
C.9 Overview of low temperature source (Port G): (A) Top view and (B) Isometric view. 112
C.10 Overview of an ion gauge: (A) Tungsten filament and (B) Triode combination of ion
gauge [114]. ................................. 114
C.11 Vacuum chamber table. ................................. 117
C.12 Sample holder stage inside vacuum chamber; the inset on the top left is the crystal
placed in the crystal holder. ................................. 118
C.13 Schematic of the sample holder. ................................. 119
C.14 Schematic representation of the sample holder: A) Position of sample holder facing at
Port A and Port G; B) Position of sample holder facing at Port D. ................................. 119
C.15 Change of the sample holder position using sample manipulation port (Port E): A) 2D
view of vacuum chamber; B) position of sample holder facing at sample input port; C)
position of sample holder facing at high temperature source; D) position of sample
holder facing at low temperature source. ................................. 120
C.16 Flow diagram of the water cooling system attached to the high temperature source of
the vacuum chamber. ................................. 121
D.1 Complete force-distance curve from NT II. ................................. 123
# List of Tables

2.1 The linear relationship between two parameters. ........................................... 20  
2.2 Comparison of results for one material system from different adhesion testing systems. 23  
3.1 Physical properties of the metals. ................................................................. 25  
3.2 Chemical names of organic materials. ............................................................ 26  
3.3 Mechanical, structural and optical properties of metal and organic materials; Here,  
FCC = Face centered cubic. ............................................................................. 28  
4.1 Combinations of metal-organic material systems. ........................................ 29  
4.2 Experimental parameters used during material deposition. .......................... 34  
4.3 Tape with known adhesive strength. ............................................................... 44  
5.1 Optical micrographs of the organic and metal interface after delamination using several  
tapes of different adhesion strength. All the images have same length scale (~1 mm). 59  
5.2 Summary of entire distribution of values ........................................................ 69  
5.3 P-value from the statistical evaluation of all good tests with the bad tests of NT II: a)  
Tape adhesion, b) Misalignment, c) Sample delamination, d) Dust on sample surface. 69  
5.4 Trend of pull off force for material systems. .................................................... 72  
5.5 Summary from chemical adhesion for Al-organic and Au-organic material systems (see  
section 3.2 for references). ............................................................................. 73  
5.6 Value of Hamaker constant and work of adhesion. ........................................ 74  
5.7 Value of material properties of metal and organic materials. ....................... 75  
5.8 Unit cell characteristics of metal and organic materials. ............................... 76  
5.9 Metal diffusion in organic compounds. ............................................................. 77
5.10 Comparison of material property trends with experimentally observed trends for
Al-organic material systems. .......................................................... 79
5.11 Comparison of material property trends with experimentally observed trends for
metal-C60 material systems. ......................................................... 79

B.1 Summary of adhesion test analysis by various research groups. ....................... 100
B.2 Summary of adhesion test analysis by various research groups (continued). ........ 101
B.3 Summary of adhesion test analysis by various research groups (continued). ........ 102
B.4 Summary of adhesion test analysis by various research groups (continued). ........ 103

C.1 Summary of all the ports at the vacuum chamber. ....................................... 107
C.2 Electrical connections attached to the ports of the vacuum chamber. ............... 113
Chapter 1

Introduction and Motivation

1.1 Introduction

Optoelectronic devices such as organic photovoltaic (OPV) and organic light emitting diodes (OLED) consist of a multilayer structure of thin films (Figure 1.1). Contact and adhesion between interfaces in organic optoelectronic devices is critical for the efficiency as well as the lifetime of the devices [1,2]. The multilayer stack consists of a transparent anode, an organic active layer or layers and a metal cathode [3–5]. Each thin layer differs from the others in their physical, electrical, chemical and mechanical properties. While designing organic devices, knowledge of characteristics such as work function [2], microstructure [6,7], diffusion coefficient [8], chemical affinity [9], mobility [10] and mechanical adhesion [1] of each component play a vital role. Among these, the influence of adhesion is not yet well understood. Adhesion is the science of describing how the interfaces of a single layer or multilayer are connected to each other. It could be due to a chemical bond or mechanical interlocking of interfaces [11,12].

In organic devices, strong adhesion at the contacts of a multilayer structure prevents them delaminating from each other. This interfacial adhesion enhances the stability of devices [13–15]. The charge transport between the active regions is also dependent on the connections at interfaces [16–19]. Adhesion at the metal-organic interface increases the likelihood of Ohmic contact formation which is the key to high device performance [20]. However, it is often hard for the multi body contacts of organic photovoltaic devices to maintain consistent adhesion between interfaces [21–25]. They can be influenced by chemical instability and mechanical properties (such as elasticity, toughness, roughness).
Recent studies [1, 9] suggest that the adhesion at the top contact (metal - organic interface) affects the efficiency and lifetime of organic photovoltaic devices.

![Schematic representation of organic devices](image)

**Figure 1.1:** Schematic representation of organic devices [(a) organic solar cell and (b) organic light emitting diode]. In these devices, the donor (hole transport layer) and acceptor (electron transport layer) are two organic layers sandwiched between two electrodes.

### 1.2 Possibility and challenges of organic photovoltaic devices

Organic photovoltaic (OPV) devices are cheaper to manufacture, lighter in weight, flexible and eco-friendly in nature [3–5]. However, low power generation efficiency of these systems limits their operation to portable device applications [26, 27]. Furthermore, OPV devices are still struggling to achieve sufficient lifetime [2, 28] for widespread use.

The bottlenecks faced by OPV devices are the high band gap of the active organic materials [29, 30], small exciton diffusion lengths [29] and the chemical instability of materials [31–33]. Several intrinsic and extrinsic characteristics of thin film layers influence the shelf life (device stability) of the organic photovoltaic devices [34]. One of the intrinsic characteristics is the instability at the top contact of the interface. The top contact (metal - organic layer) is the last deposited layer in the organic devices that starts to become unstable when exposed to the atmosphere. The primary causes of instability are the formation of dark spots, cathode delamination, metal diffusion in organic layers and oxidation of the thin film layers [2]. Cathode delamination indicates a poor adhesion between the metal - organic interfaces [1, 9]. The delamination can occur during metal deposition, device operation or device storage [2]. Encapsulation can be a partial solution to prevent the formation of dark spots. Another solution could be modifications to increase the adhesion strength of the interface [1, 35–37].
To understand the adhesion between interfaces, measurement of adhesion is essential. Although there is a variety of adhesion testing systems to measure adhesion, Normal testing can be the most simple and convenient testing method.

1.3 Objectives of the Thesis

In the present study, we focus on the measurement of interfacial adhesion strength of the top contact interface using Normal testing system. The study aims at determining whether Normal testing is a viable method to measure the adhesion force of such interfaces by evaluating the ability of Normal testing system to measure the adhesion of metal-organic interfaces. This will be accomplished by:

1. Checking the reproducibility of results from a statistical analysis for metal-organic material system.

2. Determining whether Normal testing can identify the difference of adhesion force for several metal-organic material systems.

1.4 Organization of the Thesis

The thesis is divided into six chapters. The first part starts with the importance of interfacial adhesion in optoelectronic devices and concentrates on the scope and motivation of this study. The fundamental principles of adhesion are demonstrated in chapter two. This chapter also gives a brief introduction to various adhesion testing systems and previous works performed with them for organic devices. The next chapter describes the physical properties of the metal and organic materials used in this thesis. Chapter four demonstrates all the experimental approaches and their basic principals in details. The results and analysis from the experiments are discussed in chapter five. Finally, chapter six concludes with a summary of the present work and some recommendations for future work.
2.1 Introduction

The mechanism of adhesion at the macroscopic level and molecular level are different from each other.
The macroscopic range is typically considered as above 10 $\mu m$ and molecular scale as below 100 $nm$ [38] (Figure 2.1). The range between these two levels is commonly known as the transition zone. Initially, it was assumed that adhesion at the macroscopic level and molecular level works in the same way. However, this assumption is no longer considered to be valid [38]. Macroscopic objects such as wooden blocks and bricks (Figure 2.2 (A)) are bonded to each other by some assistance such as a mortise and tenon joint (Figure 2.2 (B)). This type of bond is considered to be “complete adhesion”. Without any assisting joint there is zero adhesion at these interfaces.

Conversely, the adhesion at the molecular level does not rely on such joints. In the nanometer
range, before complete adhesion, the objects attach to each other without any assistance and are
difficult to take apart. This condition is denoted as “pre-mature adhesion” (Figure 2.2 (C)) [38].
Either force or surface contamination is required to break the joint. Thus, identifying the factors
that influence adhesion at the nanometer level has become an important task [38].

Figure 2.2: Schematics of (a) two building blocks adhering to each other in a mortise and tenon joint,
b) complete adhesion at the macro level, c) pre-mature adhesion observed at the nanometer level
(modified from [38]).

To explain the molecular adhesion, three principals have been developed [38]:

1. Molecules are bonded to each other. The bond is known as the adhesion force. During the
   separation of molecules, the force acts as a resistance.

2. Contamination in surfaces acts as adhesion force-reducing factor.

3. The value of adhesion force is not constant across the surface.

Instead of adhesion failure between film and substrate, sometimes interface cracks are initiated
within the thin film. This situation can be defined as a cohesion failure [38]. Here, the cohesive
force of the thin film is less than the adhesive force at the contacts. Thus, additional force has to
be applied between the interfaces to prevent it from further cohesive failure. The three principles
mentioned above lead to extensive research on the mechanism of adhesion for thin films, adhesion
influencing factors and the measurement of adhesion force for laboratory scale samples.
2.2 Intrinsic fracture resistance

When an external force is applied between two surfaces, the resistive force per unit area mentioned in the first principle is known as intrinsic fracture resistance \( G \) [39]. Tvergaard et al. [40] found a correlation between the intrinsic fracture resistance and the mechanical properties, for a brittle contact:

\[
G = \frac{(1 - \nu^2)K^2}{E} N/m^2 \tag{2.1}
\]

where, \( E = \) Young’s modulus \((N/m^2)\); \( \nu = \) Poisson’s ratio; \( K = \) Stress intensity factor.

Young’s modulus \( E \) and Poisson’s ratio \( \nu \) are mechanical properties of the material. Young’s modulus is the ratio of the stress over strain when a force is applied to the material. Poisson’s ratio can be represented as the relative change in the dimensions of an object in the direction of applied load. In general, it is the ratio of lateral strain and longitudinal strain.

During the application of the normal force, a crack initiates and propagates perpendicular to the direction of force until the surfaces delaminate from each other. The value when this crack propagation becomes critical and the interfaces delaminate from each other is known as stress intensity factor \( (K) \). The stress intensity factor is a function of stress and crack length [41].

Equation 2.1 is applicable only for brittle surfaces. For a ductile contact, the energy dissipation zone at the tip of the crack grows with the change of applied force; consideration of plasticity zone is essential to calculate the intrinsic fracture resistance of ductile materials [39]. Therefore, the stress intensity factor is replaced by the length of plasticity zone.

Thus, 2.1 becomes,

\[
G = \frac{3\pi(1 - \nu^2)\sigma_{ys}R_0}{E} N/m^2 \tag{2.2}
\]

\[
R_0 = \frac{K^2}{3\pi\sigma_{ys}^2} \tag{2.3}
\]
where, $R_0$ = Length of plasticity zone of the interface; $\sigma_{ys}$ = Yield strength of the material (Pa).

Yield strength can be defined as the stress when the material reaches its plasticity zone and deforms elastically [41].

In the equation 2.2, the intrinsic fracture resistance scales with the Poisson’s ratio and yield strength, and also inversely scales with the elastic modulus. Equation 2.2 of intrinsic fracture resistance is only for a homogenous interface. In considering a heterojunction, if the intrinsic fracture resistance of two materials are close to each other, there might be a possibility that they adhere more than the one whose fracture values are quite different.

2.3 Adhesion modeling for elastic contacts

The contact and crack phenomenon between two interfaces was first examined by Orbeimoff et al. [42]. They observed that cracking and contact at internal interface in mica split by a glass wedge is a reversible cyclic process. At first, molecular contacts are de-bonded by the external force of the wedge. Once the external force is removed, the surfaces again adhere to each other to reach an equilibrium state. However, the recovered energy is less than the fracture energy. They suggested that the force that separates the surfaces is converted into another force that creates a new adhesion interface. In Orbeimoff’s experiment, the fracture energy was 1.5 $Jm^{-2}$. When a vacuum pump removed all the air, the fracture energy increased up to 20 $Jm^{-2}$ which agrees with the second principle of adhesion, that is, contamination reduces adhesion.

This basic principle evolved into the current understanding of adhesion energy ($W_{Adhesion}$). When two interfaces are in contact, the work of adhesion ($W_{Adhesion}$) per unit area ($J/m^2$) can be defined as the surface energy required to separate the interfaces (equation 2.4) with some energy dissipation during surface separation [41]:

\[ W_{Adhesion} = \gamma_1 + \gamma_2 - \gamma_{1-2} \]  \hspace{1cm} (2.4)

where, $\gamma_1$ and $\gamma_2$ are the surface energy of two surfaces; $\gamma_{1-2}$ = the energy dissipation used to create surface 1 and surface 2.
The relationship between the applied force and work required to break the adhesion can be explained from the perspective of contact mechanics. Heinrich Hertz introduced the concept of contact mechanics [43]. His theory assumed that there was no contact deformation at interfaces under zero applied loads. However, Johnson, Kendall and Roberts strongly opposed the idea and established that, there is adhesion force at the contact interfaces even when there is no load applied at the interfaces. In such a case, there is deformation at the interfaces. They modified the Hertz equation into the JKR model [44,45] which takes into account the concept of adhesion force along with the surface energy.

However, JKR theory strictly neglects the Van der Waals (VdW) force that is always present between interfaces. This interaction force can be positive (attraction) or negative (repulsive) influence an adhesion. Therefore, the DMT (Derjaguin - Muller - Toporov) model has been developed to study the relation between surface energy and intermolecular force [46,47].

Though the DMT model was developed for spherical contacts, a similar, simplified version can be applied to describe the VdW interaction force between flat surfaces. To estimate the work of adhesion between two flat surfaces, considering the interaction energy in a way similar to the DMT model, can be expressed as:

\[ W_{\text{Flat}} = -\frac{A}{12\pi D_0^2} \]  

(2.5)

here, \( W_{\text{Flat}} = W_{\text{adhesion}} \) = work of adhesion

\( A = \) Hamaker Constant

\( D_0 = \) Cut-off distance in the bulk

Hamaker constant is a material property used to indicate the interfacial strength between two surfaces when they are in contact within a medium. There are two approaches to measure the Hamaker constant between two materials: Hamaker theory and Lifshitz theory.

In the Hamaker theory, the interaction of two different surfaces is considered as the sum of the individual Hamaker constants.

The equation of Hamaker constants,

\[ A = C\pi^2 \rho_1 \rho_2 \]  

(2.6)
where, $C$ = Van der Waals energy coefficient
$ho_1, \rho_2$ = number of atoms per unit volume of the materials in contact.

In equation 2.6, $A$ only holds true in the Hamaker theory, and is one of the limitations of Hamaker theory. We need to know VdW energy coefficient and the surface densities to predict the interaction of two surfaces in order to predict it. The value of the summation completely neglects the influence of neighboring atoms. Therefore, polarization of surface atoms in the presence of neighboring atoms is not taken under consideration.

The Lifshitz theory considers the effect of polarization of the interacting bodies. Easily measurable optical properties used to estimate the interaction energy between surfaces. The Hamaker constant for two flat surfaces (1 and 2) in a medium (3) such as air or vacuum is expressed as:

$$ A = \frac{3}{4} kT \left( \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \right) \left( \frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3} \right) + \frac{3h\nu_e}{8\sqrt{2}} \frac{(n_1^2 - n_3^2) (n_2^2 - n_3^2)}{(n_1^2 + n_3^2)(n_2^2 + n_3^2)} \left( \sqrt{n_1^2 + n_3^2} + \sqrt{n_2^2 + n_3^2} \right) \left( \sqrt{n_1^2 + n_3^2} + \sqrt{n_2^2 + n_3^2} \right) (2.7) $$

Where, $k$ = Boltzmann constant
$h$ = Planck’s constant
$T$ = Temperature
$n_1, n_2, n_3$ = Refractive index of the three media
$\varepsilon_1, \varepsilon_2, \varepsilon_3$ = Dielectric constants of the three media
$\nu_e$ = Absorption frequency

$D_0$ (Cut-off distance) is used to define the space between two flat surfaces when they are in contact at the microscopic range. Measurement of cut-off distance is critical and changes for different surface geometries. However, to estimate the cut off distance, a relation has been developed between $D_0$ and collision diameter ($\sigma$) for a closely packed plane solid surface by Israelachvili et al. [48]. The derivation is explained in Appendix I.

From this approach, the cut-off distance is,

$$ D_0 = \frac{\sigma}{2.5} \quad (2.8) $$
2.4 Factors that influence adhesion

Adhesion testing is performed by stripping a film from a substrate. First, an external force is applied to the film. Meanwhile, a resistive force from the film tries to counterbalance the applied force. However, with the continued application of an external force, the resistance is overcome, and the film delaminates from the substrate. While measuring adhesion between interfaces, the most useful parameter aside from $W_{\text{Adhesion}}$ is the pull off force, which is determined by the maximum load required to take apart two interlayers. However, this parameter is not consistent as mentioned in the third principle. The pull off force is influenced by surface roughness, change in load and moisture [49].

**Surface roughness**

![Adhesion between a) rough contact surface; b) smooth and rough contact surface](image)

Figure 2.3: Adhesion between a) rough contact surface; b) smooth and rough contact surface (modified from [38]). Arrows indicate the strength of the applied force to separate the surfaces.

As interfaces are not smooth all the time, surface geometry is a considerable factor to promote adhesion [38]. Kendall et al. [49] observed that, when there was contact between two rough polymer surfaces coated with silicone rubber (Figure 2.3 (A)), the peeling force to separate the two rough surfaces was three times higher in comparison to the contact between a smooth polymer surface with a rough one (Figure 2.3 (B)) [38]. During peel off of the rough interface, there was a change in the rough asperities. The rough asperities elongate from their initial position. Once the rough surfaces were detached, they could never return perfectly to their initial molecular contacts. Therefore, surface roughness at rough contacts has a higher amplification factor in comparison to the smooth surface contacts.

**Change in load**
All adhesion tests differ from each other in the mechanism of applied load. The adhesion of surfaces is affected by the magnitude of the load [50]. As shown in figure 2.4, there is no significant deformation of surface roughness for a light load. On the other hand, for a heavy load, the surfaces deforms plastically, thus making smoother contact at the interfaces.

![Figure 2.4: Influence of applied load on the adhesion test: a) light load gives an elastic asperity deformation; b) heavy load gives plastic flow (highlighted in the red box) (modified from [38]).](image)

**Effect of moisture**

![Figure 2.5: a) Roughness leaves capillary gaps in the surface; b) water condensation can occur in the gaps (modified from [38]).](image)

Most adhesion experiments occur in ambient conditions. As shown in figure 2.5, water from the atmosphere condenses in the surface gaps. The water in the surface gaps acts as a thin film layer and adheres to the surfaces in contact. Therefore, condensed water can be considered as a contamination...
and its interactive mechanism at the surface contact influences the measured adhesion [38].

### 2.5 Adhesion Testing Methods

According to Mittal et al. [51], an ideal adhesion testing system has to fulfill the following characteristics:

1. Produce quantitative data for easy interpretation,
2. Easy and convenient system for products,
3. Reproducible,
4. Non-destructive,
5. Not dependent on film thickness,
6. Useful for a wide range of sample size,
7. Flexible for all interfaces of films and substrates.

However, as yet, there is no such adhesion testing system that fulfills all the features at the same time.

There are several types of adhesion tests used to measure the pull off force of thin films. The experiments differ from each other by the technique of applying load and analysis of quantitative or qualitative result [51,52]. Figure 2.6 summarizes the types of adhesion tests, which differs by the nature of applied load.

![Figure 2.6: Schematics of different types of adhesion testing systems: a) four point bending test, b) double cantilever beam test, c) adhesion tape test, d) atomic force microscopy.](image)

2.5.1 Four point bending (FPB) test

The FPB is commonly used to measure the adhesion between two interfaces [53,54]. A pre-notch is created on top of the upper beam that helps to initiate a crack at the interface. Then, the method involves compression of the specimen by applying force from four different points (Figure 2.7 (A)) which delaminate the interfaces. The applied load that causes interface delamination through the beam is obtained from the force - displacement curves.
2.5.2 Double cantilever beam (DCB) test

The DCB test is primarily used for the measurement of the adhesive strength of thin films [37, 55]. Here, a thin film structure is sandwiched between two rectangular elastic beams. A pre-crack is created at one side of the film. On that end, a tensile load is applied by two aluminum end blocks until the films delaminate completely (Figure 2.7 (B)). The applied force through the beam and the displacement of the interfaces are obtained from the force - displacement curves.

2.5.3 Adhesion tape test

Tape test is typically used for the qualitative measurement of adhesion [52, 56]. The technique involves two steps - pressing of an adhesive tape to the top surface and delamination of the tape (Figure 2.7 (C)). The results can be classified either as complete or partial removal or no removal of the coating. The peel test is a variation of the adhesion tape test, where the delamination is controlled by an electronic device. The resultant load to peel is an indication of the adhesion force between the thin film and substrate [57, 58].

2.5.4 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) is an option for samples in the nanometer scale [59, 60]. In this approach, adhesion between surfaces is tested by using deflection of a cantilever probe. The cantilever comes in contact and is deflected. After some preload, the probe is pulled away from the surface under a negative load until they separate. Typically, the probe resists being removed and deflects strongly. The magnitude of this deflection is proportional to the adhesion force between the tip and the surface (Figure 2.7 (D)) [38]. AFM is flexible for all interfaces and non-destructive. However, the AFM tip limits interaction between contact areas [59].
2.5.5 Normal force test

The simplest approach is the Normal test method. For quantitative measurement of adhesion between two interfaces, the smooth surface of the actuator is coated with an adhesive, and then adhered with a surface of interest [51, 61, 62]. Then, load is applied in the Normal direction until the actuator delaminates the thin films from each other [Figure 2.8].

The process is simple and convenient. In some cases, however, the tensile strength is not uniform over the surface [51, 61, 62]. Thus, the resultant stress can be influenced by the combination of tensile strength and shear strength. In the present work, we used the Normal force testing system to measure the adhesion between interfaces. So, a detailed description of Normal testing system follows in section 2.6.

2.6 Detailed description of the Normal testing method

As this method is the focus of this thesis, the steps of the Normal force test during the experiment are explained in greater detail. The method starts with the approach of a moving stage towards the sample, eventually making contact with it (Figure 2.9 (A) and (B)). Then, further force is applied to the “moving” stage in contact with the sample until a particular pre-load force is reached. Often the sample is held at that preload for a fixed time to allow viscoelastic flow of the adhesive or sample [63]. After that, the moving stage moves back until the top (metal) layer attached to the adhesive detach from the sample (Figure 2.9 (C) and (D)).
Figure 2.9: Schematic showing various steps of Normal test with the movement of actuator: (a) before contact between tape and contact; (b) initial contact between tape and sample; and loading of tape towards the sample, (c) start of unloading and (d) continuation of unloading until delamination.
Figure 2.10: Graphical representation of the force-distance curve with in situ video observation where each significant stage: a) approach, b) contact, c) loading, d) unloading, e) pull off point, f) snap out point, have been identified from the video.

Figure 2.10 is a typical output force-distance curve from a Normal test showing the significant steps occurring in the adhesion testing system with images of the in situ video observations. When the adhesion between surfaces has reached its maximum resistance, it starts to fail which continues until the layers are completely delaminated from each other. In this thesis, the zone that covers the beginning of the interface failure until its complete delamination is denoted as “The adhesion transition zone”. This is a non-standard term which has been used in the region of interest from the force-distance curve. In this transition zone, the point where the force between the interfaces reaches its maxima is known as the pull off point. On the other hand, the point when the interface completely detach from each other is situated at the end of the “Adhesion transition zone”. This point is known as the snap out point [64]. The force at the pull off point and the snap out point are commonly defined as the pull off force and the snap out force respectively. After reaching the snap out point, there is no contact between the layers. In the unloading zone, the area under the curve below the baseline defines the work of adhesion [49,65,66].
2.7 Measurement of adhesion in organic electronics

As mentioned earlier in chapter one, the interface between the thin films influences the overall efficiency and stability of organic optoelectronic devices. Previous research using adhesion measurement approaches other than the Normal force method has been conducted to try to reveal the relationship of adhesion with electrical and mechanical properties of these thin film devices. Although recent studies [1] revealed that the stability of organic devices is also heavily affected by the adhesion of the organic - electrode interface, there has not been as much focus on this aspect in the literature. Most studies have focused on several commonly used organic active layers of optoelectronic devices, including polymers such as, P3HT:PCBM (Poly-(3-hexylthiophene-2,5-diyl) : phenyl-C61-butyric acid methyl ester), PEDOT:PSS (poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate), MEH:PPV (poly (2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene)) and oligomers like Alq3 (Tris ((8-hydroxyquinolinato) Aluminum)), among others.

The primary motivation of most of these studies was to examine the mechanical and electrical film properties, without much distinction between adhesive and cohesive failures. Tong et al. [59] measured adhesion of thin film layers of OPV and OLED by atomic force microscopy (AFM). Their AFM analysis concluded that the adhesive interaction of organic-organic interface was higher than that of organic-inorganic and inorganic-inorganic interfaces. In addition, their work stated surface roughness, chemical bonding and surface charge variations as adhesion influencing factors.

Although Tong et al. determined that AFM can be used as an adhesion testing system for organic devices; the application of this process is still limited. Specially, it only measured adhesion at a particular location of the interface instead of the whole surface. Additionally, the frequency of their AFM tip was of shorter range [59].

In another experiment, P3HT:PCBM bulk heterojunction (BHJ) solar cell was measured by the double cantilever beam (DCB) test [35]. In the experiment, the solar cell specimens were sandwiched between two elastic cantilever beams. In this test, the weakest interface was found to exist between the BHJ (P3HT:PCBM) and hole transport layer (PEDOT:PSS). The study identified the organic-organic interface as the weakest interlayer which contradicts the study by Tong et al. Additionally, fluctuations in the adhesion fracture energy were observed due to a change of weight (%) of P3HT in the P3HT:PCBM composition. For pure P3HT (3 wt% PCBM), the fracture energy was found to be maximum whereas for pure PCBM (2 wt% P3HT), it was found to be minimum.
The adhesion failure in the work by Dupont et al. [35] was confirmed by visual observation and x-ray photoelectron spectroscopy (XPS). Here, the interface failure of P3HT:PCBM suggested a strong bonding of P3HT with PEDOT:PSS and PCBM with the metal cathode. Additionally, the researchers also concluded that although P3HT is more hydrophobic in nature than PCBM [67], the adhesion between long chains of P3HT and hydrophilic PEDOT:PSS was due to secondary Van der Waals (VdW) bonding. In comparison to P3HT, PCBM is more stable and incapable of forming a secondary VdW bond.

As the obtained fracture energy was not satisfactory, the morphology of BHJ interfaces was modified by annealing at 110°C and 130°C. In that case, the adhesion fracture strength was improved for all the compositions. The change in the adhesion strength was attributed to the chemical morphology of the BHJ interfaces. Thus, changing the composition of P3HT and post-deposition annealing of the interfaces showed a marked improvement of adhesion strength (J/m²) of the materials.

The work of Vitali and colleagues [36], also identified the BHJ interface as the weakest interlayer by four-point bending (FPB) process [Figure 2.7 (B)]. However, it is important to point out that in the case of FPB, the resultant force is the cohesive force, rather than adhesive, as the failure occurs within the BHJ layer [36]. Similar to Dupont et al [35], they saw that the higher the composition of P3HT in BHJ, the higher will be the magnitude of cohesion, and that annealing of BHJ structure up to 200°C resulted in an increase of cohesion value significantly. AFM (atomic force microscopy) analysis after the FPB test revealed that the increment of cohesion values was due to a change in surface roughness with temperature. At higher temperatures, the cohesion between layers was found to degrade. Furthermore, the difference in cohesive strength was only seen when annealing was done after the deposition of the metal electrode (Aluminum). Another study was performed showing that the metal electrode deposition rate is a contributing factor to increase the adhesion strength [68]. Additionally, they found almost identical cohesion values (1.5 ± 0.2 Jm⁻²) for a range of BHJ thicknesses, suggesting that it plays no role in the cohesive strength [36].

The XPS (x-ray photoelectron spectroscopy) and AFM (atomic force microscopy) analysis after FPB test showed that, the BHJ layer delaminates in two interfaces. The first one was in BHJ / metal (Calcium) interface, and another one was in BHJ / hole conductor layer (PEDOT:PSS). The fracture resistance of the former interface is lower than that of the latter one. The researchers explained that similarity of mechanical properties of BHJ and PEDOT:PSS made their interface strong [69].

Table 2.1 summarizes the relationships that can affect the adhesion strength of organic optoelec-
tronic devices based on the journal articles mentioned above.

<table>
<thead>
<tr>
<th>Linear relationship</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. ( y = 1.58x + 0.06 )</td>
<td>( x = % ) of weight for P3HT (ranges from 0 – 100 unit); ( y = ) Adhesion strength (J/m²) [35]</td>
</tr>
<tr>
<td>2. ( y = 0.22x + 0.37 )</td>
<td>( x = ) Annealing time (ranges from 0 – 3 hrs); ( y = ) Adhesion strength (J/m²) [35]</td>
</tr>
<tr>
<td>3. ( y = 0.03x - 1.06 )</td>
<td>( x = ) Annealing temperature (ranges from 1000 – 200°C); ( y = ) Cohesion strength (J/m²) [36]</td>
</tr>
<tr>
<td>4. ( y = -0.3x + 4.18 )</td>
<td>( x = ) Annealing time (ranges from 0 – 3 hrs); ( y = ) Cohesion strength (J/m²) [36]</td>
</tr>
<tr>
<td>5. ( y = 1.85x + 0.6 )</td>
<td>( x = % ) of weight for P3HT (ranges from 0 – 100 unit); ( y = ) Cohesion strength (J/m²) [36]</td>
</tr>
</tbody>
</table>

Table 2.1: The linear relationship between two parameters.

Another experimental investigation of fracture toughness by Yongjin Kim [37] using the double cantilever beam test also identified the P3HT:PCBM \ PEDOT:PSS interface as the weakest interlayer (Figure 2.11 (A)). Similar results have also been obtained for the PEDOT:PSS / PBDTTT:PCBM structure. The study concluded that the weakest interlayer is due to the hydrophobic characteristics of BHJ and hydrophilic nature of the hole transport layer, similar to the results of Vitali et al. [36]. To test this, PEDOT:PSS was replaced by more stable MnO₂ where cohesive failure was observed in the P3HT:PCBM interlayer instead of at the interface, supporting that interpretation (Figure 2.11 (B)).

![Figure 2.11: Adhesion failure in a) PEDOT:PSS/P3HT:PCBM and cohesion failure in b) P3HT:PCBM interface](image-url)
Recently, AFM has also been performed at metal-oligomer organic interfaces by AFM [60]. In particular, the motivation of this experiment was to record the elastic stretching between Gold (Au) electrode and two pyridine [4,4-bipyridine (BP) and 1,2-bis(4-pyridyl)ethylene (BPE)] molecules. In this study, a home-built AFM was constructed (Figure 2.12) which facilitated the measurement of the mechanical strength of a single molecule, the adhesion between the metal and molecules, as well as the conductance of the metal-molecule-metal junction. The cantilever tip of AFM was gold-coated. In addition, the gold coated AFM substrate was covered with pyridine molecules. Continuous contacts between tip and substrate were made to calibrate the strength and stiffness of the interfaces. The fracture strength of gold-coated contacts and BP/BPE contacts were calculated from a force-distance curve (Figure 2.13).
Figure 2.13: Simulation measurement of conductance and force for a) Au, b) BP and c) BPE. The figure is divided into two regions. The upper region is showing the change in conductance of the junction. The lower region is showing the force-distance curve at the interference. The force-distance curve is showing the fluctuation of forces. Stability of force is an indication of elastic stretching and when the force drops it undergoes structural arrangement of bond lengths. From the investigation, the researchers concluded that, before complete delamination the pyridine molecules make a structural re-arrangement by themselves to prevent de-bonding (modified from [60]).

Phatak et al. [1] confirmed that cathode-organic interfacial adhesion plays a significant role in reducing the growth rate of dark spots and improves the stability of oligomer OLEDs, which is a major motivation for this thesis. They found that cathode deposition at elevated temperature reduces the growth rate of the dark spots. They correlated that to improved adhesion strength compared to normal cathode deposition, determined by four point bending system [70]. Though they also examined post annealing treatment (65°C for 40 minutes) and a metal organic mixed interlayer [mixture of tris (8-hydroxyquinolinato) aluminum, magnesium (Mg) and gold (Au)] between the cathode and organic layers, elevated temperature cathode deposition was found to be the best in terms of both improved adhesion and slower dark spot growth.

In summary, several techniques have been used to measure the adhesion between layers of organic optoelectronic devices, in both polymer and oligomer systems. Researchers modified the thin film structure at the interface and measured their adhesion over the past few years. Various forms of interface modification have studied, including high temperature processing, changing the thin film composition or thickness, or introducing interlayers. Among them, annealing and changing the thin film composition were identified as adhesion influencing factors. In Appendix II, table B.1 to table B.4 summarizes these significant changes in the value of adhesion energy including the adhesion testing technique and surface modification.
As most of the research discussed above used the same material system, ITO / PEDOT:PSS / P3HT:PCBM / metal, one can directly compare the values of the adhesion force obtained from other methods. For the different types of adhesion testing techniques, the adhesion strength of BHJ interface varies considerably (Table 2.2). For AFM adhesion testing, this strength is significantly higher than other systems. For other types of adhesion testing system, the value of adhesion energy from the FPB test is higher than DCB test. For DCB test, only shear stress develops at the interface. On the other hand, FPB test is a combination of both compression and shear stress. Creating a pre-notch over the interface of interest is an essential criterion for these two types of tests. However, the influence of pre-notch in thin film devices were ignored by the research done by Dupont et al. [35], Brand et al. [36], Kim et al. [37] and Phatak et al. [1]. Moreover, only Dupont et al. [35] briefly talked about the influence of adhesion for power conversion efficiency of the devices.

From the discussion it can be concluded that, there is an inconsistency in the adhesion energy values from different adhesion testing systems. Furthermore, there is a lack of research on the top contact interface. Therefore, this thesis focuses on adhesion force measurement between metal and organic interface using the Normal testing system.

<table>
<thead>
<tr>
<th>Interfaces</th>
<th>Adhesion Testing System</th>
<th>Adhesion energy (J/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT:PCBM / PEDOT:PSS</td>
<td>AFM test</td>
<td>40 [59]</td>
</tr>
<tr>
<td></td>
<td>DCB test</td>
<td>0.1 [35]</td>
</tr>
<tr>
<td></td>
<td>FPB test</td>
<td>1 [36]</td>
</tr>
</tbody>
</table>

Table 2.2: Comparison of results for one material system from different adhesion testing systems.
Chapter 3

Material systems examined in Normal testing system

The common structure of the organic photovoltaic device consists of a single layer or multilayer organic materials sandwiched between two electrodes. In this thesis, we only focus on the top contact interface of the device which is the metal-organic interface as it degrades first when exposed to atmospheric conditions [71,72]. As degradation is of interest, a reactive base metal (Al) and a noble metal (Au) were chosen as the metal layers and deposited on top of oligomer organic molecules. The base metals are highly susceptible to corrosion and oxidation in the atmosphere, unlike the noble metals. Organic materials such as Alq3, BCP and C60 have been adopted as organic layers as they are most commonly used in organic devices. Alq3, BCP and C60 act as electron transport layers [73], exciton blocking layers [74] and electron acceptor layers [75] to enhance the device performance in OPV devices.

3.1 Inorganic materials

The following table 3.1 is representation of the general information of the inorganic materials used for analysis.
Table 3.1: Physical properties of the metals.

<table>
<thead>
<tr>
<th>Inorganic compound</th>
<th>Molecular mass ((g/mol))</th>
<th>Work function ((eV))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum (Al) ([76,77])</td>
<td>26.98</td>
<td>4.08</td>
</tr>
<tr>
<td>Gold (Au) ([76,77])</td>
<td>196.96</td>
<td>5.1</td>
</tr>
</tbody>
</table>

3.1.1 Aluminum (Al)

Aluminum is a low work function metal and forms aluminum oxide when exposed to air. It is most commonly used as the metal cathode in the organic devices. Aluminum is chemically more stable than other low work function metals. Thus, significant improvement of device performance has been observed using Al as a cathode \([78]\).

3.1.2 Gold (Au)

Gold, which is a noble metal, is less chemically reactive in comparison to Al and can also be used as a metal electrode for organic optoelectronic devices. However, due to its high work function, it is rarely used as the cathode material \([79]\).

3.2 Organic materials

Figure 3.1 and table 3.2 summarize the chemical structure, molecular formula, full name, and common abbreviation of the organic materials used for this study. For the rest of the thesis, the common abbreviation will be used to refer to the organic compound, unless otherwise necessary.
Figure 3.1: Chemical structure of organic materials: a) Alq$_3$ [80], b) BCP [81] and c) C60 [82].

<table>
<thead>
<tr>
<th>Organic compound</th>
<th>Full name (Molecular formula)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alq$_3$</td>
<td>Tris [(8-hydroxyquinolinato) Aluminum] (C$<em>{27}$H$</em>{18}$AlN$_3$O$_3$)</td>
</tr>
<tr>
<td>BCP</td>
<td>Bathocuporine (C$<em>{26}$H$</em>{20}$N$_2$)</td>
</tr>
<tr>
<td>C60</td>
<td>Fullerene (C60)</td>
</tr>
</tbody>
</table>

Table 3.2: Chemical names of organic materials.

3.2.1 Alq$_3$

Alq$_3$ is a chelant that acts as an electron transport material [83]. This material consists of a central aluminum atom, which is surrounded by three identical conjugate base ligands [Figure 3.1 (A)]. The carrier transport property and stability at the organic - metal interfaces of Alq$_3$ help to increase the power conversion efficiency of the organic light emitting devices [84]. Metal-Alq$_3$ interface structures have been analyzed using x-ray photoelectron spectroscopy (XPS) by Turak et al. [78,79]. The study
revealed that there is no chemical reaction between Au - Alq3 interface [79]. On the other hand, deposition of Al over Alq3 surface causes oxidation at the interface [78].

### 3.2.2 BCP

Figure 3.2: Density of states for (a) BCP on Al and (b) BCP on Au using density functional theory (DFT) [81].

BCP is another electron transport material, commonly used as a buffer layer that lowers the energy band gap between the organic-metal interface [81,85]. Moreover, BCP also acts as an exciton blocking layer (EBL) like Alq3 to improve device efficiency [86–88]. This heterocyclic compound consists of carbon, hydrogen and nitrogen [Figure 3.1 (B)]. Experimental and simulation models have been established to study the electronic (and hence electrical) properties of metal-BCP interfaces [81,85]. Ultra-violet photoemission spectroscopy (UPS) spectra showed interface states (IS) at the Al - BCP interface (Figure 3.2). The interface state is an indication of chemical reaction between them. However, this state is absent in the case of Au - BCP interface.

### 3.2.3 C60

In photovoltaic applications, C60 [Figure 3.1 (C)] is widely used as an electron acceptor material for its affinity for electrons [75,89]. This molecular structure of C60 resembles a cage like structure that consists of hexagons and pentagons of carbon [82]. C60 is known to interact chemically with both Al and Au, though the nature of the bonding is different in either case. Surface analysis of Al and C60 by XPS and low-energy electron diffraction (LEED) showed the bond to be covalent in nature [90]. Due to electron affinity of C60, the noble structure of Au is disrupted by it, and an ionic bond is formed between them as shown by scanning tunneling microscopy (STM) [91].
3.3 Summary of physical properties of organic and inorganic materials of interest

Table 3.3 presents some basic properties (mechanical, unit cell structure, optical) of the materials used in the experiments. Some of the boxes left as blank, as the data for them are not available in the literature.

<table>
<thead>
<tr>
<th>Parameter (Unit)</th>
<th>Al</th>
<th>Au</th>
<th>Alq₃</th>
<th>BCP</th>
<th>C60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s modulus (GPa)</td>
<td>70 [76]</td>
<td>79 [76]</td>
<td>100 [92]</td>
<td>3.6 [93]</td>
<td>20 [94]</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>0.33 [76]</td>
<td>0.44 [76]</td>
<td>0.33 [92]</td>
<td>0.35 [93]</td>
<td>-</td>
</tr>
<tr>
<td>Yield Strength (MPa)</td>
<td>68.14 [76]</td>
<td>220 [76]</td>
<td>77 [95]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Shape</td>
<td>Sphere</td>
<td>Sphere</td>
<td>Pyramid</td>
<td>Pentagon</td>
<td>Hollow sphere</td>
</tr>
<tr>
<td>Unit cell structure</td>
<td>FCC</td>
<td>FCC</td>
<td>Triclinic</td>
<td>-</td>
<td>Face centered</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>1.26 [76]</td>
<td>0.248 [76]</td>
<td>1.698 [96]</td>
<td>1.7 [97]</td>
<td>2.2 [98]</td>
</tr>
<tr>
<td>Dielectric Constant</td>
<td>1.6 [76]</td>
<td>6.9 [76]</td>
<td>2.962 [99]</td>
<td>2.985 [99]</td>
<td>4 - 4.5 [100, 101]</td>
</tr>
</tbody>
</table>

Table 3.3: Mechanical, structural and optical properties of metal and organic materials; Here, FCC = Face centered cubic.
Chapter 4

Experimental Procedure

Two Normal testing (NT) systems from Leibniz Institute for New Materials (INM), Germany and Wageningen University, Holland have been used to measure the adhesion force between the metal-organic interfaces. The Normal testing system in Germany has been used to measure the adhesion force of six metal-organic material systems. The examined combinations of the material systems for Normal tests conducted in this thesis are showed in table 4.1. The samples were made at Max Planck institute for Metals Research, Germany. The Normal testing system in Holland was used for the statistical study of one metal-organic material system (Al - Alq₃), as well as those for the examination of tapes with different adhesion strengths. An evaporation chamber of Niagara College, Canada has been used to make these samples. The Normal testing (NT) system in Germany and Holland have been designated as NT I and NT II respectively to make discussions easier. Initially, we built a vacuum chamber at McMaster University to make the samples for NT II. However, the chamber could not meet the requirements to run the experiment. The description of that vacuum chamber has been explained in Appendix C.

<table>
<thead>
<tr>
<th>Material systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al - Alq₃</td>
</tr>
<tr>
<td>Al - BCP</td>
</tr>
<tr>
<td>Al - C₆₀</td>
</tr>
<tr>
<td>Au - Alq₃</td>
</tr>
<tr>
<td>Au - BCP</td>
</tr>
<tr>
<td>Au - C₆₀</td>
</tr>
</tbody>
</table>

Table 4.1: Combinations of metal-organic material systems.
4.1 Sample preparation

![Diagram of a sample showing all the layers.]

Figure 4.1: Schematic of a sample showing all the layers.

A structure composed of an organic layer covered by an inorganic layer, deposited on an inert substrate has been produced by vacuum evaporation [Figure 4.1]. Substrates (ITO coated glass pieces purchased from TFD) have been prepared by ultrasonic cleaning process, consisting of 15 min acetone, and 15 min ethanol washing. During deposition of the organic and inorganic layers, multiple substrates have been mounted together to test the reproducibility of samples for each material system. The dimension of each glass piece is $3\times3mm^2$, cut by a dicing saw in the Centre for Emerging Device Technologies. All materials were commercially purchased from Alfa Aesar and Sigma Aldrich and have been used as received.
4.1.1 Sample preparation for Normal Test I

![Diagram of UHV system with loading and deposition chambers, valves, and transfer bars](image1)

Figure 4.2: Top view of the UHV system consisting of a loading chamber and a deposition chamber that are separated from each other by valves and connected to with each other by transfer bars (modified from [102]).

![Image of samples mounted on substrate holder](image2)

Figure 4.3: Nine samples of a metal-organic material system mounted on a substrate holder.

The organic molecular beam deposition (OMBD) process in an ultra-high vacuum (UHV) system was performed at the Max Planck institute for Metals Research [Figure 4.2] to make six metal-organic material systems. The vacuum system consists of two different chambers [102]: 1) Loading and 2) Deposition chamber. All chambers are separated from each other by valves in order to maintain their pressure. The loading chamber is used to insert and take out the substrate from the chamber. The deposition chamber consists of several Knudsen cells. The Knudsen cell is a source used to evaporate and deposit the molecules to the substrate. The position of the sample can be manipulated in such a way that the cell and substrate are always in parallel position to ensure an uniform deposition of molecules. The system is pumped down by a turbo molecular pump to a
very low pressure \((10^{-10} \text{ to } 10^{-11}\text{ mbar})\). The turbo-pump is connected with additional ion pumps and titanium sublimation pumps to obtain this pressure. There is a quartz crystal sensor in the evaporation chamber to measure the deposition rate and film thickness of the materials. Inside the evaporation chamber, there is a C-type or K-type thermocouple to measure the temperature of the deposition source.

All the cleaned ITO substrates have been annealed at \(130^\circ C\) temperature for 30 minutes to remove all the contamination present in them. After that, 100 nm thick organic film has been deposited with a growth rate of \(10.9 \text{ Å/min}\) in the pressure range of \(10^{-9} \text{ mbar}\). After that, 100 nm of Al has been deposited by vacuum thermal evaporation rate of \(16.106 \text{ Å/min}\) with pressures below \(10^{-6} \text{ mbar}\) in a separate chamber. As the sticking quality of Au on the organic semiconductor is quite low compared to Al, 400 nm of Au has been deposited on the organic layer with the same evaporation rate. While preparing the samples, Quartz Crystal Monitor (QCM) has been used to measure the growth rate of thin films. During the deposition, nine pieces of wafers have been mounted together to test the reproducibility of samples for each material system [Figure 4.3].
4.1.2 Sample preparation for Normal Test II

![Figure 4.4](image1.png)

**Figure 4.4:** (a) Inside view of the evaporation chamber, (b) schematic of the basic components inside [103] and (c) sample holder with active layer mask at the Niagara College.

![Figure 4.5](image2.png)

**Figure 4.5:** Twenty five Al - Alq₃ samples attached to a glass slide prepared in the Niagara college facility.

One metal-organic material system (Al - Alq₃) has been evaporated in a vacuum deposition system at Niagara college. The evaporation system (Nexdep deposition system) is an electron beam physical vapor deposition (EBPVD) system used to coat the substrate with various materials [Figure 4.4 (A)]. The chamber consists of a sample holder, rate sensor, sample shutter, evaporation source, e-beam source and power supply enclosed in a vacuum chamber [Figure 4.4 (B)]. Once the substrates and
materials have been loaded [Figure 4.4 (C)] inside the evaporation chamber, it is then pumped down (Turbo V 1000 HT) to a very low pressure ($5 \times 10^{-7}$ mbar). The machine then releases electricity to the filaments. The beam of electrons with high kinetic energy from the filament is accelerated towards the crucible that holds the materials. The electrons hit the evaporation source and generate thermal energy. This thermal energy evaporates the material that hits the sample shutter. A quartz crystal sensor (Inficon SQC 310) close to the shutter is used to measure the evaporation rate of the material. Once the desired rate is reached, the shutter is opened, and the substrate is exposed to the evaporating material. The desired rate of evaporation and amount of material to be evaporated can be adjusted with the deposition controller. Once the desired amount of material has been evaporated, the shutter is closed. Finally, the pressure is increased to atmospheric pressure, and the chamber is opened to take out the samples.

In this system, 25 substrates have been mounted together on the sample holder (Figure 4.5). The deposition rate of Alq$_3$ was 0.18 Å/s and deposition rate of Al was 0.27 Å/s under vacuum pressure $1.1 \times 10^{-6}$ mbar. Thickness of each layer is 100 nm. In total, 100 samples have been produced.

### 4.1.3 Experimental parameters

Table 4.2 displays all the parameters of the metal and organic materials used while preparing the samples for testing in NT I and NT II. The MSDS data sheet of organic materials suggested to maintain the evaporation temperature below $400^\circ C$.

<table>
<thead>
<tr>
<th>Testing system</th>
<th>Material</th>
<th>Evaporation temperature</th>
<th>Evaporation rate</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>NT I</td>
<td>Al</td>
<td>$1010^\circ C$ [104]</td>
<td>16.1 Å/min</td>
<td>$10^{-6}$ mbar</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>$1132^\circ C$ [104]</td>
<td>16.1 Å/min</td>
<td>$10^{-6}$ mbar</td>
</tr>
<tr>
<td></td>
<td>Organic molecules</td>
<td>$300^\circ C$</td>
<td>10.9 Å/min</td>
<td>$10^{-9}$ mbar</td>
</tr>
<tr>
<td>NT II</td>
<td>Al</td>
<td>$1010^\circ C$ [104]</td>
<td>0.27 Å/s</td>
<td>$10^{-6}$ mbar</td>
</tr>
<tr>
<td></td>
<td>Alq$_3$</td>
<td>$300^\circ C$</td>
<td>0.18 Å/s</td>
<td>$10^{-6}$ mbar</td>
</tr>
</tbody>
</table>

Table 4.2: Experimental parameters used during material deposition.

### 4.2 Normal Testing Systems

In a Normal testing system, the vertical displacement of the sample occurs until failure. To get the force-displacement curve, adhesive tapes have been attached to a moving stage to delaminate the top surface from the substrate. The outputs from the testing system are the sample data, image of the
interfaces after delamination and video of the whole experimental procedure.

In this section, the description of the two Normal testing systems used in the experiment has been provided. The general idea of both testing apparatus are simple and identical; that is, attach the top layer of the sample to an actuator with adhesive tape and apply force in a Normal direction until sample failure. There are some instrumental setup differences between the two devices which have been summarized in section 4.3.

4.2.1 Description of Normal Test I

![Diagram]

Figure 4.6: Schematic of the Normal testing system I (modified from [105]). The inset on the top (green box) shows the side view and inset on the bottom (light blue box) shows the bottom view of the sample by the optical microscope.
Figure 4.7: Schematic of the sample arrangement for Normal testing system I. Here the force is applied to the sample from a perpendicular direction.

![Schematic of sample arrangement for Normal testing system I](image)

Figure 4.8: Setup of Normal testing system I [105].

A home built setup was developed for in situ visualization of the sample with controlled alignment at the INM (Leibniz Institute for New Materials) to measure the adhesion between surfaces (Figure 4.6) [105]. In this system, a glass cantilever with three layers double sided tape (Figure 4.7) is attached to the sample. This tape delaminates the metal layer from the organic layer by applying Normal
force. Some features of this system are a video recording of the experiment, sensitive measurement of
the quantitative values and control over the alignment of surfaces.

This Normal testing device records the side view and the bottom view of the contact area by two
horizontally positioned optical microscopes. The side video shows the table displacement, and the
bottom video shows the contact area through the glass substrate using a mirror system.

NT I consists of a glass cantilever (with spring constant $= 3541.67 \, N/m$) (Figure 4.8). For force
sensing, a laser interferometer is positioned above the cantilever. A mirror is placed on the top side of
the cantilever. The deflection of the symmetrically clamped cantilever is estimated by the changing
intensity of the laser beam. This deflection is calibrated to calculate the force. During the experiment,
the spring constant of the cantilever is fully independent of the measured force.

The whole setup is installed in an optical table to prevent it from vibration. Above the optical
table, a 6-axes positioning table with a sample positioning accuracy of 100 $nm$ is used. A 3-axes
piezo stage is mounted directly on top of the positioning table. The sample is placed on the piezo
stage. This piezo stage has mainly two purposes: 1) High-resolution movement of the sample and 2)
Positioning of the sample parallel to the tape.

In NT I, the sample is raised towards the tape. The sample is compressed by the tape at a fixed
preload. After that, the table moves back with a constant velocity of 100 $\mu m/s$ until delamination.
The output data is written using a LabView software package that includes substrate geometry,
measurement parameters and environmental data. Six combinations of metal-organic interfaces have
been examined in that adhesion tester. Optical images of the samples have been taken before and
after delamination. All the experiments have been performed under the same condition.

### 4.2.1.1 Data conversion

The most important output data from NT I are the cantilever displacement and the table displacement.
Table displacement is the vertical movement of the table towards the double sided tape during loading
and unloading. On the other hand, spring displacement gives the value of the cantilever movement.
For the calculation, spring displacement is converted to force using Hooke’s law 4.1,

\[ F = -kx \]  

(4.1)
here, $F =$ Force, $k =$ spring constant of the glass cantilever (3541.6697 $N/m$), $x =$ spring displacement.

The pull off point and snap out point, where the unloading curve reaches its maximum point and final point respectively have been selected from the force-distance graph (Figure 2.10). Work of adhesion from the area under the curve has been estimated using the trapezoidal rule.

### 4.2.2 Description of Normal Test II

![Figure 4.9: Schematic of the Normal testing system II. The inset on the top (light blue box) shows the side view of the sample by the optical microscope.](image)

![Figure 4.10: Schematic of the sample arrangement for Normal testing system II. Here the force is applied to the sample from a perpendicular direction.](image)
Figure 4.11: Setup of Normal testing system II at Wageningen University, Holland; the highlighted portion is shown in figure 4.10.

Figure 4.12: Raw data obtained from the adhesion tester in Holland showing all the resultant curves from the experiment.
NT II is the adhesion testing system at Wageningen University, Holland. In it, three layers of double sided tapes (Tesa Tape Double Sided Foam) is fixed on a glass cantilever and attached to a movable stage (Figure 4.9). The sample is fixed with two layers of double sided tape on a glass slide (Figure 4.10). The glass slide is attached to a fixed stage using glycerol. The movable stage is a Futek load cell (model LSB 200, S/N 454653 mated with USB210, S/N 454846, capacity: 250 g). The coupled actuator (Thorlabs Z825B) is attached to the controller (Thorlabs TDC001) to control the motion of the moving stage (Figure 4.11). The load cell consists of strain gauges. The compression and expansion of the strain gauge also change the electrical resistance of the gauge itself. The change in resistance of the gauge delivers signal to the load cell which is calibrated and recorded as the “force”.

For the measurement, three layer double sided tapes have been indented at $10 \mu m/sec$ over the sample until a preload force has been achieved. The sample and double sided tape are kept in contact for 10 seconds. After that, the movable stage moves backwards at $10 \mu m/sec$ until delamination occurs at the interface.

The adhesion experiments in Holland gave sample data, image and video from each experiment. All sample data give five important sets of data. The data are sample number, tracking value, peak value, valley value and time respectively. The output image shows the metal and organic interlayer after delamination. The video illustrates the experiment from initial contact to contact break.

Figure 4.12 represents the live graph of sample number vs output (N). The x-axis (sample number) represents the motion steps of the moving stage towards the fixed stage with time. The y-axis shows the change in force with the movement of the moving stage. Three types of values can be obtained from the graph: peak, valley and tracking value. The peak and valley in the figure 4.12 represent the pull off force and pre-load force, respectively. The tracking value is the complete summary of the loading and unloading forces acting over the metal-organic interface.

4.2.2.1 Data conversion

Tracking values from the output file have been used as the force for the force-distance curve. The device measures the time for the motion of moving stage. The moving stage moves at $10 \mu m/sec$. This information has been used to calculate the table displacement. The time difference is the time distance between each sample number for the unloading curve.

$$\text{Table displacement (} \mu m) = \text{Velocity (} 10 \mu m/\text{sec}) \times \text{Time difference (sec)}$$
The pull off point where the unloading curve reaches its maximum point has been selected from the peak valley. From that force-displacement data, it has been observed that for multiple steps of table displacement the change in force is nil. For that, for one value of force the average of the multiple steps of table displacement has been taken under consideration.

The next step is to find out the snap out force. For that, the video of each sample has been taken under consideration. Each video shows the entire picture of the adhesion testing system that includes contact of three layers of double sided tape with the sample, loading zone, unloading zone, contact break between the interfaces, state of tape and alignment of the tape with sample. In addition, every video helps to estimate roughly the time difference between the starting of unloading zone and contact break between the interfaces. This time difference will help to find out the last point when the metal interface delaminated from the organic interface. After taking the time difference from the video, it has been compared with the time range of the data. From that comparison, snap out force has been identified. Work of adhesion from the area under the curve has been estimated using the trapezoidal rule. A complete force-distance curve of NT II has been shown in Appendix D.

4.3 Comparison between two Normal testing systems

![Diagram of Normal testing systems](image)

Figure 4.13: Schematic of Normal testing system developed in (a) Germany and (b) Holland; the features of these two devices have been described in detail in section 4.3.

Two Normal testing systems have been examined to measure the adhesion force between the metal-organic interface (Figure 4.13). There are some similarities and some differences among them. The
similarities are:

- Both work on the same principle, that is, sample delamination in the Normal direction.
- In both, three layers of double sided tape came into contact with the sample.
- Both have visualization of the contact area using high-resolution microscope from the side.
- In both cases, experiments have been conducted under atmospheric conditions.

Though they have many similarities, there are a few critical differences:

- NT I also displays video of the contact area from the bottom view, though this was not found to yield any extra information for our purpose.
- In NT I, the adhesive tape is attached to a glass cantilever. The cantilever is mounted with rubber elastic material, between clamps. In NT II, the adhesive tape is attached to the load cell.
- For NT I, the sample is mounted on a 3-axis piezo sample holder. For NT II, the sample is attached with two layers of double sided tape on a glass slide.
- The NT I has control over the alignment of the interfaces using a laser interferometer. The changing intensity of the laser helps to control the angular movement of the cantilever. For the NT II, there is no control over the alignment.
- Measurement technique of the force is different for each testing apparatus. The force for NT I is calculated from the displacement of the cantilever using Hook’s law. For NT II, a load cell is used to measure the resistance to delamination.
- In NT I, the sample is moving and in NT II the actuator is moving.
4.4 Tape test

![Figure 4.14: Schematic of the tape testing system.](image)

A qualitative tape test has been performed to determine the best tape of known adhesive strength that can delaminate the metal interface from the organic one completely. Several tapes (Nitto Denko, Japan) with known adhesive strength have been chosen for the tape test at McMaster University.

In the manual setup (Figure 4.14) built for this thesis, the sample and the tape are in contact to each other. A force has been applied manually using a wrench at the hexagonal portion. The motion of the hexagonal part with the wrench will also rotate the rod that is attached to it. The wrench will rotate around 30° to avoid the variability of force that occurs for qualitative tape test. This mechanism will delaminate the metal layer from the organic layer. The following figure 4.15 shows the sample arrangement in the tape test apparatus.
After delaminating the metal layer, the organic interface of the substrate has been observed with the optical microscope (Barska digital microscope, model no: AY11374). From the microscope observation, the delaminated part of metal from the organic surface has been considered as the quantitative data. The peel off percentage of metal observed in the microscope for several adhesive tapes has been calculated using ImageJ.

### 4.4.1 Setup of Tape test

<table>
<thead>
<tr>
<th>Adhesive strength (N/mm)</th>
<th>Thermal release temperature (120°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>0.7</td>
<td>0.8</td>
</tr>
<tr>
<td>0.8</td>
<td>1.09</td>
</tr>
</tbody>
</table>

Table 4.3: Tape with known adhesive strength.

To do the tape test, Al - Alq₃ material system has been used using single coated thermal release tape with the adhesive strengths (N/20 mm) of 3.7, 4.8, 5.5 and 7.3 respectively. The thermal release temperature of each tape is 120°C. The unit N/20 mm represents the average adhesion strength (N) per unit width (mm) of the tape. For substrate size of 3 mm width, the adhesive strength has been multiplied with scaling factor $\frac{3}{20}$. The adhesive strength (N/mm) of several tapes has been shown in table 4.3. For each tape, ten samples of Al - Alq₃ have been used.
4.5 Statistical tests

Several statistical tools have been used to check the data in chapter 5. Graphical representation of the data is useful to identify the central tendency, dispersion and skewness of data. Initially, some visual tools such as boxplot and histogram have been selected to observe the centre, spread and overall shape of the distribution [106]. Histogram also provides information about the frequency of the data. Furthermore, for comparison of two or more datasets boxplot is very helpful.

Many statistical interference procedures assume that all sample data follow a normally distributed population [106,107]. To check the data normality, a normal quantile-quantile (Q-Q) plot has been used [108]. If the data is normally distributed, the sample quantiles will follow the theoretical quantiles straight line. In addition, Shapiro test [109] has also been performed to check the normality. The null hypothesis of this test is that the data is normally distributed. The alternative hypothesis contradicts the null hypothesis, that is, the data is not normally distributed.

For the statistical evaluation of the quantitative data (percentage of the delaminated area using different adhesive tapes) of the tape test, both parametric and non-parametric methods of statistics can be used. The methods will help to determine whether the adhesion strength of various tapes has an identical data distribution. The parametric tests are based on a restricted assumption, that is, the normal distribution of data without knowing the mean and standard deviation of the sample for large sets of data [106,107]. On the other hand, non-parametric method can be implemented without assuming the normal distribution for small sets of data [106,107]. Analysis of variance (ANOVA) has been chosen for parametric test and Wilcoxon rank sum test has been chosen for non-parametric test. The null hypothesis of ANOVA is that the sample means are identical, and the alternative hypothesis of ANOVA is that the sample means are not identical. If the alternative hypothesis is true, then at least one of the sample mean is different from the others. The non-parametric statistical assessment from the quantitative data is to determine, whether adhesion strength of several tapes has identical data distribution or not at the 0.05 significance level. The null hypothesis of Wilcoxon rank sum test states that the samples have identical median. On the other hand, the alternative hypothesis of Wilcoxon rank sum test mentions that the median of samples is not equal to zero.

For all the statistical hypothesis tests (Shapiro test, ANOVA, Wilcoxon rank sum test), the pre-determined threshold (commonly known as level of significance \(\alpha\)) has been chosen as 0.05. Therefore, if the probability value (p-value) from the tests is more than 0.05, we will accept the...
null hypothesis. On the other hand, if the p-value is less than the 0.05 then we will reject the null hypothesis [106,107]. The sample tests are independent for all statistical tests.
Chapter 5

Results and Analysis

The primary motivation of this thesis is to identify whether Normal force adhesion testing system is a viable method to measure adhesion at the top contact in organic optoelectronic devices. To answer this question, three important aspects have been considered, as described in this chapter. The first is to select a suitable adhesive tape with known adhesive strength and examine its performance in the Normal testing apparatus. The next objective is to check the reproducibility of data from the Normal testing system for one metal-organic material system. The final objective is to determine whether the Normal testing system can identify quantitatively different values for several metal-organic material systems.

5.1 Classification of tests

From the Normal testing systems, two types of tests have been observed: (a) “Good test”, where the results can be attributed to metal delamination, free of any experimental errors and (b) “Bad test”, where there is an obvious error in the experimental procedure that makes the test invalid. There were also a few tests which were not clearly categorizable in either category and they are discussed in the context of the "good tests" and how their inclusion would change the findings. This section discusses them in details.
5.1.1 Identification of “Experimental errors”

In total, 110 Normal force tests have been conducted, 56 in the NT II for one set material system and 54 in the NT I for six sets of metal-organic material systems. Additionally, 40 samples of one material system have been used to determine the best adhesive strength tape, in the tape test. From an examination of all results, there were two types of failures observed from the tests. In the first type, no quantitative information could be obtained by the end of the test (Failure I). In the second type, force-distance curves (or other quantitative data for the tape tests) were obtained but they were deemed unacceptable due to a variety of reasons (Failure II).

During the measurement with NT I, the critical importance of video observation for each test was not realized. Therefore, only eight videos have been taken from the side view, six of which showed the complete experiment. Although thirty videos were taken from the bottom view, ten of them were blurred and incomplete. They generally did not add any useful information regarding the test outcome.

5.1.1.1 Failure I: Incomplete experiment

There were a number of problems that led to incomplete experiments, without the acquisition of usable quantitative data. In some cases, before completion of the loading stage the tape on the top detach from the sample, leading to premature detachment of the metal layer of the sample.

During experiments with NT II, the load cell was unable to provide any quantitative information for data analysis of the two cases. As the force sensor in the load cell is very sensitive, there was scattering of data due to touch or movement close to the sensor during the experiment. As a result, those tests have been rejected.

For tape test, especially for the 1.09 N/mm tape, the tape was so strong that the ITO glass substrate delaminated from the double sided tape used to fix it to the stage. There is only one test where the sample was fixed in place. All the other results have not been taken under consideration because of this situation.

5.1.1.2 Failure II: Tape adhesion

Tape adhesion in NT II

In some tests, the tapes from the sample and load cell came into contact and adhered to each
other. In such cases, while unloading, the load cell measures the force of two contacts simultaneously: 1) Contact between the tape and sample and 2) Contact between the tapes. The video from the tests helps to identify this situation.

Video observation revealed two different types of tape adhesion. The first situation is when the three tape stack at the load cell is not parallel to the sample, and one side of the tape on-top adheres to a portion of the bottom tape affixing the sample to the stage. Thus, while unloading the force sensor also measures the adhesion force between tape contacts. In another case (Figure 5.1) the tape and sample are properly aligned with respect to each other. However, the tapes are larger than the sample, and the overhang from each side touch each other during loading. For all the tape adhesion failures, the pull off force was found to be greater than the preload force.

In summary, tape adhesion observed in the videos is an indication of an experimental failure, even if the force-distance curve looks suitable. Furthermore, a value of pull off force higher than the preload force suggests the possibility of tape adhesion.

Figure 5.1: Snapshots of the video observation during tape adhesion in NT II: a) before contact between tape and sample; b) contact between sample and tape; c) contact between the two tapes (in the highlighted section) observed during loading where sample was not visible; d) tape necking (in the highlighted section) observed during unloading.
We also observed these types of curves in NT II so it is not only a NT I failure. It is however maybe another type of failure. From the videos that we do have, it appears that the entire tape elongates: this is not tape adhesion (i.e. the top tape and the bottom tape touch, which is shown more by necking); it is more likely to be tape relaxation (i.e. the tape itself was compressed, and after unloading, relaxed). It may be due to tape adhesion but we don’t have proof of that. From graphical observation of the force-distance curve, it has been seen that some tests (Figure 5.2) were dissimilar from the ideal curve in NT I (Figure 2.10). For this type of sample, the unloading curve extends such that a large difference ($\Delta d$) between pull off point and snap out point can be observed.

**Figure 5.2: Force-distance curve from a material system which deviates from the ideal behavior.**

Only one of the tests with such a force-distance curve has a video from the side view showing the experiment. That video shows significant tape extension before complete delamination (Figure 5.3). The video from the bottom view does not show this tape failure (Figure 5.4 (A and B)). Therefore, it appears that all the videos taken from the bottom view are not very useful to extract any information about any experiment.
Figure 5.3: Snapshots of the video observation during tape adhesion in NT I: a) initial position of tape and sample; b) tape and sample in contact during loading; c) observation of tape adhesion (in the highlighted section) while unloading; d) tape and sample after unloading.

Figure 5.4: Snapshots of the video observation during tape adhesion from the bottom view in NT I: a) tape and sample before delamination; b) tape and sample after delamination. The video from the bottom view was not very useful to extract any information about the experiment.
Figure 5.5: Optical micrograph of the sample after delamination showing that the tape is not strong enough to delaminate the metal interface completely.

The post delamination image of that experiment with visible tape elongation showed incomplete delamination, which indicates that the tape was not strong enough to delaminate the whole interface (Figure 5.5). The difference of displacement ($\triangle d$) is more than 0.5 $\mu m$ for that sample. Additionally, the pull off force is higher than the applied preload.

There are no videos available from the rest of the experiments to identify other reasons behind the extension in the graphs. In the absence of videos, if the $\triangle d$ is more than 0.5 $\mu m$, we can consider this as a failure. Based on that particular experimental outcome, it can be concluded that tape adhesion is the main reason for the deviation of the graph from the standard curve during the rest of the observations. However, this deviation of the graph was not seen in NT II.
5.1.1.3 Failure II: Misalignment

Figure 5.6: Force-distance curve of Al - Alq3 material system for misalignment.

Figure 5.7: Misalignment between sample and tape causes incomplete delamination.
For some tests, the unloading zone is not smooth and continuous, showing several points that could be considered the pull-off point (Figure 5.6). That kind of curve also exists in NT I; probably it is also due to misalignment for those kinds of samples as well, though we do not know as we do not have the video. The difference of displacement ($\Delta d$) is more than 0.5 $\mu m$ for those samples. All the post-delamination images for those tests displayed incomplete delamination (Figure 5.7). From the video observation, it has been observed that,

1. The tape and the sample are not parallel to each other. Typically, the sample is inclined around 15° (Figure 5.8 (A)).

2. Due to that inclination, contact between the tape and the sample is non-uniform and takes a longer time than a typical test (Figure 5.8 (B)).

3. Due to that inclination, delamination between the interfaces takes longer time than usual and is accompanied by necking (Figure 5.8 (D)).
On the whole, when there is misalignment between the tape and the sample, the force has not been applied uniformly to the interface in the normal direction. From this experimental failure, it is clear that, alignment is critical to successful tests.

5.1.1.4 Failure II: Sample delamination

![Snapshots of the video observation showing sample delamination: (a) sample position before contact; (b) sample position while unloading. The highlighted portions are showing the change of position of the sample while unloading.](image)

Although no tape adhesion has been observed in the videos, the resultant pull off force is higher than the preload for four experiments. All the samples are slightly misaligned (< 15°). The metal layer is completely delaminated from the organic layer, and \( \Delta d < 0.5 \text{\( \mu m \)} \). The video observation (Figure 5.9) of those tests, however, showed an interesting case. While unloading, the tape from the load cell not only delaminates the interface but also changes the position of the sample that is attached to the bottom tape. Thus, the load cell is also measuring that force. As the pull off force is higher than the preload in this failure mode also, these results for those samples have not been taken under consideration.

5.1.1.5 Failure II: Dust on the sample surface

For one sample, some dust particles have been observed in the post-delamination image and video (Figure 5.10). The dust on the surface can influence the results of interlayer adhesion. Thus, the result for that sample has not been taken under consideration.
5.1.2 Uncategorized tests from NT

In one case, the sample and tape were not parallel to each other in NT II, and the tape was off-set, not making contact with the whole area of the sample. Although, no tape adhesion was observed, the resultant pull off force is slightly higher than the preload. We could not draw a definitive conclusion for these samples, so they have been designated as uncategorized. The result from these tests have not been taken under consideration in examining the reproducibility of data, but the implications of including them will be discussed in section 5.4.3.

Although the resultant pull off force is higher or equal to the preload, the $\Delta d$ is less than 0.5 $\mu$m in another case of NT I. There are no videos available for those tests to clearly identify the cause for this situation. These samples were initially considered in examining different metal-organic combinations (section 5.5). The implications of not including the results from these tests are discussed in section 5.6.

5.1.3 Standards for “Good tests”

After all tests that were uncategorized or could be explained as resulting from experimental failures, and therefore identified as not measuring the data of interest, were eliminated, the remaining tests were ones that were deemed as "good tests". Figures 5.11 to figure 5.13 show the typical outcomes of such good tests. From the typical results, some conclusions can be drawn regarding standards for a 'good test'. Figure 5.11 shows that the pull off point and snap out point are very close to each other ($\Delta d < 0.5\mu$m). Figure 5.12 shows that the metal layer is completely delaminated from the organic layer. There is no tape adhesion or misalignment visible from the video of the experiment (Figure 5.13).
Figure 5.11: Typical “good” force-distance curve from Normal testing system for a metal-organic material system.

Figure 5.12: Optical micrograph of (a) organic and (b) metal surface after complete sample delamination from a typical test in a Normal testing system.
5.2 Implications of adhesive strength in Normal testing

After identifying the causes of the bad tests, the next approach is to analyze the first objective, selection of adhesive tape with known adhesive strength to examine its performance in the adhesion testing apparatus. To determine the optimal ones for our Al-Alq$_3$ samples the metal layer was delaminated from the organic layer using four tapes with different adhesion strength, using the home-built tape test apparatus. Using an optical microscope, the percentage of metal delamination from the organic interface was observed.

The following table 5.1 is a summary of the metal and organic sides of the interface after a typical tape test for each adhesive tape.
5.2.1 Observations from the tape test

From the tape test with Al - Alq₃ material system, some outcomes have been noticed.

1) For 0.5 N/mm tape, none of the experiments showed complete delamination of the metal layer from the organic layer. This indicates that the adhesive strength of this tape is not enough for complete delamination.

2) As mentioned earlier for 1.09 N/mm tape, there is only one test where the sample was fixed to its place. For the rest of the tests, the ITO glass sample has been delaminated by it. Thus, the tape is stronger than tape-glass interface strength. For that, adhesive strength of 1.09 N/mm is more than enough for the weaker interface of Al - Alq₃ and complete delamination was observed. However, the tape with 1.09 N/mm is not suitable tape for further experiment.

3) In the case of 0.7 N/mm tape, some tapes completely delaminated the metal interfaces, while some of them did not.

4) The rate of metal delamination from the substrate is higher for 0.8 N/mm tape than other tapes.
5.2.2 Statistical assessment for the tape test

![Box plot showing the percentage of delamination for several tapes.](image)

Figure 5.14: Box plot is showing the percentage of delamination for several tapes.

The statistical assessment of the quantitative data (percentage of the delaminated area using different adhesive tapes) from 10 samples was performed to determine whether the adhesion strength of various tapes has an identical data distribution. The results have been plotted in a boxplot (Figure 5.14). For the statistical evaluation, both parametric (ANOVA) and non-parametric methods of statistics can be used.

The null hypothesis of ANOVA is that the sample means are identical, and the alternative hypothesis of ANOVA is that the sample means are not identical. If the alternative hypothesis is true, then at least one of the sample means is different from the others. The ANOVA analysis indicates acceptance of the alternative hypothesis i.e. that at least one of the sample mean is not identical with the others. Two sample t-test has been calculated to identify which sample mean is significantly different than others. The t-test results showed that the mean of 0.5 N/mm adhesive tape is lower than others (Figure 5.14). There was no significant change in the mean for the rest of the samples using ANOVA and a t-test. The parametric test revealed that, the percentage of delamination for 0.5 N/mm adhesive tape is significantly different from that of the other tapes.

The non-parametric statistical assessment from the quantitative data is to confirm, whether the adhesion strength of several tapes has an identical data distribution or not at the 0.05 significance level. The null hypothesis of Wilcoxon rank sum test states that the samples have identical median. On the other hand, the alternative hypothesis of Wilcoxon rank sum test mentions that the median
is not equal to zero. The result from the rank sum test is identical with the parametric test results. This indicates that the result of 0.5 N/mm tape is significantly different from the other tapes and the median difference is equal to zero for the remaining tapes. Thus, this tape has been rejected. In addition, the dispersion for 0.8 N/mm tape is less scattered than the remaining ones.

5.2.3 Microscopic image and AFM study

To determine if there is any visible difference between the interface peeling quality for the two remaining tapes, 0.7 and 0.8 N/mm, a portion of the metal and organic interface for each tape have been observed with an optical microscope. This microscopic observation was unable to show any significant difference for the organic side for any tapes (Figure 5.15). In figure 5.16 the metal side for 0.7 N/mm and 0.8 N/mm tapes looked almost identical. The metal surface of tape 1.09 N/mm seemed to be rough compared to other metal surfaces, further underscoring its rejection as a suitable tape for Normal force adhesion testing.
Figure 5.15: Optical micrographs of a typical region on the organic surface after delamination using several tapes: a) 0.5 N/mm, b) 0.7 N/mm, c) 0.8 N/mm and d) 1.09 N/mm; All the images have same length scale (~0.025 mm).
AFM has been performed on the organic side of the interface of the sample after delamination for 0.8 N/mm and 1.09 N/mm tapes to check the roughness of the sample. For 100 nm thickness of the thin film layer, the RMS (root mean squared) roughness of 0.8 N/mm and 1.09 N/mm tapes are 0.5 nm and 0.6 nm, respectively (Figure 5.17). Though the RMS roughness of tape 1.09 N/mm is slightly higher than tape 0.8 N/mm, the profile analysis did not show any significant difference between them.

Based on the surface analysis, there were no obvious differences between tapes that seemed as likely candidates and those that were deemed unsuitable.
Figure 5.17: AFM analysis: a) Surface image of organic interface after using tape 0.8 N/mm; b) Profile of organic interface after using tape 0.8 N/mm; c) Surface image of organic interface after using tape 1.09 N/mm; d) Profile of organic interface after using tape 1.09 N/mm.

5.2.4 Selection of suitable tape

All the information collected from the statistical analysis of the percentage delamination, observations during the test, and a comparison of the topography can be used to determine the optimal tape for implementation in the Normal testing system. From the initial observations that the 1.09 N/mm tape was stronger than the substrate adhesion to the stage, and only one test out of ten was successful, it was eliminated. The 0.5 N/mm tape was generally unsuccessful in completely delaminating the metal, and the statistical analysis confirmed that the mean and median were significantly less than
the other three tapes. Though no obvious difference in the topography of the two tapes were observed by optical or atomic force microscopy, the dispersion of the 0.8 N/mm tape was the smallest, making it the most suitable tape of those tested for further study in the Normal testing system.

5.2.5 Implementation of ideal tape in a Normal testing system

After choosing 0.8N/mm as the best tape, eight tests have been conducted with it in NT II. These were compared with the 'good' tests using the standard double sided tape. The 0.8 N/mm tape has a rigid backing [PET (Polyethylene terephthalate)] for the adhesive. To easily distinguish between them, the typical tape and 0.8 N/mm tape have been denoted as flexible tape and stiff tape respectively. For the flexible tape, there is complete metal delamination and the glass substrate did not detach from the fixed stage. Therefore, it has been assumed that the adhesion strength of 0.8 N/mm tape and the typical tape used in NT II are roughly the same. However, out of the eight tests conducted only three were successful using the 0.8 N/mm tape. The rest of the tests failed before the completion of the experiment, resulting in no force-distance curves. It seems that the typical tapes are much easier to use than the 0.8 N/mm tape.

The results of all good tests using the flexible tape and stiff tape have been merged together for pull off force (Figure 5.18(A)) and preload normalized pull off force parameter (Figure 5.18(B)) (see section 5.4 for details). The figures show that the results from the stiff tape and flexible tape are not comparable to each other. Though only three results from stiff tape are not enough for a statistical
comparison, it appears that stiffness of the tape can have an impact on the Normal testing system. Therefore, stiffness seems to be an important factor, along with the adhesion strength when choosing a suitable tape.

5.3 Reproducibility of data for one material system

The second objective is to check the reproducibility of data from the adhesion testing system for a metal-organic material system.

5.3.1 Statistical evaluation for Normal Test II

The total number of “good” tests is found to be 16 for Al - Alq₃ using the typical flexible tape. The boxplot and histogram of those tests have been plotted in figure 5.19 for pull off force. The boxplot shows that the mean and median are equal. However, the histogram shows that the data is not following a normal distribution.

To check the normal distribution of data, two approaches have been taken under consideration [106]: 1) Q-Q plot and 2) Shapiro test. However, the results from the Q-Q plot are not meaningful. The Shapiro test indicates that the value of pull off force follows a normal distribution (p = 0.42). So, there is a contradiction between histogram and statistical test values.
It has been observed that the value of preload is inconsistent for the 16 tests. Therefore, to see if the preload is biasing the pull-off force, a preload normalized pull off force has been examined to check the distribution of data (Figure 5.20). In comparison to pull off force, this histogram strongly follows the normal distribution. From the statistical test, the data corresponding to this parameter tends to be more normally distributed (p = 0.82). It appears that the preload has an influence on the measured pull off force and consideration of the preload normalized pull off force is important to check the data reproducibility.

The next parameter is to find the work of adhesion. In this thesis, work of adhesion parameter using the pull off force and the preload normalized pull off force have been designated as W and $w$, respectively. The boxplot and histogram correspond to the work of adhesion (W) using pull off force values are shown in figure 5.21. The histogram shows a great amount of fluctuations. The p-value is 0.09 from the Shapiro test, which is very close to the marginal value 0.05, suggesting this data is at best weakly normally distributed.
Figure 5.21: Boxplot and histogram of work of adhesion (W) for all good tests using pull off force value.

The boxplot and histogram of work of adhesion (w) using preload normalized pull off force value are shown in figure 5.22. In this case, the histogram follows a normal distribution, like the preload normalized pull off force itself did (p = 0.45).

In summary, the preload normalized pull off force and work of adhesion (w) strongly follow the normal distribution of data. It seems that the preload has an influence over the pull off force. The ratio of preload and pull off force is more significant than pull off force alone. Therefore, the results of the normalized values are more reproducible than the pull off force in the normal testing system. The mean and standard deviation of the preload normalized pull off force value and work of adhesion (w) have been shown in table 5.2. As the data follows a normal distribution for 16 tests, we can expect that for larger set of good tests the standard deviation will be very close to the mean.

Figure 5.22: Boxplot and histogram of work of adhesion (w) for all good tests using preload normalized pull off force value.
### Table 5.2: Summary of entire distribution of values

<table>
<thead>
<tr>
<th></th>
<th>Preload normalized pull off force</th>
<th>Work of adhesion (w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>0.7</td>
<td>2.3</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.13</td>
<td>0.77</td>
</tr>
</tbody>
</table>

#### 5.3.2 Implications of including “Bad test” in the statistical analysis

![Statistical evaluation of all good tests with the bad tests of NT II](image)

**Figure 5.23:** Statistical evaluation of all good tests with the bad tests of NT II

<table>
<thead>
<tr>
<th>Failure</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tape adhesion</td>
<td>$4.21 \times 10^{-8}$</td>
</tr>
<tr>
<td>Misalignment</td>
<td>$9.98 \times 10^{-8}$</td>
</tr>
<tr>
<td>Sample delamination</td>
<td>$1.1 \times 10^{-7}$</td>
</tr>
<tr>
<td>Dust on sample surface</td>
<td>-</td>
</tr>
</tbody>
</table>

**Table 5.3:** P-value from the statistical evaluation of all good tests with the bad tests of NT II: a) Tape adhesion, b) Misalignment, c) Sample delamination, d) Dust on sample surface.
Due to the small data sets, the non-parametric Wilcoxon rank sum test has been performed to check whether the median of preload normalized pull off force for the good tests is significantly different from the bad tests. As most of the bad tests occurred due to tape adhesion, their results have been compared first with the good tests. The results (Figure 5.23 (A)) showed that the median from both tests is significantly different from each other (p-value: $4.21 \times 10^{-8}$). For the rest of the failures the results are also significantly different than each other. Their images and p-values has been shown in figure 5.23 (B-D) and table 5.3. For failure due to dust on the surface, there is only one sample. Therefore, its normalized value has been merged with results of the good tests. The resultant image showed that the value from this bad test lies outside the boxplot.

From the statistical evaluation, it is clearly visible that the results from the good tests and bad tests are significantly different than each other. Consideration of any bad test can influence the reproducibility of data.
5.3.3 Implications of including uncategorized results in the statistical analysis

The results from the good tests and uncategorized data have been merged together to check whether the results of uncategorized data can affect the overall conclusions (Figure 5.24). After merging the data for pull off force, we can see that the two values of uncategorized data are inside the standard deviation of the boxplot. However, the preload normalized pull off force of uncategorized data is almost unity, indicating that the value of preload and pull off force are nearly identical. In those cases, the difference between preload and pull off force ($\Delta F$) is less than 0.01 N.

When the $\Delta F$ is greater than 0.2 N, tape adhesion is clearly observed in the videos. Thus,
the threshold value for the difference between forces is considered as 0.01 N to distinguish the uncategorized data from the rest of the bad tests. Therefore, if the pull off force and preload are almost identical \( \Delta F < 0.01 \) and there is no visible tape adhesion in the in-situ video between the interfaces, then that data can be accepted as a 'good test'.

5.4 Physical interpretations of differences between different material systems

5.4.1 Suitability of Normal testing to distinguish between different metal-organic interfaces

After validating the reproducibility of data for a metal-organic material system, the preload was found to have a significant influence on the pull off force. Initially, before determining this as a critical parameter, the results obtained from six metal-organic material systems were compared with one another. Only the non-ideal force-distance curve and a \( \Delta d \) value more than 0.5 \( \mu m \) have been considered as an indication of bad test. Based on these criteria, only five tests for each sample are considered as “Good tests” from the first three samples (Al - Alq3, Al - BCP, Al - C60). For Au - Alq3, Au - BCP and Au - C60 the number of “Good tests” are one, two and four, respectively. The boxplot of pull off force for six metal-organic material systems has been shown in figure 5.25. The boxplot shows that the median value of pull off force for Al - Alq3 is higher than other material systems. The dispersion of Al - BCP is the least compared to others. However, the non-parametric test (Wilcoxon rank sum test) on six metal-organic systems could not reject the null hypothesis. In that test, the samples have identical median for small sets of data. The trend of the data (pull off force) for each metal-organic systems has been shown in table 5.4.

<table>
<thead>
<tr>
<th>Material system</th>
<th>Trend</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al - organic</td>
<td>Alq3 &gt; BCP &gt; C60</td>
</tr>
<tr>
<td>Au - organic</td>
<td>Alq3 &gt; BCP &gt; C60</td>
</tr>
<tr>
<td>metal - Alq3</td>
<td>Al &gt; Au</td>
</tr>
<tr>
<td>metal - BCP</td>
<td>Al &gt; Au</td>
</tr>
<tr>
<td>metal - C60</td>
<td>Au &gt; Al</td>
</tr>
</tbody>
</table>

Table 5.4: Trend of pull off force for material systems.
The most likely to affect the adhesion are \([11, 12, 60]\):

I) Chemical reaction between the metal and organic compounds,

II) Van der Waals (VdW) interaction between surfaces,

III) Interfacial fracture resistance,

IV) Metal diffusion on organic compounds.

### 5.4.2 Chemical reaction

<table>
<thead>
<tr>
<th>Metal-Organic interface</th>
<th>Chemical reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al - Alq(_3)</td>
<td>Yes; Oxidation</td>
</tr>
<tr>
<td>Al - BCP</td>
<td>Yes; Orbital mixing / charge transfer reaction</td>
</tr>
<tr>
<td>Al - C60</td>
<td>Yes; Covalent bond</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Metal-Organic interface</th>
<th>Chemical reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au - Alq(_3)</td>
<td>No reaction</td>
</tr>
<tr>
<td>Au - BCP</td>
<td>No reaction</td>
</tr>
<tr>
<td>Au - C60</td>
<td>Yes; Ionic bond</td>
</tr>
</tbody>
</table>

Table 5.5: Summary from chemical adhesion for Al-organic and Au-organic material systems (see section 3.2 for references).

From table 5.5, it is clear that Au is unable to react chemically with Alq\(_3\) and BCP but it does form an ionic bond with C60. On the other hand, Al is highly reactive with all organic materials. These results have been compared with the results from the Normal test. Compared to other metal-organic material systems, there are only one successful test for Au - Alq\(_3\) and two for Au - BCP. The comparison of chemical reaction with experimental results indicates that the Normal testing system might only be useful for chemically reactive interfaces.
5.4.3 Van der Waals interaction between surfaces

Hamaker constant (equation 2.7) and work of adhesion (equation 2.5) have been calculated using the optical properties (Table 3.3) of the materials. To calculate the Hamaker constant, the absorption frequency \( \nu_e \) has been taken as \( 3 \times 10^{15} \text{s}^{-1} \) [48]. A typical value of \( \sigma \) which is \( 0.4 \text{nm} \) [48], has been used to estimate \( D_0 = 0.16 \text{nm} \) from equation 2.8.

<table>
<thead>
<tr>
<th>Material name</th>
<th>Hamaker constant (A)</th>
<th>Predicted work of adhesion</th>
<th>Calculated work of adhesion (10^{-6}N.m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al - Alq3</td>
<td>9.6 \times 10^{-20}</td>
<td>-0.09</td>
<td>1.1</td>
</tr>
<tr>
<td>Al - BCP</td>
<td>1.0 \times 10^{-19}</td>
<td>-0.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Al - C60</td>
<td>1.52 \times 10^{-19}</td>
<td>-0.15</td>
<td>1.07</td>
</tr>
<tr>
<td>Au - Alq3</td>
<td>-2.65 \times 10^{-19}</td>
<td>0.27</td>
<td>1.03</td>
</tr>
<tr>
<td>Au - BCP</td>
<td>-2.82 \times 10^{-19}</td>
<td>0.29</td>
<td>1.1</td>
</tr>
<tr>
<td>Au - C60</td>
<td>-4.11 \times 10^{-19}</td>
<td>0.42</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Table 5.6: Value of Hamaker constant and work of adhesion.

The positive Hamaker constant for Al-organic interface suggests that the VdW force is attractive. On the contrary, the force is repulsive for Au-inorganic interface as indicated by the value of Hamaker constant. Therefore, Hamaker constant can be a parameter of importance to identify whether a combination of two different surfaces is acting positively or negatively at the interface. Moreover, the predicted work of adhesion acting at the interfaces shows maximum work for Al - Alq3. From the table 5.6, the value between Au-organic interface is found to be positive which implies that there is no significant work acting between the interfaces. There should therefore be a significant difference between the Al and Au interfaces in the quantitative values obtained from the Normal testing system, and some differences from the organic materials for each metal. The calculated and predicted values are found to follow the same trend for the Al-organic interface. Though the quantitative values were not convincing for the difference between Al and Au and their interaction with the organic molecules, the number of successful tests was consistent. Al-organic interfaces all have positive work of adhesion, and almost all tests were successful. Au-organic interfaces have negative work of adhesion, and there were almost no successful tests. Further study using a material with positive Hamaker constant, but values substantially different from Al are necessary to confirm if the Hamaker constant gives a good indication of the trends in adhesion strength for these systems.
5.4.4 Intrinsic fracture resistance (IFR)

If the intrinsic fracture resistances of organic and inorganic materials are close to each other, there might be a possibility that they adhere more than those who have dissimilar fracture values [39]. Therefore, IFR of organic materials has been normalized with respect to the metals for each material system. The theoretical intrinsic fracture resistance ($G$) of metal and organic materials has been calculated using equation 2.2.

Table 5.7: Value of material properties of metal and organic materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Young’s modulus (GPa)</th>
<th>Poisson’s ratio</th>
<th>Yield Strength (MPa)</th>
<th>Intrinsic fracture resistance / Length of the interface (N/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>70 [76]</td>
<td>0.33 [76]</td>
<td>68.14 [76]</td>
<td>$5.57 \times 10^5$</td>
</tr>
<tr>
<td>Au</td>
<td>79 [76]</td>
<td>0.44 [76]</td>
<td>220 [76]</td>
<td>$46.56 \times 10^5$</td>
</tr>
<tr>
<td>Alq3</td>
<td>100 [92]</td>
<td>0.33 [92]</td>
<td>77 [95]</td>
<td>$4.98 \times 10^5$</td>
</tr>
<tr>
<td>BCP</td>
<td>5.0 [93]</td>
<td>0.35 [93]</td>
<td>48.6 [110]</td>
<td>$18.8 \times 10^5$</td>
</tr>
<tr>
<td>C60</td>
<td>20 [94]</td>
<td>0.33</td>
<td>44.12 [111]</td>
<td>$8.16 \times 10^5$</td>
</tr>
</tbody>
</table>

Table 5.7 illustrates the mechanical properties of metal and organic materials. For the calculation, interface length scale is unknown and therefore the intrinsic fracture resistance / length scale were calculated. Given that there is limited mechanical property data on these organic molecules, the yield strength has been considered equivalent to the ultimate tensile strength. Some mechanical properties of the organic molecules are not available in the literature (as shown in table 3.3). The mechanical characteristics of BCP have been assumed to be identical to the behavior of “incompressible” materials such as polymethyl methacrylate (PMMA) at 120°C [93]. PCBM, a functionalized derivative of C60, is widely studied as an electron acceptor material in bulk heterojunction devices; therefore, it can be considered as an analogue of C60. Both of them have comparable structure and chemical properties [112]. While calculating the yield strength of BCP and C60, the values of PMMA and PCBM have been taken respectively. Poisson’s ratio for C60 has been considered as 0.33.
Figure 5.26: Comparison of organic-metal ratio for intrinsic fracture resistance / length of the interface parameter: (a) Al-organic material system and for (b) Au-organic material system.

Figure 5.26 represents the normalized values of intrinsic fracture resistance for all organic-metal material systems. The figure shows that the combination of Al - Alq3 and Au - BCP shows value close to 1. Though Al - Alq3 did in fact have the highest mean pull-off force, Au-BCP did not. All the mechanical properties of BCP had to be assumed to predict the intrinsic fracture toughness. Comparison of the experimental results with the literature indicates that this assumption is not necessarily valid. After neglecting Au - BCP, the intrinsic fracture resistance of Au and C60 is closer to 1, suggesting greater adhesion compared to Au - Alq3. The measured pull off force of Al - Alq3 and Au - C60 are higher than the remaining Al-organic and Au-organic material systems, respectively. This analysis supports the work of Vitali et al. [36,68], who concluded that two interfaces with similar material properties show strong adhesion.

5.4.5 Metal diffusion

<table>
<thead>
<tr>
<th>Material name</th>
<th>Shape</th>
<th>Unit cell structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>Sphere [77]</td>
<td>Face centered cubic [77]</td>
</tr>
<tr>
<td>Au</td>
<td>Sphere [77]</td>
<td>Face centered cubic [77]</td>
</tr>
<tr>
<td>Alq3</td>
<td>Tri-clinic [80,83]</td>
<td>Tri-clinic [80,83]</td>
</tr>
<tr>
<td>BCP</td>
<td>Ellipse (Assume)</td>
<td>Simple cubic (Assume)</td>
</tr>
<tr>
<td>C60</td>
<td>Hollow sphere [82]</td>
<td>Face centered cubic [82]</td>
</tr>
</tbody>
</table>

Table 5.8: Unit cell characteristics of metal and organic materials.
In the absence of chemical reaction, inorganic materials can diffuse into the organic layers during deposition. As the inorganic materials fill the pores of the organic materials, more force should be required to separate the interface. Crystal structure and unit cell area of the organic compounds are shown in Table 5.8. The intermolecular separation within the unit cell has been calculated and an approximate number of metal atoms that can diffuse on the voids has been predicted. For the calculation of metal diffusion, the shape of BCP has been assumed as an ellipse and the unit cell is considered as a simple cube structure, in the absence of diffraction data in the literature. As the atomic radius of Al (1.43 Å) and Au (1.44 Å) are almost alike, the number of diffusing species inside the organic one is assumed to be identical (Table 5.9). Both Al-organic and Au-organic material systems follow a common trend contradicting the experimental results. Moreover, the rate of diffusion is highest for BCP and lowest for Alq₃, which is completely opposite of the Normal testing results. As most of the material properties are assumed for BCP, we cannot rely on the trends predicted for the metal diffusion in such a system. Metal diffusion is likely not a significant factor in the adhesion strength measurements from Normal testing.

### Table 5.9: Metal diffusion in organic compounds.

<table>
<thead>
<tr>
<th>Material (unit cell volume)</th>
<th>Packing Factor</th>
<th>Measurement of unit cell (empty unit cell volume)</th>
<th>Number of Al atom in organic compound</th>
<th>Number of Au atom in organic compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alq₃ (1738.98 Å³)</td>
<td>0.62</td>
<td>Alq₃ (660.8 Å³)</td>
<td>54</td>
<td>53</td>
</tr>
<tr>
<td>BCP (2206.85 Å³)</td>
<td>0.52</td>
<td>BCP (1059.28 Å³)</td>
<td>87</td>
<td>85</td>
</tr>
<tr>
<td>C60 (2835.55 Å³)</td>
<td>0.74</td>
<td>C60 (737.243 Å³)</td>
<td>60</td>
<td>59</td>
</tr>
</tbody>
</table>

5.4.6 Summary

The material property review on Au - Alq₃ revealed that, there is no chemical reaction between Au and Alq₃. The intrinsic fracture resistance is poor. In addition, negative VdW force acts between the interfaces. That helps to explain the problems encountered during deposition of Au, where a thickness of 100 nm was not enough to stick to the organic substrate. To deal with that problem, the thickness was increased up to 400 nm. Yet, there was only one test that showed quantitative results. In addition, there were no videos from those experiments. However, based on the evidence, it appears that adhesion between Au - Alq₃ is extremely poor.

For Au - BCP, there are only two tests that showed quantitative results. For this material system,
a video from the bad test showed tape adhesion. The material property review on Au - BCP revealed that there is no chemical reaction between Au and BCP interface. Although the intrinsic fracture resistance is high for that interface, all of the material properties had to be assumed for BCP. In addition, calculation of the Hamaker constant suggests a negative VdW force acting between the interfaces. The result from the rest of the experiments showed tape failure. Based on that, we can conclude that adhesion between Au - BCP is extremely poor.

For Au - C60, the experimental results and material properties are more promising than other Au-organic material systems. Despite a predicted negative VdW force acting between the interfaces, there is a known covalent bond formation within the interface. The value from IFR is moderate. There are four “Good Tests” from the experiments. Based on that review, it seems that the Normal testing system measures quantitative values when there is a chemical reaction within the interface.

For all Al - organic tests, the number of “Good tests” are same. During the experiment, thickness of 100 nm is found to be sufficient for complete delamination.

There is a known oxidation reaction between Al and Alq3. The intrinsic fracture resistance is high. There is a positive Van der Waals force at the interface. The experimental results show a high pull force in this material system. The material property review of Al - BCP revealed that there is an orbital mixing within the interface. In addition, a positive Van der Waals force acts within the interface. For Al - C60 the experimental results and literature values are promising like other Al - organic samples. There is covalent bond acting between the interfaces. The value from IFR is moderate.

The following tables 5.10 and 5.11 show the experimental and theoretical outcomes of the metal-organic material systems studied in this thesis. As the results from Au - Alq3 and Au - BCP are not reliable, they have not been included for comparison. For Al-organic material systems, the experimentally observed trend follows the material property values. However, the trend is contradictory for inorganic-C60 material systems. For such a small set of samples, we cannot compare the experimental values of the inorganic-C60 with the material property values.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Sample</th>
<th>Sample</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>High Adhesion Strength</td>
<td>Intermediate Adhesion</td>
<td>Low Adhesion Strength</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Strength</td>
<td></td>
</tr>
<tr>
<td><strong>Experimental result</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pull off force</td>
<td>Al - Alq$_3$</td>
<td>Al - BCP</td>
<td>Al - C60</td>
</tr>
<tr>
<td>Work of Adhesion</td>
<td>Al - Alq$_3$</td>
<td>Al - BCP</td>
<td>Al - C60</td>
</tr>
<tr>
<td><strong>Material property</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organic-metal ratio for</td>
<td>Al - Alq$_3$</td>
<td>Al - C60</td>
<td>Al - BCP</td>
</tr>
<tr>
<td>intrinsic fracture resistance</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical adhesion</td>
<td>Al - Alq$_3$</td>
<td>Al - C60</td>
<td>Al - BCP</td>
</tr>
<tr>
<td>Predicted work of Adhesion</td>
<td>Al - Alq$_3$</td>
<td>Al - BCP</td>
<td>Al - C60</td>
</tr>
</tbody>
</table>

Table 5.10: Comparison of material property trends with experimentally observed trends for Al-organic material systems.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Sample</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>High Adhesion Strength</td>
<td>Low Adhesion Strength</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Experimental result</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pull off force</td>
<td>Au-C60</td>
<td>Al-C60</td>
</tr>
<tr>
<td>Work of Adhesion</td>
<td>Al-C60</td>
<td>Au-C60</td>
</tr>
<tr>
<td><strong>Material property</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organic-metal ratio for</td>
<td>Al-C60</td>
<td>Au-C60</td>
</tr>
<tr>
<td>intrinsic fracture resistance</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical adhesion</td>
<td>Al-C60</td>
<td>Au-C60</td>
</tr>
<tr>
<td>Predicted work of Adhesion</td>
<td>Al-C60 (attraction)</td>
<td>Au-C60 (repulsion)</td>
</tr>
</tbody>
</table>

Table 5.11: Comparison of material property trends with experimentally observed trends for metal-C60 material systems.
5.5 Suitability for comparing different material systems

From the preliminary results described in the previous section, the Al−Alq₃ material system was chosen to check the reproducibility of one sample, as described in section 5.4. However, based on those experiments, with the introduction of new potential experimental failures, and an understanding of the critical role of the preload in determining the pull off force, the results for the six metal-organic material systems were revisited. Unlike the previous section, here the preload normalized pull off force parameter has been considered for all the previously supposed “good” tests. Due to the small amount of data, values for metal-organic material systems have been described using the dot plot (Figure 5.27). Preload normalized pull off force for six material systems indicate that two types of results have been merged together. In the first type, the preload is lower than the pull off force and in the second type the preload is higher or almost equal to the pull off force. A horizontal dotted line has been plotted along the x-axis (x=1) to show this threshold. In all cases, $\Delta d$ is less than 0.5 $\mu m$. However, there are no videos available for these tests that show the experiment clearly from the side view. There are some videos from the bottom view, but they are not useful to identify bad tests. For NT II, all the evidence to classify a test as either good or bad is available. From our statistical analysis, it was clear that erroneously including the results from the bad tests can influence the conclusions drawn. Clearly, a complete set of data (force-distance curves, post-delamination images, and in-situ video from the side) is critical to determine the success rate of a Normal testing system.
From figure 5.27, all results for Au - Alq$_3$ and Au - BCP show PL<POF. Analysis in section 5.5 showed that there is no attractive interaction energy predicted at those interfaces. For these two material systems it is likely that, PL<POF is the indication of sample failure. Based on that result, the tests where pull off force is higher than preload ($\Delta F > 0.01$) should not be used to compare different material systems.

### 5.5.1 Comparison of different material systems in NT I

![Dot plot of preload normalized pull off force for metal-organic material systems.](image)

Figure 5.28: Dot plot of preload normalized pull off force for metal-organic material systems.

For Al - Alq$_3$, Al - BCP and Al - C60 material systems the number of good tests is three, three and two respectively. The Au - C60 material system performed ideally in two tests. The preload normalized pull off force values for metal-organic material systems have been compared using the dot plot (Figure 5.28). Straight lines have been plotted along the x-axis to check the range of data. For Al - Alq$_3$, the standard deviation is lower than the other Al-organic samples and for Au - C60, the results are from the two tests are identical. The dot plot clearly indicates that due to fewer amounts of data it is hard to distinguish any metal-organic systems from the other. Thus, we can conclude that a specific amount of good tests for each material system are required for adequate comparison. For such a small data set, Normal testing is not able to distinguish the metal-organic system from each other.
Chapter 6

Conclusion and Recommendations

6.1 Summary

Interlayer adhesion at the top contact promotes device efficiency and increases life span of organic optoelectronic devices. The reported results from several adhesion measurement techniques, however, are inconsistent. Establishment of a reliable adhesion testing apparatus to measure interlayer adhesion would be helpful. In this work, a series of investigations were performed to determine whether the Normal force testing approach is a viable method to measure adhesion between metal-organic interfaces. The analysis suggests that, this approach is promising to extract quantitative information on the adhesion strength. The in situ videos and images of delaminated samples are strongly correlated with the force-distance curve, and all three are necessary to determine whether a test was successful or not.

Normal testing with a stiff tape suggests that flexibility is an important factor for a successful adhesive along with known adhesion strength.

The results from Normal testing system were found to be reproducible for one metal-organic material system, following a normal distribution with a standard deviation of 0.13 for preload normalized pull off force. The outcomes from the experiment revealed that alignment and tape adhesion are two most important parameters that need to be controlled for a successful test. Statistical analysis revealed that these parameters can highly affect the interpretation if they are included in with the measured values. Another finding is that the pull off force is significantly influenced by the preload force applied during the loading step. As a consequence, a normalized value is essential to confirm the data distribution.
Finally, it was determined that no conclusion can be drawn regarding the ability of Normal testing system to determine a trend in the values of adhesion force for six metal-organic material systems. This situation can be attributed to two reasons: 1) Too little data from each material system and 2) Incomplete information from the output data. Especially, due to the absence of videos from the side view, the comparison of different materials was inconclusive.

The significant finding of this thesis is that Normal testing appears to be a viable approach to examining adhesion in organic systems. However, there are some critical parameters that need to be considered and controlled while measuring the adhesion force with a Normal testing system. Some recommendations for issues to consider in future Normal force tests have been described in the next section.

6.2 Recommendations for future experiments with Normal testing

- As the statistical evaluation is unable to show any significant differences for small amounts of data, more data is necessary for proper analysis. For future tests, we are recommending 20 good tests from each material set to observe trends in adhesion force.

- The Hamaker constant is a significant parameter to identify if a combination of two different materials acts positively or negatively at their interfaces. Prior to the experiment, it is recommended to estimate the Hamaker constant for the interfaces to see if it is a suitable material combination.

- All the samples must be made under similar conditions.

- Force-distance curve, image after sample delamination and in situ video, are correlated. Absence of any of these data makes a test inconclusive. For future experiments, it is strongly suggested to take pictures before and after the delamination of the organic and inorganic surfaces. In addition, taking video from the side view is required for each test to compare the data with the curve. The side view video will help to control for the critical experimental failures that can occur during the experiment.

- The preload has an influence on the measured pull off force. A fixed value of the preload should
be maintained to obtain consistent data in the loading zone.

- Control over the alignment is critical for a successful test. Therefore, a sample positioning stage for Normal testing system is required to prevent sample tilting and sample delamination.

- Prevention of tape adhesion is critical for a successful test. Thus, the tape size needs to be as close to the sample size as possible.

### 6.3 Proposal for the extension of the present work

- The Normal test with a tape of known adhesive strength proved the importance of flexibility for a good test. For future experiments, double sided flexible tape with the adhesive strength of 0.8 N/mm is recommended for Normal testing.

- A common failure in Normal testing system is tape adhesion. Thus, an adhesion test between the tape and ITO substrate is recommended to check the force-distance curve from the Normal testing system. The experiment can give insight about whether the preload is really a biasing factor for the pull off force at that interface.

- In the absence of chemical reaction, the result of Normal testing system is not promising. Other metal-organic material systems can be introduced to verify this statement. Based on the performance of six metal-organic material systems, chemically reactive metal [silver (Ag)] and noble metal [palladium (Pd) and platinum (Pt)] are recommended with the used organic materials for future analysis.

- Selection of a material system which is well characterized is critical for analysis. For example, the mechanical and structural property of BCP is unknown. As a result, the contribution of metal-BCP material system is unclear in the present work. A test is recommended where all the physical properties of materials are as known as Al - Alq,

- In this work, the surface analysis of the interfaces by the end of the experiment is omitted. However, there were previous investigations on the chemical states of metal-organic interfaces [78] using x-ray photoelectron spectroscopy. Investigation on the surface properties for metal-organic interfaces after delamination is recommended.
As the Normal testing is unable to expose any significant differences between material systems because of insufficient data, the same experiment can be performed again with a large data set for the six material systems. The objective is to check whether the Normal testing system can identify any significant differences between material systems (at least 20 good tests from each material set).

Several groups ([1,35–37]) working on organic electronics proved that surface modification by annealing the interlayers can increase the efficiency of organic devices. Therefore, a comparison of the adhesion force before and after the annealing would be of interest for a metal-organic material in Normal testing system.

Several groups ([1,35–37]) measured adhesion in the polymeric BHJ materials using different adhesion testing techniques. Adhesion test in the BHJ interlayers is recommended to compare their results with those of the Normal testing system.
Bibliography


Appendix A

Estimation of cut-off distance

A relation has been developed between cut off distance \( (D_0) \) and collision diameter \( (\sigma) \) for a closely packed plane solid surface by Israelachvili et al. [48]. In this calculation, each atom at the solid surface has nine neighboring atoms instead of twelve neighbors. Once an atom comes in contact with another surface, it gains binding energy \( (w) \) of three more atoms \([ (12 - 9)w = 3w ] \).

From equation 2.5,
\[
W_{Flat} = -\frac{A}{12\pi D_0^2}
\]

The relationship between work of adhesion \( (W_{Flat}) \) and surface energy \( (\gamma) \) to separate two flat surfaces from contact to infinity can be written as,

\[
W_{Flat} = -\frac{A}{12\pi D_0^2} = -2\gamma
\]

\[
D_0^2 = \frac{A}{24\pi\gamma}
\]

\[
= \frac{A}{24\pi} \times \frac{S}{3w}
\]

\[
= \frac{A}{24\pi} \times \frac{\sigma^6S}{3C}
\]

97
\[
= \frac{A}{24 \pi} \times \frac{\sigma^6}{3C} \times \frac{\sqrt{3\sigma^2}}{2}
\]

\[
= \frac{A}{24 \pi} \times \frac{\sigma^8}{2\sqrt{3C}}
\]

\[
= \frac{A}{24 \pi} \times \frac{\sigma^2}{\sqrt{3C}} \times \frac{1}{\rho^2}
\]

\[
= \frac{A}{24} \times \frac{\sigma^2 \pi}{\sqrt{3C} \pi^2 \rho^2}
\]

\[
= \frac{A}{24} \times \frac{\sigma^2 \pi}{\sqrt{3A}}
\]

\[
= \frac{\sigma^2 \pi}{24\sqrt{3}}
\]

Therefore, cut off distance,

\[
D_0 = \frac{\sigma}{2.5}
\]

where,

- surface energy per unit area for three atoms, \( \gamma = \frac{3w}{S} \)
- binding energy, \( w = \frac{C}{\sigma} \)
- surface area of each atom, \( S = \frac{\sqrt{3}}{2} \sigma^2 \)
- bulk atom density in a closed packed solid, \( \rho = \frac{\sqrt{2}}{\sigma^2} \)
Appendix B

Summary of adhesion test analysis
by various research groups
<table>
<thead>
<tr>
<th>Material</th>
<th>Adhesion testing system</th>
<th>Cathode</th>
<th>Active layer</th>
<th>Bi-layer</th>
<th>Anode</th>
<th>Adhesion failure</th>
<th>Adhesion strength ((J/m^2))</th>
<th>Interface Modification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al / LiF / P3HT: PCBM / PEDOT: PSS / ITO / Glass substrate</td>
<td>AFM</td>
<td>Al</td>
<td>PEDOT: PSS/ P3HT: PCBM</td>
<td>LiF</td>
<td>ITO / VPP PEDOT</td>
<td>PEDOT: PSS/ P3HT: PCBM [59]</td>
<td>40 \pm 4</td>
<td>X</td>
</tr>
<tr>
<td>SiN(_x) / Epoxy / PMMA / SiNx</td>
<td>DCB</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>PMMA / SiNx [37, 55]</td>
<td>4.58 \pm 0.85</td>
<td>X</td>
</tr>
<tr>
<td>Ag / PEDOT: PSS / P3HT: PCBM / ZnO / ITO / PET</td>
<td></td>
<td>Ag</td>
<td>PEDOT: PSS/ P3HT: PCBM</td>
<td>ZnO (electron selective contact)</td>
<td>ITO</td>
<td>PEDOT: PSS / P3HT: PCBM [35]</td>
<td>0.1 (\pm 0.1)</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Table B.1: Summary of adhesion test analysis by various research groups.
<table>
<thead>
<tr>
<th>Material</th>
<th>Adhesion testing system</th>
<th>Cathode</th>
<th>Active layer</th>
<th>Bi-layer</th>
<th>Anode</th>
<th>Adhesion failure</th>
<th>Adhesion strength $(J/m^2)$</th>
<th>Interface Modification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al / Ca / P3HT: PCBM / PEDOT:PSS / ITO / Glass substrate</td>
<td>FPB</td>
<td>Al / Ca</td>
<td>P3HT: PCBM / PEDOT : PSS</td>
<td>ITO</td>
<td>P3HT: PCBM</td>
<td>1 - 20</td>
<td>II) Annealing from 100°C to 200°C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>FPB</td>
<td>Al / Ca</td>
<td>P3HT: PCBM / PEDOT: PSS</td>
<td>ITO</td>
<td>P3HT: PCBM</td>
<td>1.5 - 1.8</td>
<td>I) Al electrode deposition rate 10, 20 and 40 Å</td>
<td></td>
</tr>
<tr>
<td></td>
<td>AFM</td>
<td>Al</td>
<td>MEH: PPV / PEDOT: PSS</td>
<td>LiF</td>
<td>ITO</td>
<td>PEDOT: PSS/ MEH: PPV</td>
<td>32 ± 0.7</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>DCB</td>
<td>Ag</td>
<td>P3HT: PCBM / PEDOT: PSS</td>
<td>ZnO (hole blocking layer)</td>
<td>PEDOT: PSS/ P3HT: PCBM</td>
<td>0.13 ± 0.07</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ag</td>
<td>MoO₂ P3HT: PCBM</td>
<td>ZnO (hole blocking layer)</td>
<td>P3HT: PCBM</td>
<td>0.39 ± 0.09</td>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>

Table B.2: Summary of adhesion test analysis by various research groups (continued).
<table>
<thead>
<tr>
<th>Material</th>
<th>Adhesion testing system</th>
<th>Cathode</th>
<th>Active layer</th>
<th>Bi-layer</th>
<th>Anode</th>
<th>Adhesion failure</th>
<th>Adhesion strength ($J/m^2$)</th>
<th>Interface Modification</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO/ NPB/ Alq / Mg:Ag / Ag</td>
<td>FPB</td>
<td>Mg:Ag</td>
<td>NPB/ Alq</td>
<td>ITO</td>
<td>Alq/ Mg:Ag [1]</td>
<td>0.39 ± 0.2</td>
<td>Pre-annealing (65°C for 15 minutes)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mg:Ag</td>
<td>NPB/ Alq</td>
<td>ITO</td>
<td>Alq/ Mg:Ag [1]</td>
<td>0.84 ± 0.2</td>
<td>Post-annealing (65°C for 40 minutes)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mg:Ag</td>
<td>NPB/ Alq</td>
<td>ITO</td>
<td>Alq/ Mg:Ag [1]</td>
<td>0.73 ± 0.2</td>
<td>Mixture of metal-organic interface (Alq : Mg : Ag = 47.5 : 47.5 : 5)</td>
<td></td>
</tr>
<tr>
<td>Au-BP-BPE-Au</td>
<td>AFM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.5 nN</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.8 nN</td>
<td>X</td>
</tr>
</tbody>
</table>

Table B.3: Summary of adhesion test analysis by various research groups (continued).
<table>
<thead>
<tr>
<th>Material</th>
<th>Adhesion testing system</th>
<th>Cathode</th>
<th>Active layer</th>
<th>Bi-layer</th>
<th>Anode</th>
<th>Adhesion failure</th>
<th>Adhesion strength ($J/m^2$)</th>
<th>Interface Modification</th>
</tr>
</thead>
</table>

Table B.4: Summary of adhesion test analysis by various research groups (continued).
Appendix C

Vacuum chamber setup at
McMaster University

C.1 Vacuum chamber setup

The following section will describe the instruments that have been used to run the vacuum chamber at McMaster University including their specifications and operating procedure. Figure C.1 is the flow chart of the vacuum chamber that is divided into three columns. The first column is the seven ports attached to vacuum chamber. The next column is about the electrical components used to run the vacuum chamber system. The final column is the mountings and safety accessories that assist the whole system.

Figure C.2 is the diagram of the complete experimental setup of the vacuum chamber.
Figure C.1: Flowchart for the complete setup of the vacuum chamber.
Figure C.2: Experimental setup of the vacuum system.
C.1.1 Vacuum chamber

A stainless steel vacuum chamber, built at the Max-Plank Institute for Metals Research (Germany), has been used to produce the adhesion samples. The chamber is (Length = 13.78", Diameter = 8.85") cylindrical shaped with seven outside ports (Figure C.3). Table C.1 represents a brief introduction to all the ports connected to the central vacuum chamber. Each port has its individual name and working function. Most of the ports are assembled directly with the chamber with the exception of port A and port G.

Port A is purchased from MBE - Komponenten and port G is a home built instrument. The following sub-section will explain all the ports in details.

<table>
<thead>
<tr>
<th>Port Identification</th>
<th>Port Name</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>Port A</td>
<td>High temperature source</td>
<td>MBE-Komponenten</td>
</tr>
<tr>
<td>Port B</td>
<td>View port</td>
<td>Part of the vacuum chamber</td>
</tr>
<tr>
<td>Port C</td>
<td>Ion gauge port</td>
<td>Part of the vacuum chamber</td>
</tr>
<tr>
<td>Port D</td>
<td>Sample input port</td>
<td>Part of the vacuum chamber</td>
</tr>
<tr>
<td>Port E</td>
<td>Sample manipulation port</td>
<td>Part of the vacuum chamber</td>
</tr>
<tr>
<td>Port F</td>
<td>Vacuum source</td>
<td>Part of the vacuum chamber</td>
</tr>
<tr>
<td>Port G</td>
<td>Low Temperature source</td>
<td>Home built</td>
</tr>
</tbody>
</table>

Table C.1: Summary of all the ports at the vacuum chamber.
Figure C.4: Port A - High temperature source.

Figure C.5: Overview of high temperature source (Port A): (A) Isometric view and (B) Bottom view.
C.1.2 Port A [High temperature source]

A 6.3” (16 cm) extended port of the vacuum chamber with a 2 3/4” flange is the main port for the high temperature source (Figure C.4(A)). The source is a standard effusion cell that evaporates suitable materials under vacuum. The manufacturer of this source is MBE-Komponenten, Germany. The high temperature Knudsen thermal evaporator is used to evaporate the inorganic materials. The source is powered by a DC power supply (Delta Elektronika). The material has been placed in the crucible inside the cell that is protected by a stainless steel shroud. Besides that, there are two ports of water supply inside the shroud to cool down the source during operation. Moreover, there is a C type thermocouple connection to measure the temperature (Figure C.5(B)).

C.1.3 Port B [View port]

This 0.78” (2 cm) extended port consists of 4 1/2” view port [Figure C.6 (A)]. The port helps to observe the place of the sample holder with respect to port A and port G.

Figure C.6: A) Port B - View port; B) Port C - Ion gauge source; C) Port D - Sample input port.
C.1.4 Port C [Ion gauge source]

This portion is the combination of eight sections. At first the elongated 1.18” (3 cm) 2 3/4” port is attached to a 2 3/4” tee joint. The left side of the T-joint has been attached to a combined joint of 2 3/4” flange to 1 1/3” reducer and a 1 1/3” quartz crystal monitor. On the other side, the T-joint is attached to another 2 3/4” T joint. The hole in the right side is attached to a 2 3/4’ nude ion gauge (Agilent technologies) and the other one covered with a 2 3/4’ blank [Figure C.6 (B)].

C.1.5 Port D [Sample input port]

This port is used to insert samples on the vacuum chamber which is now enclosed with 4 1/2” blank [Figure C.6(C)].

Three Positions:
1. Sample Loading
2. High temp. source position
3. Low temp. source position

Figure C.7: A) Port E - Growth deposition port; B) Schematic of Port E representing all the positions; C) Port F - Vacuum source.
C.1.6 Port E [Sample manipulation port]

Port E consists of a 1 1/3" shutter rod that has been attached to a substrate holder stage (Figure C.7 (A)). The shutter rod allows positioning of the sample holder stage of three separate positions of the sample holder mechanism. With the manipulation, the sample holder changes to position 1, 2 and 3 (Figure C.7 (B)).

Where, position 1 = sample parking position, position 2 = position to high temperature source, position 3 = position to low temperature source.

The port rotates forward in anti-clockwise direction and moves backward in the clockwise direction.

C.1.7 Port F [Vacuum Port]

This port starts with a 2 3/4" gate valve. A CF 2 3/4” to KF 40 adapter is attached to this gate valve. On the other side of the adapter, a bellow is clamped. The bellow acts as a link between the gate valve and vacuum pump (Figure C.7(C)).
C.1.8 Port G [Low temperature source]

The port is attached to a 2 3/4” nipple CF flange joint to accommodate the low temperature source (Figure C.8(A)).

The home built low temperature source is an effusion cell. The low temperature source is used to evaporate the organic materials. The source is powered by a DC power supply. Additionally, there is a K type thermocouple connection to measure the temperature. In this source, the ceramic crucible holder is coiled by tungsten (W) wire. The crucible is shielded by molybdenum (Mo) foil. Heat is supplied to the crucible by a wired network of tungsten and copper (Figure C.9(B)).
<table>
<thead>
<tr>
<th>Port</th>
<th>Electrical equipment</th>
<th>Company (Model No)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Port A</td>
<td>Power supply</td>
<td>Delta Elektronika (ES 030-10)</td>
</tr>
<tr>
<td>Port A</td>
<td>Temperature controller</td>
<td>Eurotherm (2408 PID Controller)</td>
</tr>
<tr>
<td>Port C</td>
<td>Ion gauge controller</td>
<td>Agilent Technologies (XGS 600 multi gauge)</td>
</tr>
<tr>
<td>Port C</td>
<td>Quartz crystal thickness monitor</td>
<td>Inficon XTC</td>
</tr>
<tr>
<td>Port F</td>
<td>Turbo molecular pump and Dry scroll vacuum pump</td>
<td>TCP 121 (Pfeiffer Vacuum) and SH 110 (Agilent Technologies)</td>
</tr>
<tr>
<td>Port G</td>
<td>Power supply</td>
<td>B&amp;K Precision (1550)</td>
</tr>
<tr>
<td>Port G</td>
<td>Temperature controller</td>
<td>Eurotherm (2408 PID Controller)</td>
</tr>
</tbody>
</table>

Table C.2: Electrical connections attached to the ports of the vacuum chamber.

### C.2 Electrical Setup

Table C.2 gives a brief outline of all the electrical equipment used to run an experiment with their manufacturer name.

#### C.2.1 DC power supply and temperature controller for High temperature source

DELTA ELEKTRONIKA Power Supply ES 030-10 Specification: Voltage range (0-30)V ; Current range (0-10)A.

The power supply is connected to Eurotherm 2408 PID controller. The controller can be programmed in a way that the power supply will deliver constant power to the high temperature source to evaporate the inorganic material.
C.2.2 Ion gauge controller

For experimental purpose, the pressure inside of the vacuum chamber is measured by a multi gauge controller (Agilent Technologies). To check the pressure inside, the multi gauge is connected to one side of port C, which consists a 2 3/4" nude BA type single filament uncoated Tungsten ion gauge [Figure C.10(a)]. The ion gauge consists of a triode combination that is a central collector surrounded by a grid wire and filament (Figure C.10).

The pressure indication works on three steps: I) Constant flow of electron from the filament, II) Ionization of gas molecules, III) Pressure indication of the ion gauge.

The electron emission current and the grid voltage are fixed. After passing current to the filament (cathode), electron moves from filament towards collector wire (anode). Before electrons are collected by grid, they hit the gas molecules. Therefore, positive ions and electrons are created from gas molecules. Positive ions are collected to the central collector ground wire. The ion current is proportional with the gaseous molecular density (pressure). The range of pressure indication by the multi-gauge (Agilent Technologies) controller is the calibration result of ion current [115].

C.2.3 Quartz crystal thickness monitor

During the deposition of thin films it is very important to measure the thickness, as it is a significant parameter to observe the mechanical properties of organic molecules and metals [104]. During thin film deposition, quartz crystal thickness monitor shows how much material is deposited on the
substrate using standard sensor.

The quartz crystal thickness monitor (INFICON XTC) provides the real time progressive indication of coating thickness during deposition of thin films. The principle is based upon the measurements of frequency change of a quartz crystal sensor during deposition [116]. This frequency change is measured and processed to provide a simple real time indication of the film thickness and deposition rate. The sensor itself is an industry standard crystal having a base resonance of 6 MHz. The sensor is easily exchangeable and requires no calibration. Additionally, there is a small electronic unit with the sensor that acts as the analog to digital conveyer.

To check the thickness three most important parameters have been used as the input value. They are density, Z-ratio and tooling factor. The first two parameters depend on the material and the last one is the geometrical positioning parameter for the crystal and sensor. Usually in a vacuum chamber, the sensor and sample are in different positions. Hence, their distance from evaporation cell is not equal. For that, the ratio between positioning of sample and positioning of sensor is known as the tooling factor. The position of sensor and samples are almost same in this vacuum chamber. Therefore, the tooling factor is 1.

C.2.4 Turbo pump

The turbo molecular pump [Pfeiffer (TCP 121)] has been used to create a vacuum inside the chamber. The pump consists of a combination of rotor/stator turbine blades. Those blades are designed in a way that air inside the chamber captured by the rotor and supplied to exhaust by stator to maintain the vacuum continuously. In addition, a dry scroll vacuum pump has been added with the exhaust of the turbo pump as a backing pump. As the turbo does not compress against atmospheric pressure, it always needs a backing pump (rotary vane pump, diaphragm pump or scroll pump).

C.2.5 DC power supply and temperature controller for low temperature source

B&K Precision (model no: 1550) power supply specification : Voltage range (0-30) V ; Current range (0-3) A. The power supply setting of low temperature source is slightly different from high temperature source. The evaporation temperature of organic material is unstable. For that, the power is regulated directly to the source. The K-type thermocouple is attached to Eurotherm 2408
PID Controller to measure the temperature.
C.3 Experimental problems and solutions

While setting up the vacuum chamber at McMaster University, several challenges came across its way. The motivation is to solve those problems in an efficient way.

C.3.1 Table design

The first major problem has been the necessity of a vacuum chamber holder. The central vacuum chamber is a bent structure and also, the whole system is only supported by a bracket. For that, design of a table has become prerequisite that will solve the problems mentioned below:

1. Support the bracket that holds the vacuum chamber,

2. Easy access to all the electrical components.

The vacuum chamber has been mounted on a frame (Figure C.11). The frame has been made from Aluminum T slot (CPI automation Ltd). The motivation of the design is to make a frame that is light in weight, flexible enough to move and can be mount easily.

![Vacuum chamber table.](image)

Figure C.11: Vacuum chamber table.

The structure of this frame consists of:

I) Two 16" Al extrusion,

II) Six 12" Al extrusion,

III) Four 24" Al extrusion,

IV) Four adjustable leveling feet,
V) Accessories: brackets, bolts and washers.

The frame is strong enough to hold the weight of the vacuum chamber. Adjustable foot has been placed at the bottom of each 24" Al extrusion slot to ensure a level surface. A support bracket has been used, as seen in figure C.11 to mount the chamber on the frame. The support bracket is an Al extrusion of 12" placed at a distance of 3.68" from the side to support the plate. The dimension of the plate is 24 cm × 20 cm. In the middle of the plate, there is a column (2.75") which supports the chamber. The support collar has four bolts in threaded holes to attach to the column to ensure stiffness of the vacuum chamber. Later, a wooden block has been placed under the table to place the transformer.

C.3.2 Sample holder

![Sample holder stage inside vacuum chamber; the inset on the top left is the crystal placed in the crystal holder.](image)

Figure C.12: Sample holder stage inside vacuum chamber; the inset on the top left is the crystal placed in the crystal holder.
Figure C.13: Schematic of the sample holder.

Figure C.14: Schematic representation of the sample holder: A) Position of sample holder facing at Port A and Port G; B) Position of sample holder facing at Port D.
The next challenge is to introduce a sample input mechanism in the port D.

The sample with the sample holder is insert into the sample holder assembly (Figure C.12).

This rotating port can change its position into three directions - A) Sample loading position, B) High temperature source position, and C) Low temperature source position.

Due to change of the sample holder position it is a challenge for the sample holder to stay inside the sample holder stage. For that, a mechanism has been established.

This mechanism has multiple purposes:
I) Allowing easily the sample holder in the chamber,
II) Easy withdrawal of the sample holder from the chamber,
III) Hold the sample holder in its place while rotating towards the multiple evaporation sources.

For the first two situations a flexible spring clip has been used.

On the other hand, a “Stop” has been made (Figure C.13) that is attached to the sample holder assembly. The stop is attached to the sample holder assembly with nuts, bolts and washer. Beneath of the two posts there is molybdenum (Mo) foil that acts as a shield. At high temperature source (Port A) and low temperature source (Port G) position, the stop is fixed to the sample holder head. However, while changing its position towards sample input (Port D), the stop is flexible enough to
slide at perpendicular direction. The situation makes easier to insert and withdraw the sample holder from the assembly. (Figure C.14)

To clarify the position of the sample holder with respect to the ports of the vacuum chamber a 2D image of the chamber has been drawn. Figure C.15 is showing the manipulation of the sample holder.

C.3.3 Cooling water supply for high temperature source

![Flow diagram of the water cooling system attached to the high temperature source of the vacuum chamber.](image)

The evaporation temperature of aluminum is more than 800°C. At such high temperature a continuous cooling system is mandatory to protect the crucible. Cooling water is circulated inside the high temperature source using a water cooling system. Figure C.16 is the diagram of the complete setup of the water cooling system [117].

On the supply line a flowmeter [Swagelok (Model No: VAF-GP-A9M-1-0)] has been added to control the fluid movement of the supply line. On the other hand, a flow indicator [Delavale Barksdale (Model No: 96163-1)] has been included on the return line to observe the flow of fluid during the experiment.

C.3.4 Low temperature source

As mentioned before, the home built low temperature source is used to evaporate the organic materials. However, the Knudsen cell of the source was not heating properly. A possible reason could be the
coil of tungsten (W) wire was broken. The old coil needed to be replaced with a new coil to solve the problem. The new spiral coil has to have even spacing. A drill bit has been selected according to the radius of the spiral coil. Then, the drill bit has put inside the chuck portion of a drill machine. After that, using the chuck key the chuck has been tightened. Next, the wire is rounded once on the drill bit and then the chuck allowed to be rotated. The rotation of the chuck is also converting the wire into a spiral coil structure. After making the spiral coil, the end part of the wire was sharp. A plier has been used to flatten this part. When the new coil is used in the Knudsen cell it worked properly to evaporate the organic material.
Appendix D

Complete force-distance curve from NT II

Figure D.1 is the complete force-distance curve from NT II. The hysteresis between the loading and unloading curve is the indication of tape viscoelasticity. In this thesis we were only interested in the pull off force and snap out force. Therefore, only the unloading portion is considered for analysis.

Figure D.1: Complete force-distance curve from NT II.