UNIVERSITI TEKNIKAL MALAYSIA MELAKA

SILTERRA CLEANING SOLUTION IN POST CHEMICAL MECHANICAL POLISHING OXIDE TO MINIMIZE AMMONIACAL NITROGEN IN EFFLUENT

MUHAMMAD ASYRAF SAID

DOCTOR OF ENGINERING

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A thesis submitted
in fulfillment of the requirements for the degree of
Doctor of Engineering

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DEDICATIONS

Special thanks to my wife, Mrs. Nurtakhyatil Ezira binti Mohd Nawawi and my children; Nuraina Madihah, Nuraina Fatini, Nuraina Sofea and Muhammad Atif Farghaly for their understanding and continuous support. Many thanks to my beloved mother; Mrs. Hekmat Mabrouk Hasan Al-Farghaly and in memory of my late father, Mr. Said Bakar for their endless love and encouragement. I am also thankful to my parents-in-law, Mr. Mohd Nawawi Hussin and Ummi Kalsom for their motivations. My gratitude to Mr. Abdul Mughith and Mrs. Jihan for their comments of this thesis and thank you to all who have directly or indirectly contributed in this research, your kindness will always be remembered.

ABSTRACT

Malaysia's Department of Environment (DOE) has introduced ammoniacal nitrogen as a new parameter to be regulated under the Environment Quality (Industrial Effluents) Act effective from 1st January 2010. The penalty for not complying to any provision of the Environmental Quality Act (EQA) is a fine not exceeding RM10,000 and/or up to two years imprisonment with an additional fine of RM1,000 per day so long as the offence continues. Extensive use of ammonium hydroxide particularly in the Chemical Mechanical Polishing (CMP) process has been identified as one of the contributing factors that led to the high ammoniacal nitrogen in the final discharge. This thesis focuses on evaluating the Scrubbing cleaning efficiency using a SpeedFam IPEC (SFI) AvantGaard™ 776 polisher at CMP as high flow of effluents containing ammoniacal nitrogen is being discharged due to the rinsing of ammonium hydroxide flow mixed with ultra pure water (UPW). The main objective of this study is to formulate an alternative cleaning process at the Scrubbing stage without compromising the cleaning efficiency. The unique formulation of SCS (SilTerra Cleaning Solution) containing hydrogen peroxide, sulphuric acid and an additive has been analyzed in the Scrubbing process since it contains the necessary ingredients to oxidize and dissolve the contaminants on wafers surface. The formulated acid provides comparable capability with ammonium hydroxide on particles and metallic ions in which both cations and anions removal efficiency was higher than 97%. The chemical is a proprietary of SilTerra by four inventors registered as a trade secret invention. It was discovered that the particles on the wafers were effectively removed with 99% efficiency during the Buffing step. The attempt to eliminate the application of chemicals during Scrubbing requires further studies as the Sulphur removal was not promising with the removal efficiency lower than 84%, comparatively lower than SCS and ammonia, delivering more than 97% removal. It is generally known that mobile ions especially the metallic residuals may damage the circuits but the allowable limit of mobile anions affecting post-CMP processed wafers were not discussed in details. In addition to this, these anions are expected to be cleaned by Tungsten slurry applied during Buffing process which is acidic and contains more than 3% hydrogen peroxide. As such, application of chemical solution during Scrubbing process is considered as a redundant process. The redundancy of the second stage of post-CMP cleaning, Scrubbing, has led to the opportunity of improving the CMP SFI equipment capacity particularly for the oxide process at 15%.

LARUTAN PEMBERSIHAN SILTERRA DALAM PENGILAPAN OKSIDA PASCA KIMIA MEKANIKAL BAGI MEMINIMAKAN NITROGEN AMMONIA DALAM KUMBAHAN

ABSTRAK

Jabatan Alam Sekitar (JAS) Malaysia telah menetapkan nitrogen ammonia sebagai parameter tambahan di dalam peraturan perlepasan efluen di bawah Akta Alam Sekitar bermula 1 Januari 2010 sebagai langkah penambahbaikan dalam mengawal pencemaran. Kegagalan mematuhi mana-mana peraturan di bawah Akta Kualiti Alam Sekitar ialah denda tidak melebihi RM10,000 dan/atau penjara maksima dua tahun serta denda harian berjumlah RM1,000 sehari sepanjang tempoh kesalahan tersebut dilakukan. Pengunaan larutan ammonia secara meluas terutama di dalam proses pasca perataan secara mekanikal-kimia (CMP) telah menyumbang kepada peningkatan nitrogen ammonia di perlepasan terakhir. Kajian ini bagi menilai semula keberkesanan penyingkiran zarah silikon dioksida (SiO_2*) daripada permukaan wafer oleh larutan ammonia. Kajian tertumpu kepada proses pengoksidaan CMP menggunakan mesin SpeedFam IPEC (SFI) AvantGaard Model 776 memandangkan proses ini menghasilkan aliran efluen yang tinggi kerana pengunaan air dinyah ion untuk bilasan semasa larutan ammonia dialirkan. Tujuan utama kajian ini adalah untuk mencari alternatif supaya kandungan nitrogen ammonia dapat dikurangkan tanpa menjejaskan keberkesanan pembersihan di atas permukaan wafer. Pengunaan larutan khas SCS (SilTerra Cleaning Solution) adalah hasil inovasi empat perekacipta dari SilTerra. Formulasi SCS yang mengabungkan tiga jenis bahan kimia iaitu hidrogen peroksida, asid sulfurik dan bahan kimia tambahan mempunyai kelebihan dari segi kemampuan meyingkirkan zarah-zarah serta sisa logam setanding dengan larutan ammonia semasa proses penggosokan melebihi 97%. Hasil kajian ini mendapati proses pencucian cakera atau dikenali sebagai penggilap telah berjaya menyingkirkan 99% zarah-zarah. Usaha untuk tidak menggunakan bahan kimia semasa proses penggosokan belum dapat dilaksanakan kerana penyingkiran zarah-zarah seperti Sulfur tidak mencapai 84% berbanding 97% yang dicapai dengan pengunaan larutan ammonia dan SCS. Namun begitu, kajian tentang impak zarah-zarah ini masih belum jelas. Penggunaan bahan kimia, buburan Tungsten berasid yang mengandungi hidrogen peroksida sebanyak 3% semasa teknik penggilapan dijangka dapat menyingkirkan zarah-zarah ini. Adalah dirumuskan bahawa penggunaan bahan kimia semasa teknik penggosokan bersifat duplikasi kepada teknik penggilapan dan ini boleh meningkatkan kapasiti mesin CMP SFI sebanyak 15%.*

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LIST OF SYMBOLS AND ABBREVIATIONS

AE - Acoustic Emission
AFM - Atomic Force Microscopy
ANOVA - Analysis of Variance
APM - Ammonia Peroxide Mixture
BAF - Biological Aerated Filters
Ca - Calcium
CAS - Chemical Abstract Service
Cl - Chlorine
CMC - Critical Micelle Concentration
CMP - Chemical Mechanical Planarization/Polishing
COF - Coefficient of Friction
CSI - Colloidal Silica
DHF - Diluted Hydrofluoric Acid
DI - Deionized Water
DMA - Dynamic Mechanical Analysis
DOE - Department of Environment
EDS - Energy Dispersive X-ray Spectroscope
EIA - Environment Impact Assessment
EQA - Environment Quality Act
FEOL - Front End of the Line
FEM - Finite Element Method
FS - Fumed Silica
FTIR - Fourier Transform Infrared
HF - Hydrofluoric Acid
HPM - Hydrochloric Peroxide Mix
H_2O_2 - Hydrogen Peroxide
H_2SO_4 - Sulphuric Acid
IC - Integrated Circuit
IDLH - Immediately Dangerous to Life and Health
ILD - Interlayer Dielectric Layer
MBBR - Moving Bed Bio Reactors
Na - Sodium
NH_3 - Ammonia
NH_4OH - Ammonium Hydroxide
NIOSH - National Institute for Occupational Safety & Health
P - Potassium
PPM - Parts Per Million
PRE - Particle Removal Efficiency
PMMA - Polymethyl Methacrylate
PVA - Poly Vinyl Alcohol
RBC - Rotating Biological Contactors
RCA - Radio Corporation of America
RR - Removal Rate

SBR - Sequence Batch Reactor
SC1 - Standard Clean 1
SC2 - Standard Clean 2
SCS - SilTerra Cleaning Solution
SEM - Scanning Electron Microscopy
SFAM - Semi-conductor Fabrication Association of Malaysia
SFI - SpeedFam IPEC AvantGaard™ 776 polisher
SiO_2 - Silicon Dioxide
SIMS - Secondary Ion Mass Spectrometry
SPM - Sulphuric Peroxide Mixture
So - Sommerfeld Number
SRD - Spin Rinse Dry
SSE - Sum of Squares Error
SSR - Sum of Squares for Factors
STI - Shallow trench isolation layer in wafer fabrication
STM - Scanning Tunneling Microscopy
TEOS - Tetra Ethyl Ortho Silicate
Ti - Titanium
TFD - Thin Film Dielectric
TFM - Thin Film Metal
TMA - Thermo Mechanical Analysis
TMAH - Tetra Methyl Ammonium Hydroxide
TXRF - Total Reflection X-ray Fluorescence
UHPCS - Ultra High Purity Colloidal Silica
UPW - Ultra Pure Water
WHS - Wafer Handling System
WIWNU - Within Wafer Non Uniformity
WTWNU - Wafer to Wafer Non Uniformity
XPS - X-ray Photoelectron Spectroscopy

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LIST OF PUBLICATIONS

Indexed Journal

Asyraf, M. S., Talib, A.D., Termizi, A., Ariff, M., 2020. Ammonia Free Cleaning Solution for Post Chemical Mechanical Polishing (CMP) Cleaning. *The International Journal of Nanoelectronics and Materials UNIMAP* (*IJNeaM)* 1985-5761 2232-1535 (Vol. 13, No.3).

Conference Proceeding

Asyraf, M. S., Talib, A.D., Termizi, A., Sulong, M., Ariff, M. A., 2016. Solutions to Ammoniacal Nitrogen Presence in CMP Effluent from Oxide Process, in *2016 International Conference on Industrial Engineering & Operations Management (IEOM),* pp. 3383-3389.

CHAPTER 1

INTRODUCTION

1.1 Background

Ammonia is one of the cleaning chemicals used in wafer fabrication manufacturing. The review of the process using the chemical, ammonium hydroxide in the Chemical Mechanical Polishing (CMP) process is being conducted in view of the inclusion of Ammoniacal Nitrogen (NH_3-N) into the Industrial Effluents parameter under the Malaysia Environmental Quality Act (EQA) by the Department of Environment (DOE) Malaysia in January 2009.

Ammoniacal Nitrogen is a measure of ammonia concentration in waste products or effluents. The monitoring and reporting of Ammoniacal Nitrogen in waste water effluent analysis are made mandatory under the EQA. The DOE is the government agency and regulatory body that enforces this requirement as shown in Table 1.1 effective from January 1st, 2010.

Table 1.1 Ammoniacal Nitrogen Effluents Limit (SFAM, 2016)

Trade/ Industry	**Industrial Effluent Treatment Systems**		
	Parameter	**Standard A**	**Standard B**
Semi-conductor (Effective 2010)	Ammoniacal Nitrogen	10ppm	20ppm
Semi-conductor (1st January 2010 - 31st Dec 2019)	Ammoniacal Nitrogen	20ppm	40ppm

At the beginning of the new regulation enforcement, the effluent discharge limit for all the facilities located upstream of water catchments categorized as Standard A is 10 parts per million (ppm) and 20 ppm for facilities located downstream of water catchments (Standard B). However, the ammoniacal nitrogen limit for semi-conductor companies that started their operation before 1st January 2010 has been revised per Table 1.1 to allow existing manufacturing companies to adapt suitably their effluents to be in compliance with this regulation (SFAM, 2016). Nevertheless, this exemption is only given for a 10-year duration and all the affected companies have to comply with the same specifications by January 1st, 2020.

1.2 Overview of Wafer Fabrication Manufacturing

SilTerra has commissioned its wafer fabrication manufacturing in Kulim Hi-Tech Park in 1999 as a part of a strategic national interest in promoting the front-end semiconductor industry to attract high technology investments into the country. SilTerra has served many fabless design and global companies covering the consumers of mobile devices, computing, electronics and communications. The process of wafer fabrication starts off with a raw material called raw silicon wafers. These wafers are processed or fabricated and divided into many identical square areas each of which is a silicon chip. A wafer is a thin slice of crystalline silicon used in the wafer fabrication. A raw wafer made of silicon is used as a raw material because of its ability to form a high quality silicon dioxide. A photo of raw silicon wafers is shown in Figure 1.1. The raw silicon wafers undergo a multi-step process to add layers for the formation of electronic circuits in repeated and identical structures called dies. An integrated circuit (IC) is a set of electronic circuits built up on the silicon wafer, each of which can function as a microprocessor, an oscillator, an amplifier, a computer memory, a timer or many others.

Figure 1.1 Raw Silicon Wafers (SilTerra Training Material, 2020)

A geometrical pattern is projected on the photo resist when lights focus on a reticle top surface due to the effect of light being absorbed and passed simultaneously through the reticle as shown in Figure 1.2.

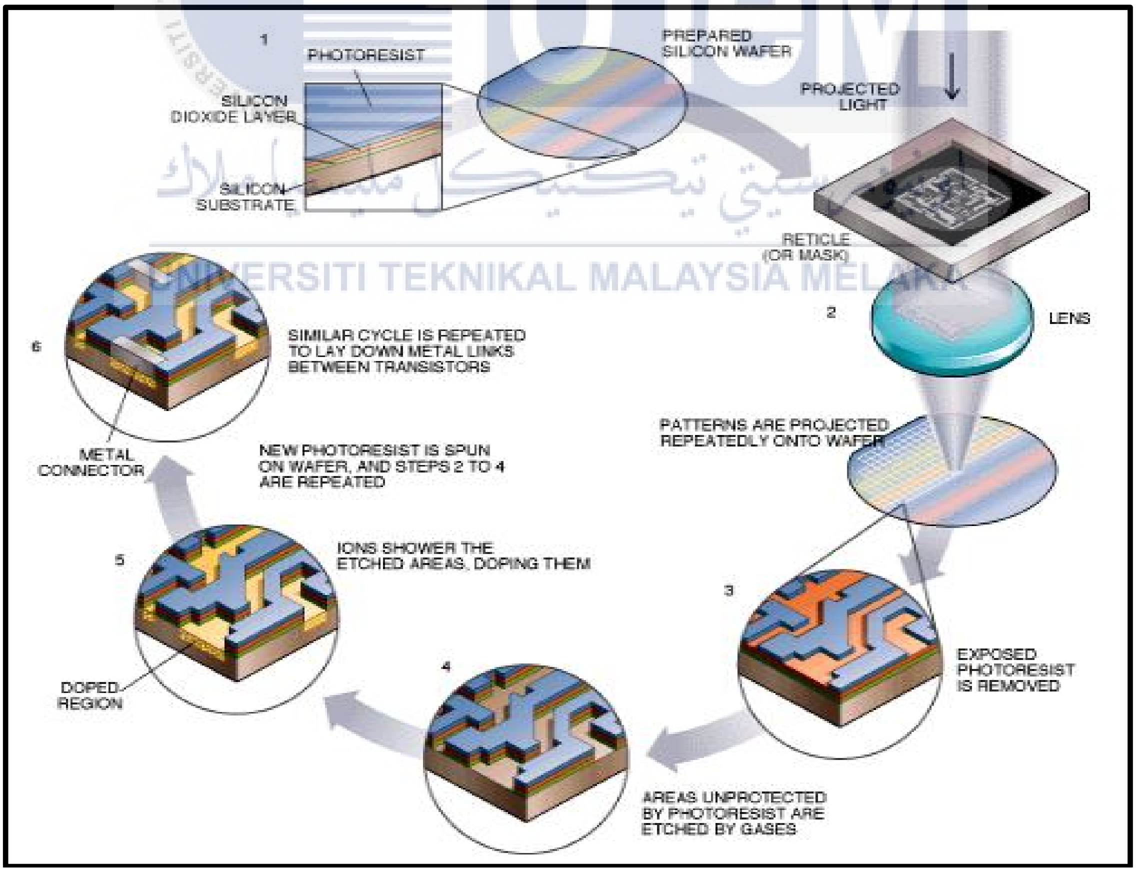

Figure 1.2 Patterning Process on a Substrate Lithography (Wachter, 2020)

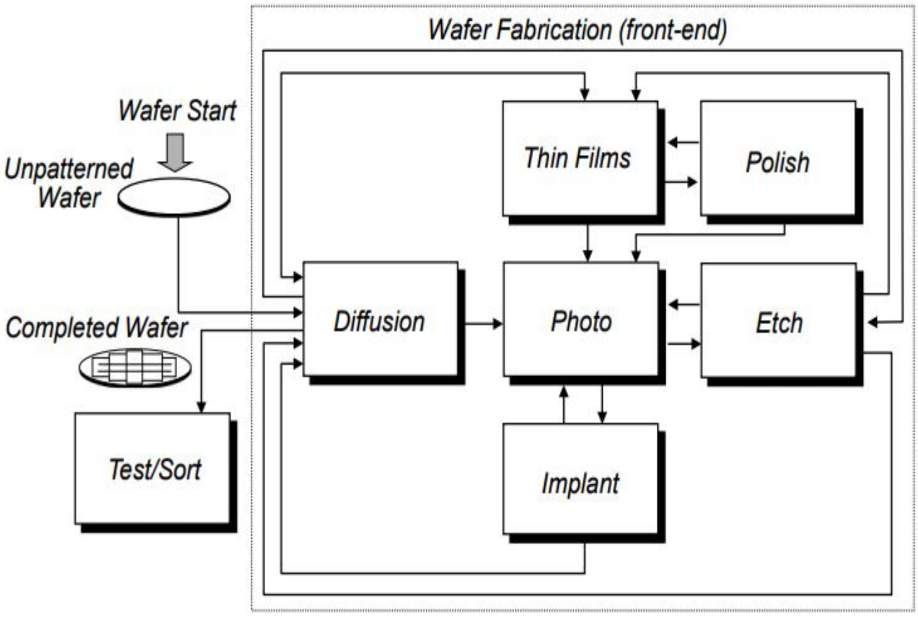

Figure 1.3 Semi-conductor Wafer Process Flow (SilTerra Training Material, 2020)

A simplified process step is shown in Figure 1.3, in which the CMP process is indicated as "Polish". The electronic circuits on wafers are produced after undergoing multiple micro fabrication process steps such as implant, diffusion, thin film, chemical mechanical planarization (CMP), photolithography and etching. The individual microcircuits are diced from a patterned wafer and packaged for use in computer components, radio frequency amplifiers, components of light-emitting diode (LED) and many other electronic devices. As the size of ICs decreases, cleaning efficiency is expected to be improved as smaller particles and contaminants may now cover part of the ICs causing yield loss and this requires more stringent contamination control mechanisms are needed (Sreenivasan, 2017).

1.3 Problem Statement

In the wafer fabrication process, ammonia is used in a concentrated form in the Wet Clean tools and the waste is discharged after a certain number of batches of wafers are processed. Thus, the collection of concentrated ammonia effluents from the Wet Clean tools for further treatment is still viable due to the small volume. CMP has two different sets of tools manufactured by Applied Materials (AMAT) and SpeedFam IPEC AvantGaard (SFI) respectively. Effluents from the AMAT tools are in a concentrated form while for the SFI tools, it is in a more diluted form since SFI tools discharge high volumes of diluted ammonia waste due to the Ultra Pure Water (UPW) rinsing during the post-CMP Scrubbing step. This resulted in a high ammoniacal nitrogen content in SilTerra's wastewater effluent (Figure 1.4) when analysis of ammoniacal nitrogen was initiated in 2010 (Ammonical Nitrogen Concentration in Effluents).

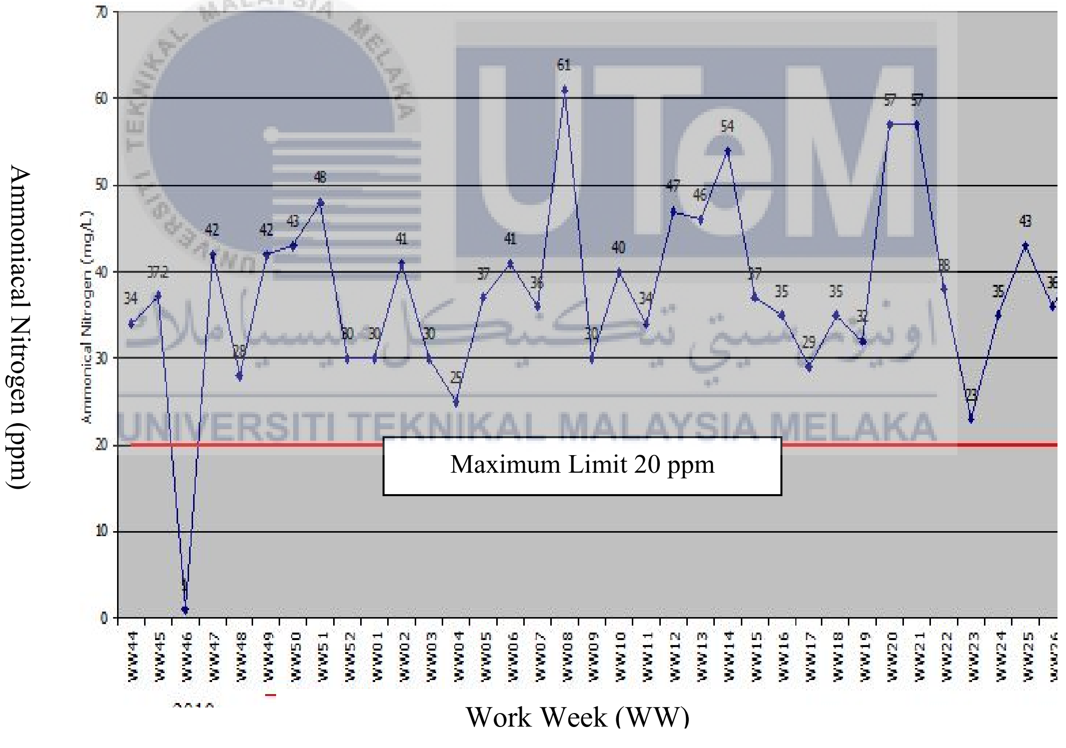

Figure 1.4 Ammoniacal Nitrogen Concentration in Effluents

SilTerra's facilities which were built in 1999 are not equipped with an ammonia treatment facility. Efforts were made to reduce ammonia usage plant-wide particularly at the SFI tools and this managed to reduce the ammoniacal nitrogen to lower than 20ppm. However, maintaining the reading consistently lower than 20ppm during an increase in production load is a challenge. Collecting effluents from CMP SFI tools for external treatment is not economical due to a high volume of wastes. Effluents from CMP SFI tools also vary in flow and concentration depending on the process steps. The waste segregation employing a membrane is not suitable to be applied due to the presence of fine residual slurry which can easily choke filters or membranes.

Another major concern is to establish a gradient of new drain lines connected to the production tools to ensure the smooth flow of the ammonia effluent to a waste treatment plant. Incorporating the new drain lines meeting the required gradient is difficult at this stage. The modification works on existing drain lines at current congested utilities in the presence of gas, chemicals, electrical cables, water and various other services are considered as high risks to safety and causing long production downtime. Currently, there is no non-ammonia-based solutions available and economical implications are expected to be discussed along with the objectives.

1.4 Objectives

The objectives of this thesis are listed below:

1) To comply on Ammoniacal Nitrogen limit in SilTerra's CMP effluent in compliance to DOE regulatory limit
2) To identify an alternative solution for the Post-CMP cleaning process on SFI CMP tools.
3) To analyze cleaning efficiency of the alternative solutions at the Post-CMP Oxide process.