1) CO - 6861 Paylaka INVC. AMS. 2/8/01

# **ELECTRODEPOSITION OF COPPER ON** POLISHED COPPER ELECTRODE

LING JIA TSUNG

UNIVERSITY OF MALAYA

2000



# ELECTRODEPOSITION OF COPPER ON POLISHED COPPER ELECTRODE

A Project Report Submitted
To
University Of Malaya
For The
Course SC 51191
In Fulfilment Of The Requirements
For The Degree Of

Master Of Science In Analytical Chemistry & Instrumental Analysis

**LING JIA TSUNG** 

2000

#### **ACKNOWLEDGEMENT**

The writer would like to express his greatest gratitude to his supervisor, Dr. Wan Jeffrey Basirun, who had contributed a great help in this project to completion. The writer also likes to thank Mr. Yusof Zaki, who had offered a great help in operating the SEM.

i

#### ABSTRACT

This project studies the surface morphology of the copper deposit from three different bath solutions on polished copper (3.1 mm in diameter) electrode by using Scanning Electron Microscopy. The behaviour of glycine as an additive in a bath solution containing 0.3 M of copper (II) sulphate and 2.2 M of sulphuric acid was studied by using cyclic voltammetry. In this project, glycine did not involved directly in the reaction of Cu<sup>2+</sup>/Cu couple but increased the potential and current density of the plating process. However, glycine has the properties for inhibiting the deposition of copper onto the copper disc. Moreover, block growth and nodules growth is observed on the surface of the copper disc.

### CONTENTS

Page	Number
ACKNOLDEGEMENT	i
ABSTRACT	ii
CONTENTS	iii
LIST OF TABLES	vi
LIST OF FIGURES	vii
LIST OF APPENDIXS	ix
CHAPTER 1: INTRODUCTION	
1.1 General Principles of Electrodeposition 1.1.1 Standard Potentials of Copper 1.1.2 Electroplating 1.1.3 Rate of Deposition 1.1.3.1 Faraday's Laws 1.1.3.2 Current Efficiency 1.1.3.3 Current Density 1.2 Nucleation and the Mechanism of the Electrodeposition of Metals 1.2.1 Nucleation 1.2.2 The Mechanism of the Electrodeposition of Metals 1.3 Electrode Kinetics 1.3.1 The Rate of Electron Transfer 1.4 Mass Transport 1.4.1 Diffusion 1.4.2 Convection 1.4.3 Migration 1.5 Voltammetry 1.5.1 Cyclic Voltammetry 1.5.2 EC Reaction 1.6 Scanning Electron Microscopy 1.6.1 Instrumentation 1.6.1.1 Electron Sources	1 1 3 6 6 6 7 8 8 10 15 20 21 22 23 24 24 25 28 29
1.6.1.2 Electron Optics 1.6.1.3 Detector 1.6.2 The Interactions of Electron Beams with Solids 1.6.2.1 Elastic Scattering 1.6.2.2 Inelastic Interaction 1.7 Properties of Copper	30 31 32 32 33 34
1.7.1 Chemical Properties	34

1.7.2 Physical Properties	35
1.7.2.1 Malleable	35
1.7.2.2 Electrical Conductivity	36
1.7.2.3 Thermal Conductivity	37
1.7.2.4 Corrosion Resistant and Application	38
1.8 Application of Copper Plating	40
1.8.1 Electrodeposition	41 44
1.8.2 Electropolishing	44 45
1.9 Objective	45
CHAPTER 2: METHODOLOGY AND MATERIALS	
2.1 Chemicals and Materials	46
2.2 Apparatus and Instruments	48
2.3 Fabrication and Polishing of Copper Working Electrode	50
2.3.1 Fabrication of Copper Working Electrode	50
2.3.2 Polishing of Copper Working Electrode	51
2.4 Experiment	52
2.4.1 Bath Solution Preparation	52
2.4.2 Instruments Setting and Operation	53
2.4.2.1 Operation of BAS 100 B/W Electrochemical	53
Workstation (Cyclic voltammetry Mode) 2.4.2.2 Operation of Model 363 Potentiostat/	53
Galvanostat (Plating)	56
2.4.2.2.1 Control E Operation	56
2.4.2.2.2 Control I Operation	58
CHAPTER 3: RESULTS AND DISCUSSION	
3.1 Cyclic Voltammetry	60
3.2 The R Square Coefficient	66
3.3 The Mechanism Study	68
3.3.1 Reversible Reaction	68
3.3.2 Irreversible Reaction	72
3.3.3 Effect of Additive	74
3.3.4 Effect of Chloride Ion	75
3.4 Plating Process	77
3.5 Rate of Copper Deposition	89
3.6 Effect of Additive	91
3.7 Surface Morphology of Plated Electrode	93
3.7.1 Dissolution of Copper	95
3.7.2 Plating at Constant Potential	96 99
3.7.3 Plating at Constant Current	100
3.8 EDX	100
3.9 Problems and Suggestion	101
CHAPTER 4: CONCLUSION	
4.1 Cyclic Voltammetry	103

4.2 Plating Process 4.3 SEM	104 104
REFERENCE	106
APPENDIX	108

#### LIST OF TABLES

Table		Page Numbe
1.1.1.1	Standard Potentials in Acidic Solution	2
2.1.1	Composition of copper (II) sulphate anhydrous	47
3.1.1	Peak currents obtained from different scan rates	60
3.1.2	Peak currents obtained from different scan rates	61
3.1.3	Peak currents obtained from different scan rates	62
3.1.4	Peak currents obtained from different scan rates	63
3.1.5	Peak currents obtained from different scan rates	64
3.1.6	Peak currents obtained from different scan rates	65
3.4.1	Current measured due to plating process on copper electrode at constant potential	77
3.4.2	Potential measured due to plating process on copper electrode at constant current	79
3.4.3	Current measured due to plating process on copper electrode at constant potential	81
3.4.4	Potential measured due to plating process on copper electrode at constant current	83
3.4.5	Current measured due to plating process on copper electrode at constant potential	85
3.4.6	Potential measured due to plating process on copper electrode at constant current	87
3.7	Appendix list for the SEM image for the surface of copdiscs due to different plating condition	per 93

### LIST OF FIGURES

Figure		Page Number
1.2.2.1	Types of site on a perfect crystal: 1, Kink site; 2, edge site; 3, adatom	11
1.2.2.2	A screw dislocation an its propagation leading to a spiral feature	13
1.2.2.3	Schematic of various growth forms observed in metal deposition: (a) layer growth, (b) ridge growth, (c) block growth, (d) pyramidal growth, and (e) dendritic growth	14
1.2.2.4	The variation of the characteristic growth modes on the normalised current density (I/I $_{\rm L}$ )	15
1.3.1.1	The variation of current as a function of the potent different	ial 19
1.4.1	Schematic of some of the processed that influence the rate of an electrode reaction	20
1.4.1.1	Diffusion to a large planar surface	21
1.5.1.1	Cyclic voltammogram for a reversible electron tran reaction	nsfer 25
1.5.2.1	Cyclic voltammograms showing the influence of chemical reaction on the observed voltammetric behaviour	27
1.6.1.1	Schematic of a SEM	29
2.2.1	A photograph of the cell used. (A) Counter electro (B) Working electrode, (C) Nitrogen gas inlet and (D) Reference electrode	de, 49
2.3.1.1	The fabricated copper working electrode	50
2.4.2.1.1	A photograph of a cell and the BAS 100B/W Electrochemical workstation	54
3.1.1	Graph of peak current versus square root of scan	rate 61

3.1.2	Graph of peak currents versus square root of scan rates	62
3.1.3	Graph of peak currents versus square root of scan rates	63
3.1.4	Graph of peak currents versus square root of scan rates	64
3.1.5	Graph of peak currents versus square root of scan rates	65
3.1.6	Graph of peak currents versus square root of scan rates	66
3.2.1	Voltammograms	67
3.3.1.1	The potential sweep (a) and corresponding current response (b) for the forward scan fragment	69
3.4.1	Graphs of current versus time for A1, A2, A3, A4 and A5	78
3.4.2	Graphs of potential versus time for A6, A7, A8, A9, A10 and A11	80
3.4.3	Graphs of current versus time for B1, B2, B3 and B4	82
3.4.4	Graphs of potential versus time for B6, B7, B8, B9, B10 and B11	84
3.4.5	Graphs of current versus time for C1, C2 and C3	86
3.4.6	Graphs of potential versus time for C6, C7, C8, C9, C10 and C11	88
3.7.2.1	Surface of copper deposit viewed at 19.42 KX magnification	97
3.7.2.2	Nodules growth viewed at 801 X magnification	99
3.7.3.1	Surface of the copper deposit on copper disc, viewed at 15.61 KX magnification	100

# LIST OF APPENDIXS

Appendix		Page Number
Α	Voltammograms	108
В	Voltammograms	114
С	Voltammograms	119
D	Voltammograms	125
E	Voltammograms	131
F	Voltammograms	135
G	SEM images for A1, A2, A3, A4 and A5	139
Н	SEM images for A6, A7, A8, A9, A10 and A11	144
I	SEM images for B1, B2, B3, B4 and B5	150
J	SEM images for A	155
K	SEM images for B6, B7, B8, B9, B10 and B11	156
L	SEM images for C1, C2, C3, C4 and C5	162
М	SEM images for C6, C7, C8, C9, C10 and C11	167
N	SEM-EDX spectrum	173
0	SEM-EDX spectrum	174
Р	SEM-EDX spectrum	175