# ULTRAFILTRATION TREATMENT FOR SPENT TUNGSTEN SLURRY GENERATED BY CHEMICAL POLISHING PROCESS IN WAFER FABRICATION INDUSTRY FOR REUSE

NUR FATIN AMALINA BINTI MUHAMMAD SANUSI

UNIVERSITI SAINS MALAYSIA

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**by**

**NUR FATIN AMALINA BINTI MUHAMMAD SANUSI**

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# LIST OF SYMBOLS

| | |
|---|---|
| M | Molar |
| Wt | Weight |
| n.a | Not available |
| Kda | Kilo Dalton |
| t | Time |
| $\zeta$ | Zeta Potential |
| $P_F$ | Feed pressure |
| $P_R$ | Retentate pressure |
| $P_P$ | Permeate pressure |
| R | Retention rate |
| $C_P$ | Solute concentration permeate |
| $C_R$ | Solute concentration retentate |
| $C_f$ | Solute concentration feed |
| $J_w$ | Membrane pure water flux |
| $t_{ss}$ | time of steady state |

# LIST OF ABREVIATIONS

| | |
|---|---|
| CMP | Chemical mechanical polishing |
| W | Tungsten |
| Fe | Iron |
| Cu | Copper |
| Al | Aluminium |
| Na | Natrium |
| Ti | Titanium |
| TiN | Titanium Nitride |
| Ta | Tantalum |
| TaN | Tantalum Nitride |
| ILD | Inter-level dielectric |
| STI | Shallow trench isolation |
| IC | Integrated circuit |
| W-CMP | Tungsten chemical mechanical polishing |
| IEP | Isoelectric pH |
| $\mu$m | Micro meter |
| $WO_3$ | Tungsten trioxide |
| $WO_2$ | Tungsten dioxide |
| $SiO_2$ | Silica |
| $H_2O_2$ | Hydrogen peroxide |
| $Fe(NO_3)$ | Ferric nitride |
| $KIO_3$ | Potassium iodate |
| $AI_2O_3$ | Aluminium oxide |

| | |
|---|---|
| $K_3Fe(CN)_6$ | Potassium ferricyanide |
| $K_2SiO_3$ | Potassium silicate |
| $H_2SO_4$ | Sulfuric acid |
| $K^+$ | Potassium ion |
| $H^+$ | Proton |
| $H_2O$ | Oxygen |
| $SO_4^{-2}$ | Sulfate |
| SiOH | Silica silanol |
| EDL | Electrical double layer |
| DLS | Dynamic light scattering |
| $OH^-$ | Hydroxide |
| UF | Ultrafiltration |
| PS | Polysulfone |
| MF | Microfiltration |
| HCI | Hydrochloric |
| Nm | Nanometer |
| MPa | Mega Pascal |
| TMP | Trans-membrane pressure |
| PES | Polyethersulfone |
| MWCO | Molecular weight cut off |
| $HNO_3$ | Nitric acid |
| NaOH | Sodium Hydroxide |
| $C_2H_5OH$ | Ethanol |
| PVDF | Polyvinilydinefluoride |
| NTU | Nephelometric Turbidity Units |

| | |
|---|---|
| SEM | Scanning Electron Microscope |
| EDX | Energy Dispersive X-ray Spectroscopy |
| TEM | Transmission Electron Microscopy |
| Ra | Mean roughness |
| V | Volume of permeate water |
| A | Area of the flat sheet membrane |
| P | Pressure |
| Psi | Pounds per square inch |
| DI | Distilled water |
| $H_2O$ | Water |
| ICP- OES | Inductively coupled plasma optical emission spectrometry |
| AFM | Atomic Force Microscopy |

# ULTRAPENAPISAN BAGI BUBURAN TUNGSTEN TERPAKAI DARIPADA PROSES PENGILATAN KIMIA TUNGSTEN DALAM INDUSTRI PEMBUATAN WAFER UNTUK DIGUNA SEMULA

## ABSTRAK

Proses pengilatan kimia diaplikasi secara meluas terutamanya dalam industri mikro elektronik bertujuan untuk meratakan permukaan wafer. Proses ini melibatkan mengilatkan permukaan bersalut logam oleh proses kimia dan diikuti pembuangan lapisan logam yang telah terjejas oleh proses mekanikal untuk mencapai pengilatan yang sempurna menggunakan buburan tungsten. Ia terdiri daripada campuran komponen yang kompleks di mana sifat fizikal dan kimianya boleh berubah bergantung kepada jenis dan keadaan rawatan yang diterima. Oleh itu, pencirian kimia dan fizikal buburan tungsten terpakai merupakan maklumat penting dalam usaha mempertimbangkan kaedah pemulihan yang sesuai. Penggunaan semula butiran silika bersaiz nano diperkenalkan sebagai salah satu langkah untuk mengurangkan kos pembuatan dan jumlah pengeluaran air sisa di mana ia memberi kebaikan dari segi kos dan alam sekitar. Sistem ultrapenapisan aliran silang telah dipilih sebagai kaedah untuk merawat dan kitar semula buburan tungsten terpakai hasil daripada proses pengilatan kimia. Ujikaji membran ultrapenapisan telah dijalankan menggunakan terhadap tiga jenis membran yang berbeza (polysulfone, polyethersulfone and polyvinylidene fluoride) dengan MWCO yg berbeza iaitu 10, 30, 50 dan 100KDa. Kesan kesan tekanan dalaman (TMP) membran dan kadar aliran fluks telah juga diuji. Analisis terhadap pemilihan, pengekalan butiran silica dan pengubahsuaian nilai pH pada buburan tungsten terpakai telah dijalankan untuk

menentukkan prestasi kecekapan membran penapisan dan fenomena pengotoran. Tekanan membran 1 bar memberikan kadar terbaik dan tahap kotor yang paling rendah berbanding tekanan dalaman yang lain. Keputusan terbaik ditunjukkan oleh membran PS 50KDa yang mempamerkan pencapaian 92% dalam pengekalan butiran silika dan cuma 42% dalam pengekalan tungsten. Ia juga mencapai purata saiz paling rendah di mana perbezaan purata saiz hanya pada tahap 0.5% berbanding purata saiz asal butiran silika isitu 125 nm dalam retentate berbanding membran PVDF dengan MWCO yang sama. Pemulihan buburan tungsten terpakai boleh ditingkatkan dengan pengubahsuaian nilai pH 9 telah mencapai prestasi yang baik kerana mempunyai nilai saiz purata 126 nm berbanding nilai saiz purata asal 125 nm dan memberi pengekalan butiran silika terbesar sebanyak 42% dalam retentate. Ia juga mencapai nilai negatif terbesar -40 mV dalam nilai zeta potensi yang menunjukkan kestabilannya. Secara kesimpulan, membran PS 50KDa menunjukkan potensi terbesar dalam penapisan dan pemekatan butiran silika hasil proses pengilatan kimia dengan keadaan nilai pH 9.

**ULTRAFILTRATION TREATMENT FOR SPENT TUNGSTEN SLURRY GENERATED BY CHEMICAL POLISHING PROCESS IN WAFER FABRICATION INDUSTRY FOR REUSE**

## ABSTRACT

Chemical Mechanical Polishing (CMP) is a widely used process to planarize wafers for microelectronic applications. It involves the polishing of metallic surface by chemical action followed by the removal of the modified layer by mechanical action using tungsten slurry. It is a rather complex mixture that both physical and chemical properties of the components in the slurry are expected to change depending on the condition and type of treatments that they receive. As such, characterization of the spent tungsten slurry and knowledge on its physical and chemical properties are critical in order to consider suitable recovery methods. Recycling of the abrasive slurry is one of the options to reduce the manufacturing cost and to achieve environmental benefits that arise from the reduction of wastewater volume. Crossflow ultrafiltration system was used as a method to recycle the silica based slurry. It investigated using three membrane materials i.e. polysulfone (PS), polyethersulfone (PES) and polyvinylidene fluoride (PVDF) with different molecular weight cut off (MWCO) of 10, 30, 50 and 100KDa. Effects of transmembrane pressure (TMP) on flux flow rate were characterized. Analyses of selectivity, retention and pH adjustment of feed water were done to demonstrate the membrane performance and fouling phenomena. A TMP of 1 bar gave the lowest fouling result as compared to the other TMPs. The PS 50KDa membrane demonstrated the best results with 92% retention of silica particles and only 42% retention of tungsten. It also achieved the lowest mean size particle of 125nm in the

retentate or only 0.5% value difference compared to that of the original spent tungsten slurry than those of other membranes especially PVDF membrane with the same MWCO. The performance in spent tungsten slurry recovery could be improved by adjusting the pH to 9 that gave the best performance in terms of having the lowest mean size of 126 nm which was close to 125 nm of the original size of particles in the spent tungsten slurry. It gave the highest retention of silica particles of 42% in the retentate. It also had the largest negative value of -40mV in zeta potential to suggest its stability. In conclusion, PS ultrafiltration with 50KDa of MWCO membrane showed the highest potential in filtrating and concentrating the spent tungsten slurry of CMP process with the best result achieved at a pH value of 9.

# CHAPTER ONE

# INTRODUCTION

## 1.1 Research Background

Chemical mechanical polishing (CMP) is a process of polishing the device side of a semiconductor wafer by applying a chemical action followed by applied mechanical action to eliminate the modified layer. The primary fundamentals of CMP is to ensure the metallic surface of the wafer is polished with a pad together by adding abrasive slurry to remove the excess of metal deposited on the wafer surface, with the purpose of obtaining the required planarization of wafer surface (Xiao, 2001). The CMP process is depicted using the scheme as presented in Figure 1.1.

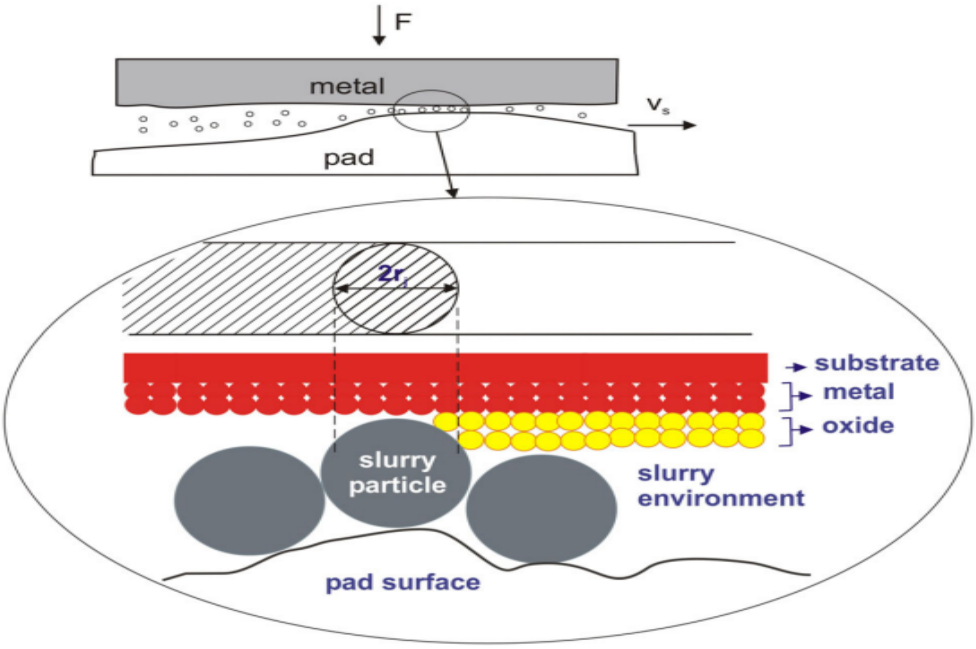


Figure 1.1 Scheme of CMP process (Stojadinovic et al., 2016)

Throughout the manufacturing process, a thick conductive layer is deposited on the surface wafer with the purpose to fill the vias and trenches. Tungsten is one of the common deposit layers with low resistivity for multilevel interconnection structures of wafers (Kang *et al*., 2010). The oxidation of wafer surface on the metallic upper layer along with chemical reactants such as mixing of oxidizer, surfactant and catalyst and the abrasive particle of slurry as function of mechanical action will remove the excess tungsten on the wafer surface (Stein, 2004).

Slurry consists of abrasive particles such as silica, alumina, ceria and also other aqueous medium that assists the abrasive slurry suspension, which acts to combine the chemical and mechanical polishing process (Luo and Dornfield, 2001). The slurry is acidic, which has to combine with appropriate oxidizing agent for surface layer polishing by metal passivation and then by the metallic film dissolve process (Wang *et al*., 2012). Tungsten slurry is designed to polish the conductive layers on the wafer surface, which is important to cover the vias on the surface of inter-level dielectric ILD. One of the important roles in CMP process is the chemical composition of the abrasive particle slurry, especially when mixing with chemical reactants such as the oxidizer (Stein *et al*. 2004). Commonly, the tungsten CMP slurries consist of silica or alumina which is suspended, in the aqueous solution of oxidizing agents (Kang *et al*., 2010). Tungsten slurry usually contains metal contaminants in the waste slurry to cause some difficulty for their removal in order to recycle the slurry. Hence, developing a method for the removal of metal contaminants in the used slurry is deemed necessary.

Testa *et al.,* (2014) attempted the method to recycle the acidic-based silica for the polishing tungsten CMP. Various studies have been focused on recycling and regeneration of CMP slurry using filtration (Ndieye *et al*., 2004; Singh and Song, 2007; Coetsier *et al*., 2011; Testa *et al*., 2014). After the polishing CMP process, the properties of the abrasive slurry are often disrupted and usually a small portion of the slurry is degraded. Besides, during rinsing step of the polishing CMP process, all the chemical components and abrasive slurry particles are highly diluted (Ndieye *et al*., 2004). The reduction of wastewater through filtration and recycling of the used slurry after polishing are among the common goals of research in semiconductor industry.

The most suitable method for recycling the used CMP slurry is the ultrafiltration processes, in view of the abrasive particle size of slurry (Singh and Song, 2007; Coetsier *et al*., 2011; Testa *et al*., 2014). Besides the economic interest of recycling the used slurry, a potential reduction the amount of wastewater generated from the CMP process using ultrafiltration, can promise clear benefits to the environment. The initial step in recycling of the used slurry is to concentrate the slurry with the purpose of recovering the abrasive silica particles (Kurisawa, 2001). Then, readjustment of the concentrated used slurry should be done by injection of chemical components (Testa *et al*., 2014). Through ultrafiltration processes the slurry chemical constituents are not reinstated, so, the regeneration of abrasive slurry particles should be done before recycling back into the CMP process (Testa *et al*., 2014). The chemical composition of the abrasive particles in the slurry acts as a main role in controlling CMP parameter, uniformity and defective value of wafer surface in the CMP process. Because of this major requirement, there is a need for chemical adjustment for the concentrated spent tungsten slurry (Coetsier *et al*., 2011). This is important so that the recovered slurry can have specific chemical properties and necessary stability.

On the other hand, ultrafiltration is the critical step in the separation of liquid and solid phases of the slurry. Ultrafiltration permeate can be recycled for rinsing water in the CMP process and the solid is recovered out for CMP usages. Ndiaye *et al.*

(2004) investigated the possibility using an ultrafiltration pilot equipped with a module of polysulfone hollow fibers to concentrate the used slurry and reducing the waste volume sent to wastewater treatment plant. Moreover, backwashing the ultrafiltration is one of the important elements to maintain its operating life and also to reduce the maintenance cost to avoid frequent membrane change. Ultrafiltration showed good recovery of large fraction of initial effluent (almost 95%) so that the relatively transparent and colorless water could be recycled back into the CMP operation. This was a good indication for the use to concentrate CMP, used slurry (Ndieye *et al*., 2004).

As reviewed by several authors, it was essential to use pretreatment or prefilter. It usually be made up of a single filter to get rid any waste and agglomerated particles in order to obtain particular particle sizes and also as a prevention from quick deterioration of the membrane module (Testa *et al*., 2014; Coetsier *et al*., 2011; Ndieye *et al*., 2004).

Recovery process of spent tungsten slurry involves the removal of dissolved and undissolved metals in the slurry suspension. Abdullah *et al*. (2007) concluded that the recovery method is not an easy task as the composition of the spent tungsten slurry is quite complex. Both physical and chemical properties of the slurry components are expected to change depending on the conditions and type of treatment that they receive.

## 1.2 Problem Statement

Tungsten slurry for use in the CMP operation is a rather complex mixture with the presence of multi components, each of which serves an individual purpose. Both physical and chemical properties of the components in the slurry are expected to change depending on the condition and type of treatments that they receive. The composition of spent slurry could significantly change as multi foreign components could be introduced into the slurry. As such, thorough characterization of the spent tungsten slurry is general critical for knowledge on its physical and chemical properties is critically needed in order to consider suitable recovery methods. Various methods for recovering abrasive silica from the spent slurry should be considered based on the composition and also their conditions. Therefore, membrane technology is one of the potential methods to treat and recycle the spent tungsten slurry into the CMP process. The treatment of spent tungsten slurry using ultrafiltration membrane process resulted high retention of silica particles of about 93% (Sheikholeslami et al., 2000). Good recovery of water from ultrafiltration of spent tungsten slurry of approximately 95% which good indication for its potential in concentrating spent slurry and reducing pollutants (Ndiaye et. al., 2004). However, the chemical components of spent slurry might not be fully reinstated and it may contain metal contamination that may disturb overall quality of slurry.

The critical problem generally encounter in using ultrafiltration membrane separation process as the recovery system for spent tungsten slurry is membrane fouling. Membrane fouling of the ultrafiltration membrane process is affected by the deposition and build up of silica particles from spent tungsten slurry on the membrane surface and its internal pores. Besides, the extent of membrane fouling by silica particles is greatly influenced by the solution chemistry (ionic strength and pH solution), operating conditions of membrane system (TMP and velocity), membrane type, module configuration and process itself. Too high of TMP and velocity will lead to severe fouling condition causing to high usage of energy and operational cost.