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SELF-ASSEMBLY OF MOLECULAR WIRES ON AU AND CU FOR MOLECULAR ELECTRONICS

by

AISYAH BINTI MOHAMAD SHARIF

B.Sc., M.Sc.

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

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Supervisors

Dr. Christophe Silien

Prof. D. Noel Buckley

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Declaration

Self-Assembly of Molecular Wires on Au and Cu for Molecular Electronics.

Supervisors: Dr. Christophe Silien and Prof. D. Noel Buckley, University of Limerick, Ireland

External examiner: Prof. Manfred Buck, University of St. Andrews, Scotland, UK

Internal examiner: Dr. Fernando Rhen, University of Limerick, Ireland

Chair (of Viva Voce): Dr. Ian Clancy, University of Limerick, Ireland

This thesis is presented in fulfilment of the requirements of the Degree of

Doctorate of Philosophy

"I declare that: this thesis is entirely my own work and has not been submitted to any other university or higher education institution, or for any academic award in the University of Limerick; and where use has been made of the work of other people, it has been fully acknowledged and referenced."

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AISYAH MOHAMAD SHARIF

Student ID Number : 0890391

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Publications

This work has been disseminated through the following publications.

Selected Peer Reviewed Journals:

- **Sharif, Aisyah M.;** Buckley, D. Noel; Buck, Manfred and Silien, Christophe. Bonding Asymmetry and Adatoms in Low-Density Self-Assembled Monolayers of Dithiols on Au(111), Journal of Physical Chemistry C, Vols. 115, 2011, 21800-21803.

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- **A. Sharif**, C. Silien and D.N Buckley, The Involvement of Adatoms in Low Density Self-assembled Monolayers of Dithiols on Au(111) : STM Approach, Agilent seminar, CRANN, Trinity College Dublin (TCD), Ireland, 6 December 2011

- **A. Sharif**, C. Silien and D.N Buckley, Bonding Asymmetry and Adatoms in Low Density Self-Assembled Monolayers of Dithiols on Au(111), COST Action Meeting: Action Conference and Management Committee Meeting, Kilmurry Lodge Hotel, Limerick, Ireland, 12th – 14th October 2011

Posters:

- **A. Sharif,** C. Silien and D.N Buckley, Morphology of Aromatic and Aliphatic α,ω-Dithiol Self-Assembled Monolayers Grown from Dilute Solution: Bonding Asymmetry and Adatoms, European Conference on Surface Science (ECOSS 28), University of Wroclaw, Poland, 28th August – 2nd Sept 2011
- **A. Sharif**, C. Silien and D.N Buckley, Morphology of Dithiol Self-Assembled Monolayers on Au(111) Surfaces, 1st annual UK-MALAYSIA-IRELAND Engineering Science Conference (UMIES) 2010, Queens University Belfast, Northern Ireland, 23rd – 25th June 2010
- **A. Sharif**, C. Silien and D.N. Buckley, Morphology of Dithiol Self-Assembled Monolayers on Au(111) Surfaces, Institute of Physics (IOP) Spring Weekend meeting: 'The definite particle' Hodson Bay Hotel in Athlone, Ireland, 26th -28th March 2010

Dedication

TO MY

BELOVED HUSBAND

(ANUAR AHMAD)

&

CHILDREN

(AMIR ASYRAF ANUAR

AND AMIRUL ADLI ANUAR)

The source of all good in me

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Abstract

Self-assembled monolayers (SAMs) of thiols, dithiols, or other bonding moieties are attractive molecular systems with expected applications in novel areas such as molecular electronics, biotechnology and chemical and bio-sensing. With two thiol or two dicarboxylic acid moieties, with aromatic and/or aliphatic backbone structures, these molecules have the ability to connect two metal electrodes, and have been chosen for this fundamental work on molecular wires.

Our work was first concerned with a study of the morphology and structure of self-assembled monolayers of such molecules on Au(111), at low and at high molecular coverage. We used scanning tunneling microscopy (STM) to investigate the self-assembly of two prototypic symmetric dithiols (1,6-hexanedithiol and biphenyl-4,4'-dimethanethiol) from dilute aqueous solutions and were able to correlate their growth with the deconstruction of the Au(111) herringbone pattern known to produce adatoms. For both molecules, we observed the formation of an initial low-density monolayer where the molecules are lying down and paired by 0.45 Å tall protrusions, assigned to Au adatoms. The other thiol terminal group is imaged differently, revealing a strong asymmetry in the dithiol bonding. The formation of vacancy islands and, thus, the extraction of additional adatoms from terraces were detected only after substantial molecular rearrangement and loss of bonding asymmetry. It is a first important result of our work to highlight the involvement of Au adatoms in the interfacial structure of dithiols on Au(111).

The self-assembly of dithiols is complex and for the sake of refining preparation methods of dithiol monolayers, we pursued by studying the interfacial implication of the solvent on the growth. More specifically, our work address the development of 1,4-benzenedimethanethiol SAMs on Au(111) in water and in hexane, which correspond to polar and non-polar solvent, respectively. Our investigations revealed that complete and ordered SAMs of lying-down dithiols can form on clean Au(111) in water within a few seconds, and that in hexane the adsorption is initially impeded by the rapid growth of an ordered hexane film that is gradually replaced by disordered domains of dithiol until completion of a saturated monolayer of standing-up dithiols. In the study, the STM data were complemented by electrochemical desorption (EC) and x-ray photoelectron spectroscopy (XPS) measurements. Our work has resolved the progression of the self-

assembly in both these polar and non-polar solvents, giving a new and clearer understanding on their implication on the interface evolution. The work further stresses the need for considering the whole trio solvent-dithiol-substrate when describing the self-assembly process.

In the third part of our work, we report our study of the evolution of the metal-molecule interfaces during the formation and measurement of metal-molecule-metal break-junctions prepared by STM. The latest are templates of nanoscale molecular electronic devices. Statistically relevant samples of current-distance curves were recorded using a Python script written for this purpose and conductance histograms were built from the data. Our work focused on dithiol and dicarboxylic acid BJT made when using tip and sample electrodes made of different metal or allied: the substrates were Au(111) surfaces unmodified or modified with a Cu monolayer prepared by underpotential electrochemical deposition (UPD) or modified with a Cu multilayer prepared by overpotential deposition, and the tip was made of Au or Cu. An important result of this section is to show that, even for small amount of Cu, Cu-molecule-Cu BJT are always preferred. Even at the very low voltage conditions (1 mV) of our study, metal transfer is thus important. An important corollary of our study is that using ambient-stable Cu UPD-modified Au(111), it is possible to reproduce Cu-metal-Cu molecular nano-junctions, which are otherwise difficult to measure due to the reactivity of Cu electrodes.

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List of Acronyms.

LSV	Linear sweep voltammetry
STM	Scanning tunnelling microscopy
XPS	X-ray photoelectron spectroscopy
EC	Electrochemistry
SERS	Surface-enhanced Raman spectroscopy
BJT	Break junction technique
BDMT	1,4-benzenedimethanethiol
HDT	1,6-hexanedithiol
BPDMT	Biphenyl-4,4'-dimethanethiol
NDT	1,9-nonanedithiol
BDMC	*p*-phenylenediacetic acid
DDT	1,12-dodecanethiol
SAMs	Self-assembled monolayers
Au	Gold
Cu	Copper
N_2	Nitrogen gas
RT	Room temperature
HOMO	Highest occupied molecular orbital
LUMO	Lowest occupied molecular orbital
UPD	Underpotential deposition
OPD	Overpotential deposition

CHAPTER 1. INTRODUCTION

1.1. Introduction

1.1.1. Molecular electronics

Molecular electronics is defined as the technology utilising single molecules or small groups of molecules to perform electronic functions. This idea had already been suggested since 1959 by the visionary physicist, R. Feynman. He proposed that the ultimate integrated circuits will be constructed at the molecular or atomic level.[1] The field of molecular electronics started to receive extensive attention in 1974 when Aviram and Ratner proposed a special diode designed from single organic molecule connected at either end to metallic electrodes.[2] The speciality of organic molecules in electronic components offers unlimited possibilities for technological development since the properties and functionality of these molecules can be precisely tailored during chemical synthesis. The employment of molecules in electronics offers the possibility to make use of self-assembled monolayers (SAMs), which influences the spontaneous organisation of components into patterns or ordered structures without human intervention.[3] SAMs are further discussed in the following section.

1.1.2. Self-assembled monolayers (SAMs)

SAMs offer a unique combination of physical properties that allow fundamental studies of interfacial chemistry, solvent-molecule interactions and self-organisation. Their well-ordered arrays and ease of functionalization make them ideal model systems in many fields.[4-8] The first self-assembly of alkylthiolate monolayer on gold was produced by Allara and Nuzzo at Bell laboratories in 1983.[9] They realised the utility of combining a relatively inert gold surface with a bifunctional organic molecule in a well-ordered, regularly-oriented array.

Applications of SAMs in nanotechnology relate to very different areas. Among them are molecular recognition,[4] biomimetic systems,[6] micro and nanofabrication,[7,10] nanodevices and molecular electronics.[8,11] Interest in molecular electronics is increasing due to the usage of organic molecules as a key electronic component. SAMs with ω-functional groups have been widely used for this purpose because of their unique advantages such as ease of preparation, highly ordered structure, and well-documented properties.[12-16] The functionalities on the top of SAMs mainly control the surface properties of the organic film. Among them, thiol-terminated surfaces, with their high affinity to metals, can serve as templates for the formation of metal film or metal wires at the SAM ambient interface by preventing the diffusion of metal into SAMs and the formation of a short circuit. The most suitable constituent for the formation of a thiol-terminated SAM is a linear dithiol. The ability of these dithiols to bond to two metal electrodes makes these molecules pertinent to the development of molecular electronics.[17] Dithiol SAMs have been utilised to make nanodevices, for measurements of electrical transport, and for multilayer formation.[12-15]

1.2. Purpose of study

α,ω-dithiol molecules show excellent properties as nanowires where they can be used as spacers in multilayer growth and as linkers for the attachment of nanoparticles for studying charge transfers in nanodevices. Thus, investigations of the behaviour of α,ω-dithiol in self-assembled monolayers on Au(111) and Cu surfaces are interesting for both academic researchers and engineers in the nanoelectronics field. The potentials of α,ω-dithiol as nanowire can only be fully exploited if structural properties and the conductivity of single molecule or molecular domains are understood with respect to each other. Therefore, the main objective of this study is to discuss the properties of dithiols SAMs when the molecules are attached to Au and Cu substrate for molecular electronics. More specifically, the aims of this study can be summarised as follows:

1. To investigate the morphology and structure of self-assembly of two symmetric dithiols (1,6-hexanedithiol and biphenyl-4,4'-dimethanethiol) on Au(111) in diluted aqueous solution.
2. To investigate the effect of solvent on the growth and structure of SAM of 1,6-benzenedimethanethiol (BDMT) on Au(111).
3. To investigate the Au and Cu metal transfer during the formation of metal-molecule-metal junctions.

1.3. Outline of thesis

This thesis is organised in eight chapters. A brief and comprehensive overview of the main points of the research process is shown in Figure 1.1. The thesis contains an introductory chapter which gives a general introduction on molecular electronics and self-assembled monolayers (SAMs) especially for readers who are not familiar with the subject. Each chapter in this thesis ends with a brief summary outlining the conclusions, achievements and findings that are established in the chapter. The remainder of this thesis is organised as follows:

Chapter 2 is a review of the literature on molecular wires self-assembly. The chapter presents previous research findings leading to the definition of the objectives of this study.

Chapter 3 is a review of the literature on molecular conductivity. The chapter presents the background study and previous research findings leading to the definition of the objectives of the study.

Chapter 4 covers the experimental procedures and methods for this work, including a summary of the basic principles of scanning tunneling microscopy (STM) imaging, scanning tunneling microscopy - break junction technique (STM-BJT), electrochemical desorption using electrochemical scanning tunnelling microscopy (ECSTM), x-ray photoelectron spectroscopy (XPS), cyclic voltammetry characterisation and potentiostatic electrodeposition techniques are presented.

Chapter 5 elaborates the results and discussions with respect to the involvement of Au adatoms in the interfacial structure for two prototypic symmetric dithiols (1,6-hexanedithiol, HDT and biphenyl-4,4'-dimethanethiol, BPDMT) on Au(111) from dilute aqueous solutions. The study was carried out by using STM imaging.

Chapter 6 presents the results and the discussions on the interfacial implications for water and hexane in the self-assembly of dithiols on Au(111) at low molecular concentration. BDMT was investigated in this study. The observations were made by STM, EC desorption and XPS to resolve the progression of the self-assembly in both polar and non-polar solvents and also to highlight the importance for considering the whole trio solvent-dithiol-substrate when describing the self-assembly process.

Chapter 7 is furnished with results and discussions on the metal transfer in molecular break-junction of dithiol and dicarboxylic acid on Cu and Au electrodes. The study was performed by employing STM-BJT.

Chapter 8 highlights the conclusions, the novel contributions of this study and recommendations for future research work.

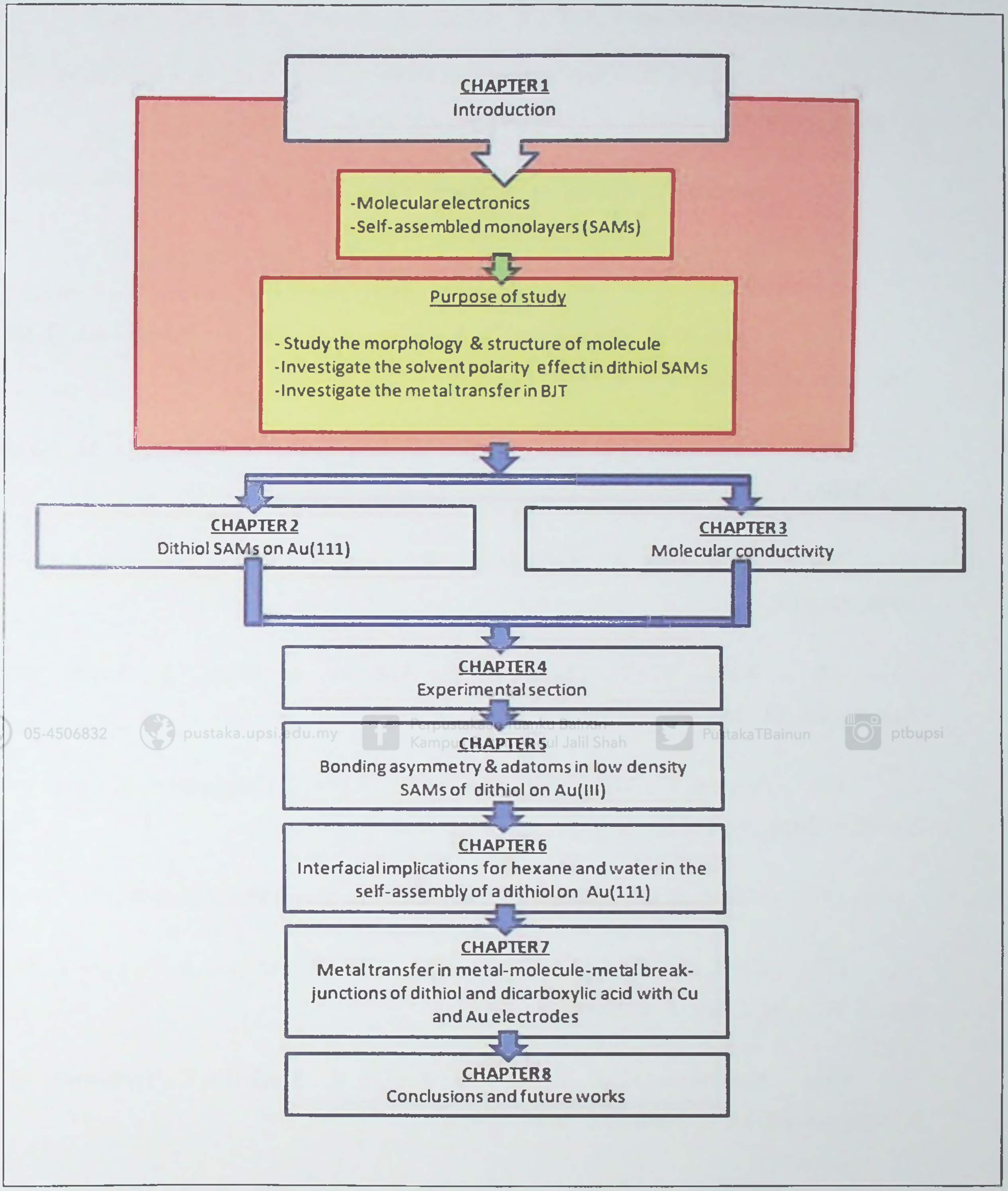

Figure 1.1 Summary of Chapter 1 and Thesis Framework.

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