Acknowledgements

首先要由衷感謝我的指導教授羅正忠教授與國家奈米元件實驗室蔡明蒔副主任在這兩年細心的指導，使我在研究所的求學過程中受益良多。也感謝論文口試委員葉清發教授、邱碧秀教授以及龔正教授能夠在百忙之中抽空前來指導，並且給予我寶貴的建議，讓我獲益匪淺。

感謝國家奈米元件實驗室賴明志先生、李美儀小姐、劉育彬先生、孫旭昌先生和趙子綾小姐等人在實驗中的協助。

感謝方政煜學長在我做實驗沮喪時，能給我安慰和鼓勵；在我做實驗茫然時，能適時的指引我方向，使我能夠順利完成實驗。也感謝實驗室同學蔣陳偉和施俊宏在試片製作的大力協助。同時也感謝學長薛國欽、黃秉緯；同學陳昶維、鍾漢邠、洪啟哲、張祐慈、黃俊傑、魏伸紘；學弟呂國源、傅文煜和紀伯翰在其它方面所給予的協助。

最後感謝我的父母吳正義先生、吳羅甘妹女士，感謝他們的照顧與關懷，也感謝我的姊姊、姊夫和弟弟在精神上的支持與鼓勵，使得我得以順利完成碩士學位。

Contents

Abstract (in Chinese)……………………………………………………………………….i

Abstract (in English)…………………………………………………………..................iii

Acknowledgement……………………………………………………………………….v

Contents………………………………………………………………………………....vi

Table Captions…………………………………………………………………….....ix

Figure Captions……………………………………………………………………….....x

Chapter 1 Introduction

1.1 Background ………………………..………...……………………...……..…………1

1.1.1 Copper Interconnect in IC manufacture…..………………….……..………….………1

1.1.2 Post-Cu CMP Cleaning……………………………………………………………...2

1.1.2.1 Particle Contamination Cleaning………..……………………….………………3

1.1.2.2 Metallic Contamination Cleaning……………………………………………....4

1.2 Motivation…………………………………...……………………..…………………5

1.3 Thesis Outline……………………………………………………………….…………6

Chapter 2 Fundamental Concepts of Post-Cu CMP Cleaning

2.1 Mechanisms for Particle Contamination….…………………………………………...15

2.1.1 Particle-Wafer Interaction………………………..………………….…………...15

2.1.1.1 Van der Waals forces……………………………………………….……………15

2.1.1.2 Electrostatic Forces………………………………………………..……………16

2.1.1.3 Chemical Bonding………………………………………………………...….16

2.1.2 Embedding of Particles………………..…..………..…………….....…………...17

2.2 Particle Contamination Removal…..…………………………………….……………17

2.3 Mechanisms for Metallic Contamination……………………..…….……………………18

2.4 Metallic Contamination Removal……………………………………………………..…19

Chapter 3 Cu Contamination Removal with Metal Chelators

3.1 Introduction………………………………………………………………………………...21

3.2 Experimental Procedures…..………………….……………………………………….....21

3.2.1 Wet Ability Test with Metal Chelators on Oxide Surface……………………....22

3.2.2 Corrosion Test with Metal Chelators on Copper Surface.………...……..…..22

3.2.3 Electrochemical Measurement..…..……………………………………………22

3.2.4 Cleaning Efficiency with Metal Chelators……………………………………..…23

3.2.4.1 Sample Preparation……………………………………………………..23

3.2.4.2 CMP and Post-CMP Cleaning Process…………………………..……....23

3.3 The Performances of Metal Chelators………………………………………..……….....24

3.4 Results and Discussions……………………………………………………………………27

3.4.1 Wetting Ability……………………………………….……………………...……27

3.4.2 Copper Corrosion……………………….……..……………………………………27

3.4.3 pH Effect on Copper Corrosion…………….……….……………………..……27

3.4.4 Cleaning Efficiency……………………..…………………………………………28

3.4.5 pH Effect on Cleaning Efficiency…………………..…………..……….....……28

3.5 Summary……………………………………………………………………………………30

Chapter 4 Effect of Novel Corrosion Inhibitors on Electrical Properties of Cu Interconnect

4.1 Introduction………………………………………………………………………………...45

4.2 Experimental Procedures……….…………………………..……………………………..46

4.2.1 Effect of Temperature on Passivation Layers..………………………...…………..…46

4.2.2 Effect of Metal Chelators on Passivation Layers……………………………..46

4.2.3 Surface Morphology after Post-Cu CMP Cleaning…………………….……….47

4.2.4 Effect of Passivation Layers on Surface Leakage Current…………………..…47

4.3 Results and Discussions……..……………………………………………….………..50

4.3.1 Thermal Stability of Passivation Layers………..…..……..….…..…………….50

4.3.2 Chemical Durability of Passivation Layers in Metal Chelators……..…..…..50

4.3.3 Copper Surface Morphology…………………………………….……....……….51

4.3.4 Result of Evaluating Passivation Effect on Surface Leakage Current……...…51

4.4 Summary………………………………………..……………..…..……....……….52

Chapter 5 Conclusions

5.1 Conclusions………………………………………………………………………………77

References...………………………………………………………………………………79

Vita..……………………………………………………………………………………..…84

Table Captions

Table.1-1 Properties of various metals

Table.1-2 Major post CMP cleaning methods

Table.3-1 Polishing parameters for cleaning experiment

Table.3-2 The cleaning steps and parameters of SSEC-M50

Table.3-3 Result of contact angle with metal chelators

Table.4-1 Polishing parameters for surface morphology evaluation

Table.4-2 Polishing parameters of evaluating passivation effect on surface leakage current

Table.4-3 The cleaning steps and parameters of SSEC-M50

Table.4-4 The contact angle of passivation layers after immersion of metal chelators

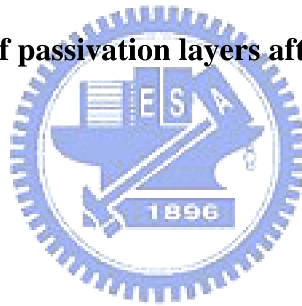

Figure Captions

Figure.1-1 Comparison of intrinsic gate delay and interconnect delay (RC) as a function of the feature size

Figure.1-2 Cross-sectional view after the different process steps for the damascene technique

Figure.1-3 Proposed mechanism of planarization of patterned features by CMP

Figure.1-4 Interacting factors in a CMP process

Figure.1-5 colloidal silica chemisorbed onto the copper oxide layer by means of oxygen bridging bonding

Figure.1-6 (a) Pourbaix diagram for the Cu-H_2O system

(b) Regions of corrosion, passivation, and immunity

Figure.1-7 (a) Chemical structure of dinonylnaphthalenesulfonic acid (DNNS)

(b) Chemical structure of 2-Phosphonobutane-1,2,4-tricarboxlic acid tetrasodium salt (PBTC-Na_4)

Figure.2-1 Electrostatic double layer around a particle

Figure.2-2 Geometry of an embedded particle into the wafer surface during CMP

Figure.3-1 Metal chelators used in this study

Figure.3-2 Contact angle measuring points in the wafer surface

Figure.3-3 The cleaning experiment flow

Figure.3-4 (a) Schematic diagram of the Westech Model 327M CMP polisher

(b) Platen assemblies of the Westech Model 327M CMP polisher

Figure.3-5 Diagram of a liquid drop showing the contact angle

Figure.3-6 Schematic of 4-point probe configuration

Figure.3-7 A schematic diagram of the three-electrode cell for in situ electrochemical measurements

Figure.3-8 (a) Arrangement for TXRF analysis

(b) Path of the X-rays in a commercially available TXRF instrument

Figure.3-9 The etch rate for copper with metal chelators

Figure.3-10 The etch rate as a function of citric acid concentration with different pH

Figure.3-11 Tafel diagram of acetic acid with different pH

Figure.3-12 The etch rate as a function of acetic acid concentration with different pH

Figure.3-13 Tafel diagram of acetic acid with different pH

Figure.3-14 The cleaning efficiency as a function of cycle with concentration=$5E^{-4}$M

Figure.3-15 The cleaning efficiency as a function of concentration with Cleaning cycle=40

Figure.3-16 The cleaning efficiency as a function of citric acid cleaning cycle with concentration=$5E^{-4}$M

Figure.3-17 The cleaning efficiency as a function of citric acid concentration with cleaning cycle=40

Figure.3-18 The cleaning efficiency as a function of acetic acid cleaning cycle with concentration=$5E^{-4}$M

Figure.3-19 The cleaning efficiency as a function of acetic acid concentration with cleaning cycle=40

Figure.4-1 (a) Comb structure interconnect

(b) Cross-section of comb structure interconnect

Figure.4-2 Schematic illustration of an AFM

Figure.4-3 ESCA measurement schematic

Figure.4-4 ESCA spectra of copper film after immersed in HNO_3/DNNS

Figure.4-5 ESCA spectra of copper film after immersed in HNO_3/PBTC-Na_4

Figure.4-6 Contact angle analysis of temperature effect on passivation layers

Figure.4-7 TDS spectra of pattern copper wafer after immersed in HNO_3/DNNS

Figure.4-8 TDS spectra of pattern copper wafer after immersed in HNO_3/PBTC-Na_4

Figure.4-9 AFM images of polished copper film with HNO_3/BTA =0.6/1E^{-4}M buffing, buffing time=1min (a) 3D diagram (b)roughness analysis

Figure.4-10 AFM images of polished copper film with HNO_3/DNNS=0.1/5E^{-2}M buffing, buffing time=1 min (a) 3D diagram (b)roughness analysis

Figure.4-11 AFM images of polished copper film with HNO_3/DNNS=0.1/5E^{-2}M buffing, buffing time=3 min (a) 3D diagram (b)roughness analysis

Figure.4-12 AFM images of polished copper film with HNO_3/DNNS=0.1/5E^{-2}M buffing, buffing time=6 min (a) 3D diagram (b)roughness analysis

Figure.4-13 AFM images of polished copper film with HNO_3/DNNS=0.1/1E^{-2}M buffing, buffing time=1 min (a) 3D diagram (b)roughness analysis

Figure.4-14 AFM images of polished copper film with HNO_3/DNNS=0.1/1E^{-2}M buffing, buffing time=3 min (a) 3D diagram (b)roughness analysis

Figure.4-15 AFM images of polished copper film with HNO_3/DNNS=0.1/1E^{-2}M buffing, buffing time=6 min (a) 3D diagram (b)roughness analysis

Figure.4-16 AFM images of polished copper film with HNO_3/PBTC-Na_4 =0.6/5E^{-3}M buffing, buffing time=1 min (a) 3D diagram (b)roughness analysis

Figure.4-17 AFM images of polished copper film with HNO_3/ PBTC-Na_4=0.6/5E^{-3}M buffing, buffing time=3 min (a) 3D diagram (b)roughness analysis

Figure.4-18 AFM images of polished copper film with HNO_3/PBTC-Na_4=0.6/5E^{-3}M buffing, buffing time=6 min (a) 3D diagram (b)roughness analysis

Figure.4-19 AFM images of polished copper film with HNO_3/ PBTC-Na_4=0.6/1E^{-3}M buffing, buffing time=1min (a) 3D diagram (b)roughness analysis

Figure.4-20 AFM images of polished copper film with HNO_3/ PBTC-Na_4=0.6/1E^{-3}M buffing, buffing time=3min (a) 3D diagram (b)roughness analysis

Figure.4-21 AFM images of polished copper film with HNO_3/ PBTC-Na_4=0.6/1E^{-3}M

buffing, buffing time=6 min (a) 3D diagram (b)roughness analysis

Figure.4-22 distribution of surface leakage current for Cu-comb interconnect measured at 90V

Figure.4-23 Dielectric degradation mechanism