

TUNGSTEN REMOVAL FROM CHEMICAL MECHANICAL POLISHING (CMP)

SPENT SLURRY USING DOWEX MONOSPHERE MR-450

ULTRAPURE WATER (UPW) RESIN

HASLINA BINTI SHAMSHUDDIN JAYA

UNIVERSITI SAINS MALAYSIA

2018

**TUNGSTEN REMOVAL FROM CHEMICAL MECHANICAL POLISHING (CMP)
SPENT SLURRY USING DOWEX MONOSPHERE MR-450
ULTRAPURE WATER (UPW) RESIN**

by

HASLINA BINTI SHAMSHUDDIN JAYA

**Thesis submitted in partial fulfillment of the requirement
for the degree of Bachelor of Chemical Engineering**

June 2018

ACKNOWLEDGEMENT

First and foremost, I would like to convey my sincere gratitude to my supervisor, Prof Dr. Ahmad Zuhairi Abdullah for his precious encouragement, guidance and generous support throughout this Final Year Project research work.

Next, I would also extend my gratitude to the PHD students under Prof Dr. Ahmad Zuhairi Abdullah that always shares their valuable knowledge without any hesitation. They are willing to sacrifice their time in guiding and helping me. I felt thankful for their kindness assistance in guiding me throughout the project for me to carry out the lab experiment.

Apart from that, I would also like to thank all SCE staffs for their kindness cooperation and helping hands. Indeed their willingness in sharing ideas, knowledge and skills are deeply appreciated.

Once again, I would like to thank all the people, including those whom I might have missed out and my friends who have helped me directly or indirectly. Their contributions are very much appreciated. I wish to thank all members of my family especially to my parents Mr. and Mrs. Shamshuddin Jaya for their tremendous moral support and encouragement which had brought me until the end of this subject.

Haslina Binti Shamshuddin Jaya

June 2018

TABLE OF CONTENTS

ACKNOWLEDGEMENT	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	vi
LIST OF FIGURES	vii
LIST OF SYMBOLS	ix
LIST OF ABBREVIATIONS	x
ABSTRAK	xiii
ABSTRACT	xiv
CHAPTER ONE : INTRODUCTION	1
1.1 Research background	1
1.2 Problem statement	4
1.3 Research objective	5
1.4 Scope of study	5
1.5 Organization of the thesis	6
CHAPTER TWO : LITERATURE REVIEW	8
2.1 Chemical Mechanical Polishing (CMP) Technology	8
2.1.1 CMP process	9
2.1.2 CMP slurry	12
2.1.2.1 Role of CMP slurry	12

2.1.2.2 Spent slurry	14
2.1.2.3 Solution for metal slurry	16
2.1.2.4 Removal of tungsten polishing	17
2.2 Methods of removing heavy metals	17
2.3 Ion exchange	21
2.3.1 Application of ion exchange for heavy metal ions removal	23
2.3.2 Ion exchange resin	23
2.3.3 Mixed bed ion exchange resin	24
CHAPTER THREE : MATERIALS AND METHODS	29
3.1 Materials and chemicals required	29
3.2 Characterization of chemicals and physical properties of spent tungsten slurry	30
3.2.1 pH and conductivity	30
3.2.2 Turbidity	30
3.2.3 Viscosity	31
3.2.4 Metal contents	31
3.2.5 Particle size distribution and zeta potential	32
3.3 Characterization study on Dowex monosphere MR-450 UPW mixed resins	33
3.3.1 Scanning electron microscopy (SEM)	33
3.3.2 Energy-dispersive X-ray (EDX) spectroscopy	34
3.4 Experimental procedure	34
3.5 The influence of resin loadings	36

3.6 Research methodology	37
CHAPTER FOUR : RESULTS AND DISCUSSION	38
4.1 Analysis of spent tungsten slurry	38
4.1.1 Characteristic of spent tungsten slurry before and after resin loading	38
4.1.2 Metal contents in spent slurry before and after resin loadings	39
4.1.3 pH values of slurry solution after 2 hours of contact time with resin	44
4.1.4 Zeta sizer and zeta potential	45
4.1.5 Intensity distribution for after loading resin	47
4.2 Characterization of Dowex monosphere MR-450 UPW mixed resin	50
4.2.1 Scanning Electron Microscope (SEM) analysis	50
4.2.2 Energy Dispersive X-Ray (EDX) Analysis	56
CHAPTER FIVE : CONCLUSIONS AND RECOMMENDATIONS	58
5.1 Conclusions	58
5.2 Recommendations	58
REFERENCES	59
APPENDICES	67
Appendix A: Calibration curves	67
Appendix B: Calculation of percentage removal using equation (3.1)	69
Appendix C: Calculation for sorption capacity using equation (3.2)	70

LIST OF TABLES

	Page
Table 3.1 Properties of mixed-bed Dowex monosphere MR-450 UPW resin	29
Table 4.1 Characteristic of spent tungsten slurry for before and after resin loading at pH 3.87 ± 0.02	38
Table 4.2 Removal percentage for W ions	40
Table 4.3 Removal percentage for Fe ions	41
Table 4.4 Sorption capacity	43
Table 4.5 The initial pH and the pH values after 2 hours of contact time with Dowex monosphere MR-450 UPW resin	45
Table 4.6 Ion exchange chemical composition obtained from elemental analysis via energy dispersive x-ray for mixed bed resin	56
Table A.1 Calibration curve of W, 183	67
Table A.2 Calibration curve of Fe, 57	68

LIST OF FIGURES

		Page
Figure 2.1	Importance of CMP in layer stacking of chip	9
Figure 2.2	CMP schematic on wafer-slurry-pad contact region	11
Figure 2.3	Particle size distribution of conventional and Dowex monosphere resins	25
Figure 2.4	Expanded view of polystyrene bead	26
Figure 2.5	The sorption capacity of ion exchangers depending on pH	27
Figure 2.6	The structure of gel and macroporous ion exchangers	28
Figure 3.1	Inductively Coupled Plasma Mass Spectrometer (Perkin Elmer ICPMS Nexion 300)	31
Figure 3.2	Zeta Sizer (Nano ZS, Malvern)	32
Figure 3.3	Scanning electron microscope (Quanta FEG450)	33
Figure 3.4	Constant temperature magnetic stirrer	35
Figure 3.5	Schematic flow diagram of experimental activities	37
Figure 4.1	Plot of resin loading against percentage removal of W ion	41
Figure 4.2	Plot of resin loading against percentage removal of Fe ion	42
Figure 4.3	Plot of sorption capacity against concentration for W and Fe	43
Figure 4.4	The intensity size distribution of W spent slurry with 5g mixed resin versus particle diameter in nanometers	48
Figure 4.5	The intensity size distribution of W spent slurry with 10g mixed resin versus particle diameter in nanometers	48

Figure 4.6	The intensity size distribution of W spent slurry with 15g mixed resin versus particle diameter in nanometers	49
Figure 4.7	The intensity size distribution of W spent slurry with 20g mixed resin versus particle diameter in nanometers	49
Figure 4.8	SEM micrographs of Dowex monosphere MR-450 UPW for before resin loading at magnifications of (a) 500X, (b) 1000 KX and (c) 2000 K X	51
Figure 4.9	SEM micrographs of Dowex monosphere MR-450 UPW of 5g after resin loading at magnifications of (a) 500X, (b) 1000 KX and (c) 2000 K X	52
Figure 4.10	SEM micrographs of Dowex monosphere MR-450 UPW of 10g after resin loading at magnifications of (a) 500X, (b) 1000 KX and (c) 2000 K X	53
Figure 4.11	SEM micrographs of Dowex monosphere MR-450 UPW of 15g after resin loading at magnifications of (a) 500X, (b) 1000 KX and (c) 2000 K X	54
Figure 4.12	SEM micrographs of Dowex monosphere MR-450 UPW of 20g after resin loading at magnifications of (a) 500X, (b) 1000 KX and (c) 2000 K X	55

LIST OF SYMBOLS

	Symbol	Unit
	σ Conductivity	S/m
	C_0 Initial concentration of metal	mg/L
	C Final concentration of metal	mg/L
	μ Viscosity of slurry	cP
	T Turbidity	NTU
	q_e Sorption capacity	mg g ⁻¹
	R Removal percentage	%
	V Sample volume	mL
	W Mass of dry resin	g
	ζ Zeta potential	mV

LIST OF ABBREVIATIONS

CMP	Chemical mechanical polishing / chemical mechanical planarization
W-CMP	Tungsten chemical mechanical polishing
FEOL	Front end of the line
BEOL	Back end of the line
MOL	Middle of the line
UPW	Ultrapure water
W	Tungsten
Ta	Tantalum
Ti	Titanium
Co	Cobalt
Cu	Copper
TiN	Titanium nitrate
Si	Silicon
WO ₃	Tungsten trioxide
SiO ₂	Silicon dioxide
Al ₂ O ₃	Aluminum oxide
KOH	Potassium hydroxide
NaOH	Sodium hydroxide
H ₂ O	Water
O ₂	Oxygen
H ₂ O ₂	Hydrogen peroxide

KiO ₃	Potassium iodate
H ₅ IO ₆	Periodic acid
Fe(NO ₃) ₃	Ferrum (III) Nitrate
H ₂ S	Hydrogen sulphide
Mo	Molybdate
pH	Potential of hydrogen
AC	Activated carbon
IC	Integrated circuit
RR	Removal rate
MRR	Material removal rate
REE	Rare earth element
PGM	Platinum group metals
S-DVB	Styrene-divinylbenzene
SAC	Strong acid cation
WAC	Weak acid cation
SBA	Strong basic anion
WBA	Weak basic anion
FFA	Free fatty acids
NTU	Nephelometric Turbidity Units
ppb	parts per billion
ICP-MS	Inductively Coupled Plasma Mass Spectrometer
SEM	Scanning electron microscopy
EDX	Energy-dispersive X-ray spectroscopy

DLS	Dynamic light scattering
ELS	Electrophoretic light scattering
ZP	Zeta potential

**PENYINGKIRAN BAGI BUBURAN TUNGSTEN TERPAKAI DARIPADA
PROSES PENGILAPAN KIMIA-MEKANIKAL DENGAN MENGGUNAKAN
RESIN DOWEX MONOSPHERE MR-450 ULTRAPURE WATER (UPW)**

ABSTRAK

Dalam proses pembuatan semikonduktor yang moden, pengilapan kimia-mekanik telah menjadi faktor yang penting dalam penghasilan litar bersepadu. Proses ini melibatkan pengilapan permukaan bersalut logam oleh proses kimia dan diikuti pembuangan lapisan logam yang telah terjejas oleh proses mekanikal untuk mencapai pengilapan yang sempurna menggunakan buburan tungsten. Pertukaran ion merupakan suatu proses yang menjadi pilihan untuk menghilangkan ion yang tidak diinginkan dengan memindahkan ion-ion tersebut ke resin yang sesuai. Oleh itu, pertukaran ion ialah salah satu cara penyingkiran logam beban daripada buburan terpakai untuk mencapai faedah persekitaran. Tujuan kajian ini adalah untuk mempelajari mekanisma penyingkiran bagi tungsten sebagai logam microelektronik yang dipengaruhi oleh kuantiti resin yang berlainan. Pencirian untuk campuran resin telah dianalisis dengan menggunakan analisa mikroskopi elektron imbasan (SEM) dan analisa X-Ray tenaga sebaran (EDX). Kepekatan ion bagi tungsten telah dinilai dengan menggunakan spektroskopi jisim induktif gandingan plasma (ICP-MS) pada kuantiti campuran resin Dowex monosphere MR-450 ultrapure water (UPW) yang berlainan (5g, 10g, 15g dan 20g) pada pH buburan yang tetap dalam proses kelompok. Campuran resin ini efektif untuk kuasa penyingkiran tungsten sebanyak lebih 96% bagi buburan tungsten terpakai pada pH 3.87 ± 0.02 . Walau bagaimanapun, terdapat penurunan peratus dari 98% kepada 96% sekiranya kuantiti resin meningkat. Hal ini kerana semakin meningkat kuantiti resin, semakin meningkat keluasan penyerapan. Kuantiti resin yang optimum ialah 5g untuk 100mL buburan tungsten terpakai iaitu penyikiran sebanyak 98%.

**TUNGSTEN REMOVAL FROM CHEMICAL MECHANICAL POLISHING (CMP)
SPENT SLURRY USING DOWEX MONOSPHERE MR-450
ULTRAPURE WATER (UPW) RESIN**

ABSTRACT

In the modern semiconductor manufacturing processes, chemical mechanical polishing (CMP) has grown to be an essential part of the production of integrated circuit (IC) manufacturing. It involves the polishing of metallic surface by chemical action followed by the removal of the modified layer by mechanical action using tungsten slurry. Ion exchange process is used extremely for the removal of ionized impurities with proper resin selection. Therefore, ion exchange is one of the options to remove the heavy metal from spent slurry and to achieve environmental benefits that arise from the removal. The aim of this research is to study the removal mechanisms of tungsten, W, as a typical microelectronic metal under different resin loadings. Furthermore, surface analysis techniques which are scanning electron microscope (SEM) analysis and energy dispersive X-Ray (EDX) analysis were performed to study the characterization of the mixed bed resin with the CMP spent slurry. Concentration of tungsten removal was evaluated using inductively coupled plasma mass spectrometer (ICP-MS) by varying the amount of Dowex monosphere MR-450 UPW mixed resin loadings (5g, 10g, 15g and 20g) at constant pH slurry under batch process. It is found that this mixed resin is effective to remove tungsten for more than 96% from spent tungsten CMP slurry at $\text{pH } 3.87 \pm 0.02$. However, the removal percentage decreases from 98% to 96% as the resin loadings amount increases due to an increase in the availability of more sorption sites. Optimum resin loading was found to be 5g for 100 mL of spent slurry as it give the highest removal of tungsten which is 98%.

CHAPTER ONE

INTRODUCTION

1.1 Research background

Chemical mechanical polishing (CMP) technology was first suggested by Monsanto in 1965. This is a completely necessary process step in semiconductor device fabrication, common method used in wafer polishing for dynamic memory, microprocessor applications and glass mechanical polishing. It is one of the key new nanotechnology fabrication processes, a true advance that could be made to use despite enormous odds and technical difficulties early on. CMP is widely used in the semiconductor industry to produce mirror like surfaces with no measurable subsurface damage (Sivanandini et al., 2013).

Applications of CMP in microelectronics can be applied in all three main areas of semiconductor device manufacturing. The transistor device part is called the front end of the line (FEOL), the contact metal (usually tungsten, W) level is known as the middle of the line (MOL), and the interconnect part is called the back end of the line (BEOL) (Krishnan et al., 2009). The FEOL is used to produce devices such as transistors within silicon, and the BEOL is the second part in which interconnects are formed on the wafer as the metallization layer. Metals are used as the conductor between individual electronic components for transporting electrons in the device. The metals incorporated into the IC fabrication of the semiconductor device are tantalum (Ta), titanium (Ti), cobalt (Co), tungsten (W), and copper (Cu). W is used to fill the via and hole on the dielectric in order to connect the interlayer metal line and the plug to improve the step coverage and alleviate electromigration (Lee et al., 2016).

Kaufman et al. (1991) was the first to suggest a model explaining the mechanism of tungsten CMP in a slurry containing an oxidizer. In that model the W film is first oxidized to W trioxide (WO_3) by the oxidizer in the slurry, and then WO_3 is removed by the mechanical abrasion due to the polishing pad and the abrasive in the slurry. These two steps are repeated during the CMP process. The WO_3 layer is easily removed by abrasion because of its mechanical hardness is lower than that of metallic W, so the rate at which the W film is polished can be increased by enhancing the formation of the WO_3 layer on the tungsten surface (Lim et al., 2013).

CMP that actually stands for chemical mechanical polishing or chemical mechanical planarization has been introduced in semiconductor industry in the 80s to planarize wafers used in microelectronic. A thick layer of conductive metal is deposited on the wafer to fill the vias and trenches during manufacturing. Tungsten is mostly used as a deposit layer for the wafers multi-level interconnection structures which serves as low-resistive metallic interconnects. CMP removes the excess of tungsten deposited, in order to obtain the planarization of the surface. The principle of CMP is to polish the metallic surface of a wafer with a pad while adding slurry. Slurry acts combining chemical and mechanical polishing processes. Action of chemical reactants (mix of oxidizers and catalyst) oxidizes the wafer surface by passivation of metallic upper layer. While, the abrasive particles remove the excess of tungsten by mechanical action. When an oxidizer enters in the composition, the chemical composition of abrasive slurry is very important in CMP process (Coetsier et al., 2011).

The process of CMP was initially developed and implemented for planarization of SiO_2 which is used as interlayer dielectric in multilevel metallization scheme. The initial

developmental focus of CMP was oxide planarization. Tungsten is used as an interconnect plug to the source, drain, and gates of transistors in Si microprocessor chips. Initially Ti and TiN barrier layers are deposited, followed by chemical vapor deposition of W to fill the contact vias. Beyond from achieving local and global planarization of SiO₂ removal of excessive tungsten from the horizontal surfaces on the wafer pattern proved to be an asset for subsequent Al metallization. Hence CMP was developed with a two-fold approach of planarizing oxide and removing the via fill metal from the horizontal surfaces (Zantye et al., 2004).

Spent slurry contains pad debris from the conditioning process and normal pad wear, diamond chips that may get dislodged from diamond discs, and chemical by-products. These contaminants can decrease material removal rate and increase wafer-level defects. Therefore, large amounts of ultrapure water (UPW) are used to rinse the pad between polishes in order to mitigate such issues (Meled et al., 2011). The tungsten CMP slurry usually contains oxidizer, iron catalyst, complexing agents and stabilizers in a pH adjusted abrasive particles solution (Coetsier *et al.*, 2011). There are two main types of slurry used to flatten a surface layer. The first type of slurry is basic with a pH between 10 and 11, it permits to polish both silicon and silicon dioxide. The second one is acid combined to an oxidizing agent permits to polish the layer by passivating the metal, then by dissolving the metallic film thus formed (Testa et al., 2014).

Tungsten layer is hard to polish mechanically due to its high hardness. Thus, it is necessary to create brittle surface by oxidizing reaction from the oxidant in slurry to achieve high removal rate for polishing (Hosokawa et al., 2014). Examples of steps of semiconductor processing that involve tungsten at a surface of a substrate include preparing tungsten “plug”

and “interconnect” structures within a dielectric layer. By these methods, tungsten is deposited over a dielectric layer that includes openings, with the tungsten flowing into the openings to fill the openings. Excess tungsten will also be deposited over the dielectric layer and must be removed. The tungsten is removed by CMP polishing to leave behind the tungsten plugs and tungsten interconnects filled into the initial openings of the dielectric layer, as components of a planarized substrate surface (Seo et al., 2017).

1.2 Problem statement

Conventional treatment methods for heavy metal removal from wastewaters include chemical precipitation, chemical reduction, flocculation, filtration, evaporation, solvent extraction, bio-sorption, activated carbon adsorption, ion exchange, electro-dialysis, and membrane separation processes. Among the heavy metal removal processes, ion exchange process is very effective to remove various heavy metals and can be easily recovered and reused by regeneration operation. Ion-exchange resins are a variety of different types of exchange materials, which are distinguished into natural or synthetic resin. Furthermore, it can be as well categorized on the basis of functional groups such as cationic exchange resins, anion exchange resins, and chelating exchange resins. Ion exchange resin can deal properly with several heavy metals such as copper, nickel, cobalt, cadmium, zinc, aluminum, and tungsten which depend on the functional groups (Zewail and Yousef, 2005).

Dowex Monosphere MR-450 UPW grade resin is a non-separable homogeneous mixed bed resin. It is recommended as a point of use or non-regenerable mixed bed in the polishing loop to achieve sub ppb levels of soluble silica, boron, potassium, sulfate, chloride, zinc, iron and aluminum. This non-regenerable mixed bed resin is used for two to three years

before replacement. This study was conducted to explore the potential use of mixed resins to remove tungsten from spent slurry solution via ion exchange as well to achieve environmental benefits that arise from the removal.

1.3 Research objective

The main objectives of this study are:

- a) To characterize the physical and chemical properties of the spent tungsten, W slurry.
- b) To study the effect of the mixed resin used for the removal of tungsten, W and iron, Fe ions from the spent slurry by varying amount of resin loading.
- c) To demonstrate the performance of Dowex monosphere MR-450 UPW mixed resin before loading and after loading with W-CMP slurry solution and characterize the physical and chemical properties of the resin.

1.4 Scope of study

In this study, the sample was prepared via ion exchange method which involve Dowex monosphere MR-450 UPW mixed resin and slurry containing tungsten, W. The characterization of tungsten slurry was done in terms of was tested for characterization test such as pH, conductivity, turbidity, viscosity, metals content, particle size distribution and zeta potential. For comparison purpose, results were compared to identify the effect of resin loading amounts for the ion exchange process towards establishing a feasible system to remove tungsten, W from the spent tungsten slurry samples.

On the other hand, the characterization of mixed resin were done by analyzed using, scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) spectroscopy.

Batch experiment investigation was done in order to carry out the analysis by studying the effect of resin loadings on removing tungsten from CMP spent slurry.

1.5 Organization of the thesis

This thesis is organized into five chapters which provide necessary general information and all the details of research findings. These chapters are the introduction, literature review, research methodology, results and discussion and conclusion and recommendations.

Chapter one briefly provide the introduction of the CMP process, application of CMP, spent slurry, importance of tungsten removal, problem statement, research objective, scopes of study and thesis organization.

Chapter two reviews all related technical information on CMP technology and process, CMP slurry, methods of removing heavy metals, ion exchange process and properties of mixed bed ion exchange resins.

Then, chapter three provides details on research methodology used throughout this thesis. This chapter is divided into six subsections (3.1 to 3.6). The first and second sections are on brief introduction to the chapter and all the materials and chemicals used in this study. The third and fourth sections provides detail information on the experimental works done in the form of a process flow and characterization works of properties of spent tungsten slurry needed for ion exchange analysis. Meanwhile, the fifth and last sections of this chapter describe the investigation on the effects of resin loadings on the performance of the resin in removing heavy metals (W and Fe) from the spent slurry solution.

In chapter four, the obtained results of all the studies done are discussed and explained in details in order to achieve the research objectives. This chapter is divided into two sections

(4.1 and 4.2). The first section briefly discusses on the work done to address the first objective. The second section provides the detail discussion about the heavy metal removal analysis to address the second and third research objective.

Last but not least, chapter five is on summary on the findings made throughout the work is provided. This chapter highlights the conclusions made and several recommendations for future research purpose.

CHAPTER TWO

LITERATURE REVIEW

2.1 Chemical Mechanical Polishing (CMP) Technology

Two terms have been used in this field, the chemical mechanical planarization and the chemical mechanical polishing. The chemical mechanical planarization is related to the polishing for the purpose of planarizing integrated circuit structures and other microelectronic devices. The chemical mechanical polishing is a more general term, including traditional polishing for example optics, semiconductor wafer preparation and metal polishing. Effectively planarized surface has enormous amount of benefits such as higher photolithography and dry etch yields, elimination of step coverage concerns minimization of prior level defects, elimination of contact interruption, undesired contacts and electro-migration effects reduction of high contact resistance and inhomogeneous metallization layer thickness and limitation in the stacking height of metallization layers. Integrated circuit (IC) is produced by deposition and modification of different metals layers (Zantye et al., 2004).

An integrated circuit, sometimes called a chip or microchip, is a semiconductor wafer on which thousands or millions of tiny resistors, capacitors and transistors are fabricated. IC can function as an amplifier, oscillator, timer, counter, computer memory, or microprocessor. A particular IC can be categorized as either analog or digital, depending on its intended application. The IC density is constantly increasing and the dimensions are decreasing. Therefore, instead of building a chip in the form of a printed circuit board with wires taking up most of the chip area, the patterned metal layers are placed above the chip. The layers are

separated by insulators creating multilevel interconnect system required for high-density integrated circuits. This is the one of the reasons for introducing the planarization into IC fabrication process. Other reasons are related to the fact that the optimal photolithography is achieved on flat surfaces and also planarization is necessary for shallow trench isolation and damascene technologies. Figure 2.1 shows the importance of CMP in layer stacking of chip.

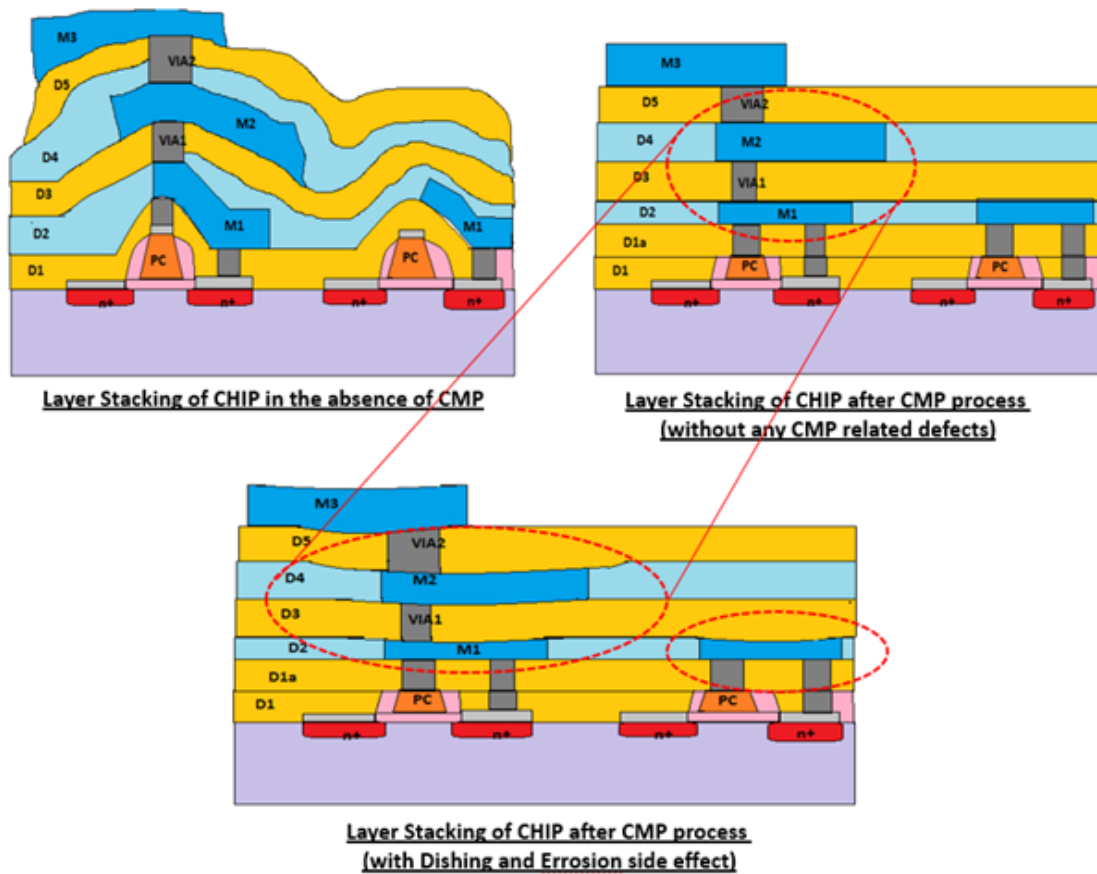


Figure 2.1: Importance of CMP in layer stacking of chip (Mithal, 2015).

2.1.1 CMP process

CMP is a process to remove material and to smooth surface, which is possible by the combination of chemical and mechanical interactions. The surface of the oxide layer is removed at different rates depending on the depth of removal and the pH of the solution (Ilie

and Ipaté, 2017). Current semiconductor fabrication technology for logic and memory devices requires CMP to achieve the required multilevel interconnections densities. Indeed, each silicon wafer can be exposed to 15 or more CMP steps before final device assembly. During CMP, the wafer is pressed face down against a rotating polishing pad, while a chemically and physically (abrasive) active slurry planarizes the wafer. As wafer size grows, devices sizes shrink and process requirements grow more stringent, within wafer uniformity and removal rate increase becomes a greater concern. Different CMP processes attempt to achieve a balance between removal rate and local or global planarization through a combination of solution chemistry, speed, applied pressure and pad properties. Often a change in slurry or operating conditions will cause a conflict performance (Zantye et al., 2004).

A schematic diagram of the CMP process is shown in Figure 2.2 shows the schematic of a wafer-abrasive slurry and pad contact during the CMP process. The CMP slurry consists of abrasives and chemicals that are homogeneously suspended in water. The chemically reacted layer formed by chemical reaction between the wafer and slurry is removed with the mechanical abrasion caused by the sliding of abrasives and asperities of the pad. In the case of the metal CMP, the general removal mechanism is the repetition of a generating passivation and its removal by mechanical abrasion. The passivation layer is a chemically reacted layer, such as stabilized oxide on the surface, to protect the final surface from corrosion. Thus, the necessity and mechanism of metal CMP are generally proposed in terms of the chemicals used in the slurry. The slurry consists of a highly basic or acidic solution, which results in pH changes in natural water and to toxic wildlife. Further, it is a short lifespan consumable unlike the long life span consumables such as pads, retaining rings,

backing films, and conditioner. Thus, the use of slurry is an important aspect of reducing consumption through the ideal slurry that can increase the material removal rate (MRR) and uniformity and defect free (Lee et al., 2016).

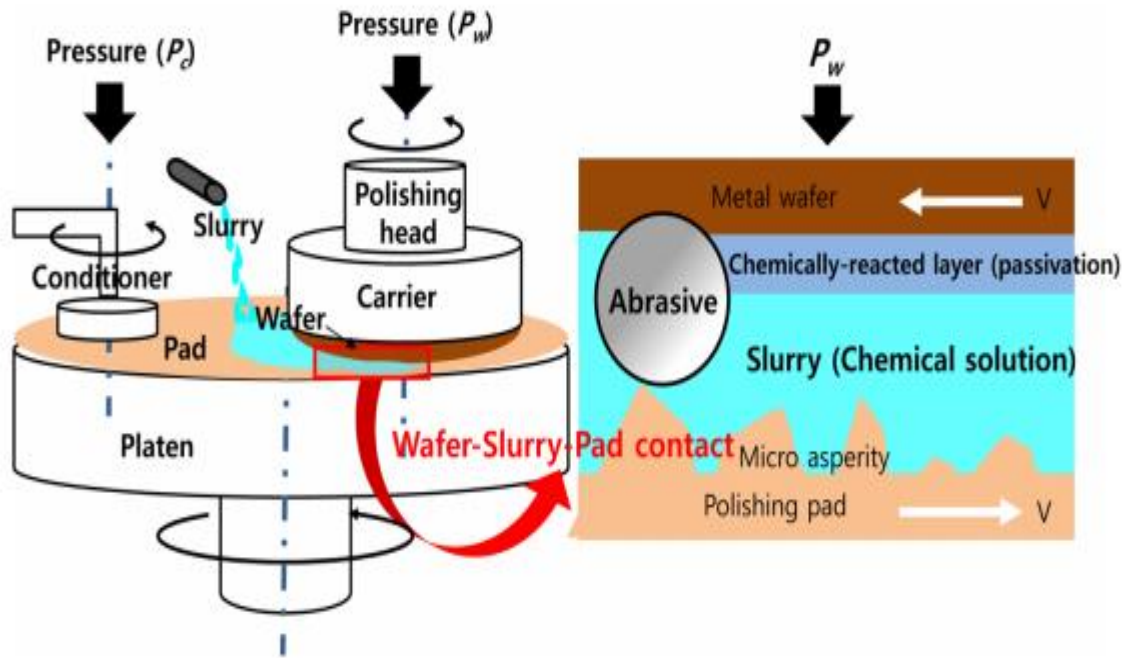


Figure 2.2: CMP schematic on wafer-slurry-pad contact region (Lee et al., 2016).

Removal rate (RR) is defined as the average thickness change of a deposited layer during polishing on the CMP machine divided by polishing time. Kaufman et al. (1991) mechanism explains the removal of specific metals used in microelectronics. It describes the material removal in the CMP as a cyclic sequence of abrasion of the passive oxide film covering the metal (depassivation) followed by anodic oxidation of the bare metal exposed to the oxidizing slurry (repassivation). By adjusting the oxidizing power of the CMP slurry it is possible to increase the thickness of the passive oxide film formed on the metal and to accelerate the material removal rate and thus the CMP process rate.

2.1.2 CMP slurry

One of the critical consumables in the CMP process is slurry which typically containing both abrasives and chemicals acting together, that directly affects CMP efficiency and the yield. Slight changes in slurry properties due to contamination, chemical degradation, abrasive content or applied shear can change polish performance and impact yield. Correlation of slurry property measurements with evaluations of wafer polish rate, planarity and defectivity provides insight into the root cause of degradation in polishing. The conventional slurry consists of abrasive particles of the solid state suspended in a liquid state chemical solution containing one or more of various chemicals such as oxidizers, pH stabilizers, metal ion complexants and corrosion inhibitors. An abrasive in the slurry provides both mechanical action with nanometer-sized abrasive particles and chemical action from the solution additives with a synergistic effect that causes material removal. The abrasive-liquid interactions play an important role in determining the optimum abrasives' type, size, shape and concentration through chemical and physical actions. The slurry designed for optimal performance should produce reasonable removal rates, acceptable polishing selectivity with respect to the underlying layer, low surface defects after polishing and good slurry stability. Thus, it is very important to choose slurry which provides good removal rates without causing defects in CMP process (Sivanandini et.al, 2013).

2.1.2.1 Role of CMP slurry

In CMP slurry, chemical reagents are reacting with the wafer surface being polishing to form a chemically modified top layer with desirable properties compared to the initial wafer surface. The modified layer has to be protective to achieve topographic selectivity.

Effect of slurry particle size and concentration on CMP material removal rate have been investigated by a number of researchers. CMP process is influenced by numerous slurry parameters such as pH, solution chemistry, charge type, concentration and size of abrasives, complexing agents, oxidizers, buffering agents, surfactants and corrosion inhibitors. An ideal CMP slurry should be possible to achieve high removal rate, excellent global planarization, should prevent corrosion (in case of metal, especially Cu), good surface finish, low defectivity and high selectivity (Zantye et al., 2004).

During CMP, slurry is spread over the pad. The function of the slurry is to continuously deliver the chemical components and abrasive particles to the entire wafer and to provide a means of removing reaction layers of the protrusion on the wafer surface. Different materials have different properties and characteristics, and the CMP processes for each material require different slurries. Therefore, it is important to understand the properties of slurry in order to predict its behavior during polishing. The abrasive component of slurry is delivered in solution phases and abrades in a solid phase to provide the mechanical part of the CMP (Lee et al., 2016). Most metals are thermodynamically unstable because of exposure to ambient environment, and they have the tendency to be oxidized. Thus, the chemical solution parameter of slurry is important in metal CMP, whereas the abrasiveness of slurry is vital in dielectric CMP because of its hydration mechanism.

Silicon dioxide, SiO_2 and aluminium oxide, Al_2O_3 abrasives are most commonly used in metal CMP because of their high hardness and stability. The oxidizer is a chemical species that removes an electron from a metal surface. The anions of the carboxylic acid react with metal ions to form insoluble or soluble salts as a passivation layer. In addition, the chelating agent forms complexes with metal ions. A combination of the oxidizer and

chelating agent would help to obtain a better passivation layer and high dissolution rate of the metal. The corrosion inhibitor protects the surface of the metal from the oxidizer in order to minimize dishing and erosion defects. There is a need for metal slurry because the excessive chemical etching and oxidation deteriorate the surface roughness of wafers.

A surfactant is a compound that changes the interfacial properties by lowering the surface tension between a liquid and a solid for post CMP cleaning. Surfactants have a hydrophilic polyethylene oxide group and a hydrocarbon hydrophobic group. Dylla-Spears et al. (2014) reported that a small amount of surfactants in polishing slurries can prevent agglomeration. (Li et al., 2005) showed that surfactant containing slurry can reduce the coefficient of friction (COF). At low pressures and velocities, the MRR was independent of the surfactant content, while at high pressures and velocities, surfactant-containing slurries caused an increase in the MRR. Finally, electrochemical equilibria depend largely on the pH condition of the slurry. The pH adjustor controls the acidity (less than pH 7) or basicity (greater than pH 7). The examples of pH adjustors are NaOH and KOH. Kang et al. (2004) reported that the pH of slurry affected the etch rate, passivation, corrosion, and the removal mechanism. In the solution, the metal exists in various states such as metal, metal ions, and metal hydroxide. Each of these components performs a significant role during the CMP process (Lee et al., 2016).

2.1.2.2 Spent slurry

As the spent slurry contains polishing by-products, it may decrease material removal rate and cause polishing defects. In the current standard CMP processes, because polishing by-products and pad debris are generated on the pad surface, large amount UPW is used to rinse the pad surface between wafer polishing. This is referred to as the pad rinsing step. At

the end of the pad rinsing step, there is appreciable amount of UPW staying on the pad surface and inside the pad grooves. When the fresh slurry is injected onto the pad surface to polish the next wafer, the fresh slurry will mix with the residue UPW and get diluted, resulting in a lower material removal. Therefore, the current standard pad center area slurry application method and previously proposed slurry application methods do not provide efficient slurry utilization and leave significant room to improve polishing performance (Meled et al., 2011).

Spent slurries contain hazardous chemicals and metal contents with large amounts of nano-abrasive particles. Even though the recovery and reuse of spent slurries have been investigated, no IC manufacturer has reported to reclaim and recycle CMP slurries. This is because of the complex chemical constituents and reaction products in the spent slurries. Therefore, optimizing slurry usage is the best solution to achieve a more cost effective and environmentally benign CMP process. During polishing, pad rotates while a large amount of fresh slurry flows directly off the pad surface without entering the pad–wafer interface due to the centrifugal forces. This causes a very low slurry utilization. Several alternative methods have been proposed to apply the slurry onto the pad surface during polishing. Mok (1999) proposed an apparatus for spraying slurry onto the pad surface rather than pumping the slurry onto the pad center area. Chamberlin et al. (1999) proposed a slurry injection technique involving spraying the slurry onto the pad under pressure through multiple nozzles. Chiou et al. (2002) proposed a slurry injector having multiple adjustable nozzles. Chang (2005) proposed a method for dispensing slurry through multiple nozzles to distribute the slurry over the entire wafer track. While these proposed methods aid to deliver fresh slurry to the pad–wafer interface, none of these methods avoid mixing of spent slurry with the fresh slurry during CMP processes.

2.1.2.3 Solution for metal slurry

CMP slurries are mostly complex mixtures of water, alkali or acid, abrasives, additives for specific purposes, which may or may not physically or chemically interact with each other. The slurry properties are highly sensitive to slurry chemistry, temperature as well as the effect of shearing during delivery. As a result of shearing agglomeration of particles might occur in the slurry solution. Viscometer tests which determine viscosity at a particular temperature in steady-state mode have been previously used to determine the changes in the slurry due to shear.

Zantye et al. (2004) reported that there are four different commercial tungsten slurries which are $\text{Fe}(\text{NO}_3)_3$ -based, H_2O_2 -based, KIO_3 -based, and H_5IO_6 -based slurries. Ferric nitrate $\text{Fe}(\text{NO}_3)_3$ was used as the first oxidizer at the starting stage. $\text{Fe}(\text{NO}_3)_3$, KIO_3 and H_2O_2 individually or in mixture as oxidants for W CMP. Generally, the $\text{Fe}(\text{NO}_3)_3$ -based, the KIO_3 -based and the H_5IO_6 -based oxidizer will dissociate into cations and anions (with different NOx and IOy complexes), and the anions will oxidize tungsten. While, H_2O_2 -based slurry break down into H_2O (water) and dissolved oxygen (O_2). Then O_2 directly reacts with tungsten. Basically, the oxidizing ability is in the order of $\text{H}_2\text{O}_2 > \text{Fe}(\text{NO}_3)_3 > \text{H}_5\text{IO}_6 > \text{KIO}_3$. However, $\text{Fe}(\text{NO}_3)_3$ causes excessive oxidation and results in contamination by Fe^{3+} ion-formed tungsten oxidation of FeCuO_2 or $\text{Fe}(\text{WO})_4$. The H_2O_2 -based slurry performed the best in slurry evaluation and used widely as an oxidizer in CMP slurry due to its simplest and most stable peroxide, and a powerful oxidizing agent without contaminated wafers (Lee et al., 2016). However, it has problems with plug recess and field oxide erosion (Meled et al., 2011).

2.1.2.4 Removal of tungsten polishing

In the case of tungsten polishing (W-CMP), the aqueous medium contains a strong oxidizer hydrogen peroxide, H_2O_2 and an iron catalyst such as ferric nitrate, $Fe(NO_3)_3$. The removal of the tungsten layer is achieved by chemical as well as mechanical action. The oxidizer mixture induces the passivation of the tungsten upper layer. The removal of the oxidized tungsten layer requires two processes which are passivation (abrasion) and chemical dissolution. Moreover, it is known that the dissolution static etch rate has to be low to prevent corrosion and planarization defects. Other additives may be included in the chemical composition for a better control of the slurry stability and of the tungsten layer formation and removal kinetics (Testa et al, 2014).

2.2 Methods of removing heavy metals

Heavy metals are the environmental priority pollutants and are becoming one of the most serious environmental problems. So these toxic heavy metals should be removed from the wastewater to protect the people and the environment. Many methods that are being used to remove heavy metal ions include chemical precipitation, ion-exchange, adsorption, membrane filtration and electrochemical treatment technologies. Heavy metals removal from aqueous solutions has been traditionally carried out by chemical precipitation for its simplicity process and inexpensive capital cost. However, chemical precipitation is usually adapted to treat high concentration wastewater containing heavy metal ions and it is ineffective when metal ion concentration is low. Plus, chemical precipitation is not economical and can produce large amount of sludge to be treated with great difficulties. (Fu and Qi, 2011).

Chemical precipitation is effective and by far the most widely used process in industry (Ku and Jung, 2001) because it is relatively simple and inexpensive to operate. In precipitation processes, chemicals react with heavy metal ions to form insoluble precipitates. The forming precipitates can be separated from the water by sedimentation or filtration and the treated water is then decanted and appropriately discharged or reused. The conventional chemical precipitation processes include hydroxide precipitation and sulfide precipitation. However, there are potential dangers in the use of sulfide precipitation process. Heavy metal ions often in acid conditions and sulfide precipitants in acidic conditions can result in the evolution of toxic H₂S fumes. It is essential that this precipitation process be performed in a neutral or basic medium. Moreover, metal sulfide precipitation tends to form colloidal precipitates that cause some separation problems in either settling or filtration processes.

There are some research on chemical precipitation in combination with ion-exchange treatments. Papadopoulos et al. (2004) reported using ion-exchange processes individually and then combining with chemical precipitation in removing nickel from wastewater streams from a rinse bath of aluminum parts. They found that the individual application of ion exchange led to the removal of nickel up to 74.8%, while using the combination of ion exchange and precipitation processes, higher removal from 94.2% to 98.3% was obtained. Besides, treating acid mine water by the precipitation of heavy metals with lime and sulfides, followed by ion exchange was also researched by (Feng et al., 2000). Conventional chemical precipitation processes have many limitations and it is difficult to meet the increasingly stringent environmental regulations by application of conventional precipitation processes to treat the heavy metal wastewaters especially containing coordinated agents.

Adsorption is now recognized as an effective and economic method for heavy metal wastewater treatment. The adsorption process offers flexibility in design and operation and in many cases will produce high-quality treated effluent. In addition, because adsorption is sometimes reversible, adsorbents can be regenerated by suitable desorption process. The high cost of activated carbon (AC) limits its use in adsorption. Many varieties of low-cost adsorbents have been developed and tested to remove heavy metal ions. However, the adsorption efficiency depends on the type of adsorbents. Biosorption of heavy metals from aqueous solutions is a relatively new process that has proven very promising for the removal of heavy metal from wastewater. Membrane filtration technology can remove heavy metal ions with high efficiency, but its problems such as high cost, process complexity, membrane fouling and low permeate flux have limited their use in heavy metal removal. Using coagulation-flocculation heavy metal wastewater treatment technique, the produced sludge has good sludge settling and dewatering characteristics. But this method involves chemical consumption and increased sludge volume generation. Electrochemical heavy metal wastewater treatment techniques are regarded as rapid and well-controlled that require fewer chemicals, provide good reduction yields and produce less sludge. However, electrochemical technologies involving high initial capital investment and the expensive electricity supply, this restricts its development (Fu and Qi, 2011).

Ion-exchange method have been widely used to remove heavy metals from wastewater due to their many advantages, such as high treatment capacity, high removal efficiency and fast kinetics (Kang et al., 2004). Ion-exchange resin, either synthetic or natural solid resin, has the specific ability to exchange its cations with the metals in the wastewater. Among the materials used in ion-exchange processes, synthetic resins are commonly

preferred as they are effective to nearly remove the heavy metals from the solution (Alyuz and Veli, 2009). The most common cation exchangers are strongly acidic resins with sulfonic acid groups ($-\text{SO}_3\text{H}$) and weakly acid resins with carboxylic acid groups ($-\text{COOH}$). Hydrogen ions in the sulfonic group or carboxylic group of the resin can serve as exchangeable ions with metal cations. The uptake of heavy metal ions by ion-exchange resins is rather affected by certain variables such as pH, temperature, initial metal concentration and contact time (Gode and Pehlivan, 2006). Thus, ion exchange has been widely applied for the removal of heavy metal from wastewater. However, ion-exchange resins must be regenerated by chemical reagents when they are exhausted and the regeneration can cause serious secondary pollution. Furthermore, it is expensive, especially when treating a large amount of wastewater containing heavy metal in low concentration, so they cannot be used at large scale.

Heavy metals are usually treated by adjusting solution pH to form metal precipitates, followed by coagulation, clarification, and filtration in industrial wastewaters. Although the precipitation method is quite effective to remove the heavy metals from industrial wastewaters, the resultant heavy metal sludge is classified as hazardous waste and generates other disposal problems. Several methods including solidification, extraction, bio-leaching, electrodialysis, microwave radiation and ion-exchange have been used for detoxifying of metal sludge. Ion-exchange is a possible and effective method to recover heavy metal species from solution or solids by directly contacting with ion exchange resin. For the recovery processes by metal dissolution, an essential limit of the recovery efficiency is the thermodynamic equilibrium, the solid dissociates to such an extent that traces of heavy metal species are saturated in the solution. The sludge solid and the slightly dissolved metal ions

equilibria in the solution can be disturbed in the presence of cationic ion-exchange resin according to the Le Chatelier principle (Lee et al., 2007).

2.3 Ion exchange

Ion exchange is the process through which ions in solution are transferred to a solid matrix which, in turn releases ions of a different type but of the same polarity. Ion exchange is a physical separation process in which the ions exchanged are not chemically altered. The main advantages of ion exchange are recovery of metal value, selectivity, less sludge volume produced and the meeting of strict discharge specifications. Ion-exchange resins are variety of different types of exchange materials, which are distinguished into natural or synthetic resins. Among the materials used in ion exchange processes, synthetic resins are commonly preferred as they are effective and inexpensive. Ion exchange is a mass transfer process. There are two main rate-determining steps which are considered in most of the ion exchange reactions. Diffusion of ions inside the material defined as intra- particle diffusion or diffusion of ions through the liquid film surrounding the particle defined as film diffusion. The rate of ion exchange is determined by both or the slower of these two processes. Industrially ion exchange reactions are conducted in either fixed bed or fluidized bed columns. The performance of fixed and fluidized bed is a strong function of equilibrium, kinetic and hydrodynamic factors, of which the hydrodynamic factor is the most important (Zewail and Yousef, 2015).

The advantages of ion exchange are can be used with fluctuating flow rates, makes effluent contamination impossible and resins are available in large varieties from suppliers and each resin is effective in removing specific contaminants. However, the limitations of ion exchange are pretreatment is required for most surface waters, waste is highly

concentrated and requires careful disposal, unacceptable high levels of contamination in effluent and units are sensitive to the other ions present (Reddy et al.,2014).

In recent research approaches (Huo et.al, 2014), shows that the separation between W and Mo has been a difficulty due to their extremely similar physicochemical properties, resulting from the lanthanide contraction. Thus, to separate W from molybdate solution depends on changing the properties of W or Mo compounds and exploiting these property differences. The chemical species of W and Mo essentially depend on the pH values and the metal-ion concentrations. By taking advantage of the tendency difference to polymerize at pH around 6.5–7.5 between Mo and W, basic adsorbents particularly those containing tertiary amino groups or macroporous anion exchangers were investigated. Hence, the result were presented good W removal efficiency. At pH around 6.5–7.5, W in aqueous solutions would be preferentially polymerized into polymeric ions while Mo still mainly exists as monomeric ions. The separation is effective and promising, except for the difficulty of controlling the pH within the narrow range of 6.5–7 without adding extra precipitation reagents. Due to the higher electrovalence of the polytungstate anions than the monomeric ion, W polymeric ions will be preferentially adsorbed using anion adsorbents. Besides, some other researches also proposed to add precipitation agents, such as the divalent ions and tin (IV) oxide hydrate that would preferentially form precipitations with W under certain conditions. The separation was effective but a large number of precipitation agents were required and the impurity ions accompanied with the added reagents were inevitable, increasing the impurity-removal burden (Zhu et al., 2016).

2.3.1 Application of ion exchange for heavy metal ions removal

Ion exchange technique can remove traces of ion impurities from water and process streams and give a product of desired quality. Ion exchangers are widely used in analytical chemistry, hydrometallurgy, antibiotics, purification and separation of radioisotopes and find large application in water treatment and pollution control (Clifford, 1999; Luca et al., 2009). The list of metals which are recovered and purified on an industrial scale by means of ion exchange include are uranium, thorium, rare earth elements (REEs), gold, silver, platinum group metals (PGMs), chromium, copper, zinc, nickel, cobalt and tungsten.

2.3.2 Ion exchange resin

Besides synthetic resins, natural zeolites, naturally occurring silicate minerals, have been widely used to remove heavy metal from aqueous solutions due to their low cost and high abundance. Many researchers have demonstrated that zeolites exhibit good cation-exchange capacities for heavy metal ions under different experimental conditions. Though there are many reports on the use of zeolites and montmorillonites as ion-exchange resin to remove heavy metal, they are limited at present compared with the synthetic resins and the application of zeolites is on the laboratory experiments scale. More work is needed for the application of zeolites at an industrial scale (Fu and Qi, 2011). There are two basic types of resins which are cation exchange and anion exchange resins. Cation exchange resins will release Hydrogen (H^+) ions or other positively charged ions in exchange for impurity cations present in the water. Anion exchange resins will release hydroxyl (OH^-) ions or other negatively charged ions in exchange for impurity anions present in the water (Reddy et al., 2014).

The extent to which the exchange takes place can be measured and ion exchange resins can be used in methods of analysis. For example to determine the amount of sodium ions in a solution, the sodium ions is mixed with a cation exchange resin. Then, the amount of hydrogen ions that exchange can be determined by titrating of the resulting solution with sodium hydroxide. The amount of hydrogen ions that measured will be the same as the sodium ions that were in the original solution because in this case they exchange in a 1:1 ratio. The hydrogen ions released from the cationic ion-exchange resin will neutralize the hydroxide ions so that the equilibrium will shift until all the metal ions are leached into solution and adsorbed onto the ion exchange resin (Lee et.al, 2007). An experimental study of heavy metal sludge extraction was conducted by the authors (Lee et al., 2007) using both Amberlite IRC-718 and Amberlite IR-120. The stronger cationic exchange resin, Amberlite IR-120, was found to favor a lower heavy metal residue in the sludge. Therefore, another study aimed at understanding the heavy metal extraction kinetics in the presence of Amberlite IR-120 is being conducted.

2.3.3 Mixed bed ion exchange resin

Mixed resins of Dowex monosphere MR-450 UPW is a uniform particle size mixed bed ion exchange resin for ultrapure water production. It is a bifunctional styrene-divinylbenzene(S-DVB)-based nonseparable, gel-type, ion-exchange resin with sulfonic acid (350 UPW) and quaternary ammonium (550 UPW) functionality. S-DVB resins are stable across a range of reaction temperatures and do not degrade easily because of high-shear mixing rates (De Rezende et al. 2008). Its components are design to be non-separating to maintain quality when hydraulically transferred. The UPW grade product is characterized by the very high conversion to ionic sites (95.0% min.), excellent rinse profiles for conductivity