

ACU 7198



**FORMATION OF COPPER DOTS IN  
COPPER DECORATION TECHNIQUE**

**By**

**PUNG SWEE YONG**

**A dissertation submitted in partial fulfillment for the  
Degree of Master of Technology (Material Science)**

**at the**

**Institute of Postgraduate Studies**

**University of Malaya**

**April 2002**



# Contents

<b>ACKNOWLEDGEMENTS</b>	i
<b>ABSTRACT</b>	ii
<b>CHAPTER ONE: INTRODUCTION</b>	1
<b>CHAPTER TWO: LITERATURE REVIEW</b>	
2.1 Overview of copper decoration technique	4
2.1.1 Growth of silicon dioxide (SiO <sub>2</sub> ) layer	7
2.1.2 Defects in the SiO <sub>2</sub> layer	10
2.1.3 Electrolysis process	16
2.1.3.1 Ions transportation in electrolyte	17
2.1.3.2 Effects of ions concentration on the conductivity of electrolyte	18
2.1.3.3 Voltage drop in electrochemical cell	20
2.2 Gate oxide integrity	22
2.2.1 Oxide breakdown in Metal-Oxide-Semiconductor (MOS) structure	22
2.2.2 The mechanism of oxide breakdown	23
2.2.3 Gate Oxide Integrity (GOI) measurement	27
2.2.3.1 Time Zero Dielectric Breakdown (TZDB) method	28



3.2.2.6	Effect of stressed field on defect density of copper decorated wafers	50
3.2.2.7	Analyzing the composition of gray ring surrounded copper dots by using TOF-SIMS	51
3.2.3	Determination of stressed field by $V_{ox}/V_{app}$ ratio measurement	52
3.2.4	Effects of copper concentration in methanol on copper decoration process	54
3.2.4.1	Effect of copper concentration on the conductivity of methanol	54
3.2.4.2	Effect of copper concentration on the size (average diameter) of copper dots	56

## **CHAPTER FOUR: RESULTS AND DISCUSSIONS**

4.1	Formation of copper dots on oxidized wafer surface	58
4.1.1	Analyzing the purity of anode using Energy Dispersive X-ray Spectroscopy (EDS)	58
4.1.2	Determination of copper concentration in methanol using Inductive Couple Plasma – Optical Emission Spectroscopy (ICP-OES)	61
4.1.3	Transportation of copper ions in methanol	65
4.1.4	Detection of permanent damages extended to wafer surface as a result of oxide breakdown	66
4.1.5	Studying distribution of copper dots size on copper decorated wafer	70

4.1.6 Studying the impact of size of D-defects on the size of copper dots	72
4.1.7 Effect of stressed field on defect density of copper decorated wafers	79
4.1.8 Analyzing composition of grey ring surrounded copper dots by using TOF-SIMS	82
4.1.9 Formation of copper dots on copper decorated wafer	93
4.2 Determination of stress field by $V_{ox}/V_{app}$ ratio measurement	98
4.3 Effects of copper concentration in methanol on copper decoration process	102
4.3.1 Effect of copper concentration on the conductivity of methanol	102
4.3.2 Effect of copper concentration on the size (average diameter) of copper dots	105
<b>CHAPTER FIVE: CONCLUSION</b>	107
<b>REFERENCE</b>	111
<b>APPENDIX</b>	115

## ACKNOWLEDGEMENTS

I am deeply indebted to my supervisor, Dr. Burhanuddin for his unfaltering support during my research and thesis preparation. His numerous suggestions and critical remarks have contributed immensely to the thesis.

Appreciation is also expressed to my advisor, Mr. G.A. Tan in S.E.H. (M) Sdn. Bhd. for his helpful discussion and penetrating criticism to make this thesis a success and presented in proper form. I am grateful to him for going through the thesis very carefully and helping me to improve it in many ways although he is really tight up with his work.

My sincere thank to Mr. F. M. Lim, Mr. W.P. Lee, Dr. Seow Wilson, and fellow colleagues of Materials Characterization Department, S.E.H. (M) Sdn. Bhd. for their support, encouragement and allowing me to use the necessary facilities.

Finally, special gratitude is expressed to my family and my girlfriend, Ms. M.K Liang, for their cares, understanding and encouragement during the entire period of this research.

Pung Swee Yong

April 2002

## ABSTRACT

Copper ions are dissolved from highly pure copper plate into the methanol during copper decoration process. As a result, copper concentration in methanol is increased with time. The copper concentration in methanol measured by ICP-OES is correlated well with the calculated value based on the magnitude of current and time during the process. Consequently, higher magnitude of current can be applied to build up copper concentration in methanol in shorter period.

When copper ions are ejected in methanol, they are positively charged. They experience force from electric field and migrate towards oxide surface. Eventually, these copper ions will be discharged and deposited at localized breakdown spots on oxide surface as copper dots. These copper dots are surrounded by grey ring. TOF-SIMS analysis on these copper dots shown that Na, Mg, K and Ca are responsible for the formation of the grey ring.

Copper dots are formed on oxide breakdown spots when oxide layer is subjected to stress field. When these defects are subjected to constant field, weaker spots will breakdown. In fact, these permanent damages are created not only at the oxide but extended to the wafer surface. Damages on wafer surface can be revealed and enlarged by preferential etching. These damages also provide localized conducting paths that allow electric current to flow through the oxide layer. Since electrons are supplied to these breakdown spots, copper dots are formed on wafer surface.

It is believed that defects integrated in the oxide layer degrade the oxide layer differently. This phenomenon is observed when higher defect density of copper dots is obtained with increasing of applied field. When higher electric field is applied to the oxide layer, those weak spots that do not breakdown initially will not be able to withstand the stress field. Consequently, more copper dots will be grown on the wafer surface. In addition, different size of copper dots on copper decorated wafer further support the above hypothesis.

The existence of the peak on the copper dot can be due to the oxide underneath the copper dot peak is the origin of a localized breakdown spot. Therefore, the spot has longer time for copper ions deposition. Moreover, the oxide underneath the copper peak might experience most severe breakdown. This allows higher current density to flow through it. Consequently, more ions are deposited at the particular spot and copper dot's peak is formed on the oxide surface.

Our experimental results also show that copper concentration in methanol plays an important role in copper decoration technique. Increasing of copper concentration is correlated with increasing conductivity and increasing of the average size of the copper dots. By controlling copper concentration in methanol in a proper range, it is possible to obtain repeatability and reproducibility copper decoration results.