EFFECT OF pH ON TUNGSTEN REMOVAL FROM CHEMICAL MECHANICAL POLISHING (CMP) SLURRY USING DOWEX MARATHON C RESIN OF ION EXCHANGE

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by

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In the name of Allah Most Gracious and Most Merciful

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LIST OF SYMBOLS

°	Temperature	°C
T_w	Shear rate	s^{-1}
V	Velocity	m/s
P	Pressure	atm
W	Dry weight	g
µ	Viscosity	cp
S	Turbidity	NTU
Q_{eq}	Ion Adsorption Capacity	mg/g
C_i	Initial Concentration	mg/L
C_t	Final Concentration	mg/L
V_f	Volume of Feed Solution	mL
t	Time	hour
ζ	Zeta potential	µE

NOMENCLATURE

Chemical Vapor Deposition	CDV
Chemical Mechanical Polishing	CMP
Energy-Dispersive X-ray spectroscopy	EDX
Integrated Circuit	IC
Iron	Fe
Inductively Couple Plasma – Mass Spectroscopy	ICP-MS
Material Removing Rate	MRR
Sodium Hydroxide	NaOH
Scanning Electron Microscope	SEM
Tungsten	W

KESAN pH TERHADAP PENYINGKIRAN TUNGSTEN DARIPADA BUBURAN PROSES PENGILATAN KIMIA MENGGUNAKAN PROSES PERTUKARAN ION OLEH DOWEX MARATHON C RESIN

ABSTRAK

Buburan proses pengilatan kimia digukan secara menyeluruh di dalam industri semikonduktor sebagai agen penggilap untuk meratakan permukaan wafer. Proses penggilapan ini membabitkan tindakan kimia dan mekanikal untuk menyingkirkan lapisan logam yang telah terjejas di atas permukaan wafer dengan menggunakan buburan tungsten. Pemulihan terhadap buburan tungsten ini amat penting untuk mengurangkan kos operasi seterusnya mengurangkan jumlah pengeluaran air sisa daripada industri. Oleh itu, kajian terhadap pemulihan terhadap buburan tungsten telah dijalankan menggunakan kaedah pertukaran ion iaitu dengan menggunakan kation resin secara spesifiknya. Kation resin yang digunakan ini tergolong dalam kumpulan pertukaran kation asid kuat iaitu Dowex Marathon C resin. Faktor yang dipertimbangkan dalam kajian ini adalah perbezaan pH oleh buburan tungsten terpakai. Kajian terhadap karakter buburan tungsten sangat penting untuk memahami metod yang terbaik untuk pemulihan buburan tungsten tersebut. Oleh itu, beberapa kajian terhadap karakter buburan tungsten telah dilakukan iaitu meliputi pH, kandungan logam, konduktiviti, zeta berpotensi dan juga purata saiz partikel di mana perubahan pH akan mempengaruhi semua aspek di atas. pH yang digunakan semasa kajian adalah 3.84, 5.26, 8.50 dan juga 10.84 dengan jumlah resin sebanyak 5 g, isipadu buburan tungsten terpakai sebanyak 150 mL dan masa campuran selama 120 minit. Oleh itu, rumusan daripada kajian ini mendapati bahawa penyingkiran tungsten berlaku lebih efisien pada pH yang berasid iaitu 9.70% penyingkiran di pH 3.84 berbanding penyingkiran ferum yang terbaik berlaku pada pH 10.84 dengan peratus penyingkiran sebanyak 39.49%.

EFFECT OF pH ON TUNGSTEN REMOVAL FROM CHEMICAL MECHANICAL POLISHING (CMP) SLURRY USING DOWEX MARATHON C ION EXCHANGE RESIN

ABSTRACT

The chemical mechanical polishing slurry is widely used in the semiconductor industry as a polishing agent to polish the surface of wafer. The polishing process involve the chemical and mechanical action to remove the modified layer on the surface of the wafer by tungsten slurry. The recovery of the tungsten slurry is important to help reducing the cost of operation and reduce the production of wastewater by the industry. The recovery of spent tungsten slurry is study by using the ion exchange process by using the cation resin. Cation resin used is classified as strong acid cation exchange which is the Dowex Marathon C resin. The parameter that consider in this study is the pH different of the spent tungsten slurry. The study on the characterization of the tungsten slurry is vital to understand the best recovery method for the tungsten slurry. The study of characterization of tungsten slurry involve the pH, metal content, conductivity, zeta potential and mean particle size where the change in pH of slurry will affected the conductivity, zeta potential and mean particle size of the slurry. The pH used in this study is 3.84, 5.26, 8.50 and 10.84 with amount of resin used is 5g, volume of spent slurry is 150 mL and time contact between resin and slurry is 120 minutes. As a conclusion, the removal of tungsten showed that the best removal in the acidic pH with 9.70% removal at pH 3.84 and the iron removal from slurry showed that the best removal is when the pH is alkali with 39.49% at pH 10.84.

CHAPTER ONE

INTRODUCTION

1.1 Research Background

Chemical mechanical polishing or planarization (CMP) is the technology for integrated circuit (IC) manufacturing in semiconductor industry to attain the local and global planarity of wafer surface (Xin et al., 2010). The CMP process is done to modify the surface roughness on the surface of the wafer where the roughness will cause the wafer to be malfunction. Other application of the CMP process also to remove the thin metal, semiconductor film and insulator film (Cadien, 2001). The CMP process have three significant components: a semiconductor wafer, a polishing slurry and a polishing pad (Liang et al., 1997). The schematic of the CMP process is shown in the Figure 1.1 below.

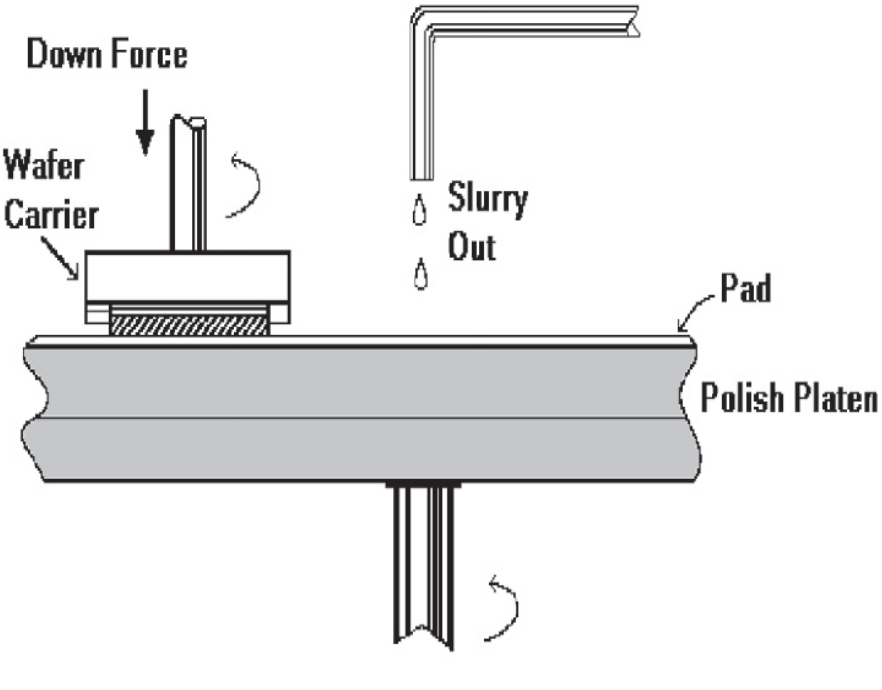

Figure 1.1: A schematic polishing process (Cadien, 2001)

The wafer is placed at the bottom of the wafer carrier and pressed on the polishing pad with the known pressure. The polishing slurry is pumped on the surface of pad at the centre and the centripetal force help to spread the slurry over the surface of the polishing pad where the polishing pad is install at the rigid base plate that is rotated on their own axial position (Cadien, 2001). To improve the life of the pad, the wafer also rotating on radial position because the usage of space of wafer on the pad surface increase, thus lowered the chance for the pad to exhausted.

In the manufacturing of wafer, tungsten (W) is commonly used to form conductively layer on the surface of the wafer. W is used for the establishment of contact, via and hole for linked the inter-layer metal line in the integrated circuit manufacturing (Kang et al., 2010). The tungsten in the slurry help to form the tungsten oxide layer at the surface of the wafer. The tungsten oxide layer will be polished using the abrasive materials in the slurry to remove the excess tungsten on the surface of the wafer.

The polishing slurry used in the CMP process contain abrasive materials that is crucial in removing the excess materials on the surface of wafer. Silica is one of the content in the slurry that give the colour of the slurry is chalky. The content of the silica also effected the turbidity of the slurry. Another content in the slurry is alumina or ceria and an aqueous medium that assist the suspension of the abrasive materials in the slurry (Testa et al., 2014;Testa et al., 2011). Besides that, slurry can be highly acidic or basic that will cause the effect to the environment and toxic to life either animal or plant. The tungsten slurry is acidic and the slurry is added with the oxidizer where it take part in the improving the removal rate of unwanted tungsten layer which is the layer of the tungsten oxide that formed on the surface of the wafer (Kang et al., 2010). The layer is softer than the tungsten on the wafer’s surface.

The recovery of the slurry is significant to make sure that the slurry can be recycle back for other polishing purpose. The recovery of slurry also help to minimize the cost of manufacturing microchip processor in the microelectronic industry (Testa et al., 2014). The method that can be used to recovery of slurry or recycling the used slurry by using ion exchange resin. According to the Helfferich (1962), ion exchanger is the insoluble solid substance that conduct the cation and anion for exchange with other cation and anion in the electrolyte solution. On the other hand, ion exchanger is the crucial and very effective in cost minimization techniques for the removal or treatment the metal ions that contain in water or aqueous solution (Nabi, 2012). The advantages of the ion exchange are the higher recovery for the metals, selectivity is higher towards metals and have potential to meet exact discharge requirements for the wastewater (Gode and Pehlivan, 2006).

The purpose of using ion exchanger in recycling the slurry is to remove the tungsten in the tungsten slurry by using the cation exchanger. Tungsten have positive charge that suitable to be remove by using cation exchanger. Cation exchanger normally consist of sulfonic acid group, phosphoric acid group, sulphonamides and azole derivatives (Ran et al., 2017). Those of the group mentioned is the functional group for the ion exchange resin that differentiate the type of resin. Sulfonic acid group give the resin with strong acidic resin while amino group in the ion exchange resin give the characteristic of the resin with strong basic. The resin with different functional group have their own chemical properties for the removing the metals in aqueous solution but it have the same physical properties (Al-Saidi, 2016).

1.2 Problem Statement

Tungsten slurry used in the semiconductor industry contain many components that help in the CMP process for the wafer manufacturing industry. The content of the spent tungsten slurry can be recycled to be used for another CMP process. The chemical properties of that slurry is changed when it used to polished the wafer surface due to the slurry will mixed with the tungsten oxide layer that form on the surface of wafer when the process is take place. In order to reduce the cost of producing the tungsten slurry, the recovery of the spent tungsten slurry is significant. Therefore, the method that can be used to recover the spent tungsten slurry is by using the ion exchanger due to the method used does not give significant effect to the composition of the slurry. The ion exchange procedure for removal of tungsten from spent tungsten slurry is the prospective procedure to recover the spent tungsten slurry. Up to that point, the research must be conducted due to the information of removing the tungsten from spent tungsten slurry is limited.

1.3 Research Objectives

The research objectives for this work are shown below;

1. To determine the physical and chemical properties of the spent tungsten slurry.
2. To study the effect of tungsten removal using (i) varying the pH of spent slurry on the Dowex Marathon C resin and (ii) the selectivity of removal the tungsten (W) and iron (Fe) using the cation resin as parameters.
3. To analyse the surface of the cation resin (Dowex Marathon C resin) before loading and after loading with tungsten.

1.4 Scope of Study

The study is concern on the spent tungsten slurry recovery from the polishing process in the wafer fabrication process by using the ion exchanger resin. The resin used is cation resin which is Dowex Marathon C resin. The first part for this study is focused on the characterization of the spent tungsten slurry in term of the physical and chemical properties such as turbidity, pH and conductivity, metal content and viscosity. After the characterization of the spent tungsten slurry is carried out, the analysis of the amount of tungsten remove from the spent tungsten slurry by varying the pH of the spent tungsten slurry and also the amount of the resin loading used is conducted. The last part in this study is to analyse the behaviour of the Dowex Marathon C resin on the terms of physical properties before and after loading with tungsten.

1.5 Organization of the Thesis

This thesis contain five chapters that will provide the general information for the work that have done. These chapters include the Introduction, Literature Review, Methodology, Result and Discussion and Conclusion and Recommendation.

Chapter one in this thesis discuss about the background of the CMP process that cover the CMP slurry and the ion exchange resin. The problem statement, research objective and also scope of the thesis also provided in this chapter. Chapter two is the literature review that review all the aspects that include the CMP technology, CMP slurry, tungsten polishing and also the ion exchange especially the cation resin.

Then, chapter three is the research methodology. In this chapter, the information is about the method that been used for the research. The chapter is divided into six section. The first section is describe about the introduction to the experiment, the second section is about chemicals and material used in the experiment. The third section is about the characterization of the spent tungsten slurry in terms of physical and chemical properties. The fourth section provide information about analysing of the tungsten removal from the spent tungsten slurry. The last section is about addressing the last objective.

Chapter four is the result obtained is discussed and explained in details to achieve the objectives of the project. This chapter discusses about (i) the analysing the spent tungsten slurry on characterization, (ii) the different of the parameters that affected the spent tungsten slurry behaviour (iii) the analysing the removal of tungsten and iron from the spent tungsten slurry and (iv) analysing the surface of resin also been covered.

The last chapter is chapter 5. In this chapter, the overall findings is summarized and conclude. The several recommendations also been proposed for this project.

CHAPTER TWO

LITERATURE REVIEW

2.1 Background of Chemical Mechanical Polishing technology

In the last 40 years, lapping and polishing was used in preparation of the single crystal substrate or known as wafer in the semiconductor field. To insure flatness and parallelism, lapping is done on both side of the wafer (Cadien, 2001). Another technique that was used to obtain the high quality of polished surface was electrolyte polishing that was widely used in 1960s (Liang et al., 1997). This technique was replaced after a few decades with the chemical mechanical polishing (CMP). The new technique help to remove the thin metal, insulator and semiconductor film that used in the integrated circuit (IC) manufacturing (Cadien, 2001).

Besides that, CMP also introduced to the world for the semiconductor processing that used to planarize the inter-level dielectric (ILD) (Chen et al., 2012). The problem arise for the manufacturing the ILD when the first level of metal was fabricated and the second level have a few fabrication problem that take into account of deposition, resist patterning and also etching. Another technology also been introduce before the CMP technology where it known as spin-on glass (SOG), unfortunately this technology gave troubles where the process was difficult but it had its own advantage such as reduce the problem of multi-level integration in IC fabrication. To overcome those problems, the CMP technology is introduce to the semiconductor industry.

2.2 Description of Chemical Mechanical Polishing process

Chemical mechanical polishing (CMP) process is the tribochemical process that are require three components which are semiconductor wafer, polishing slurry and polishing pad (Liang et al., 1997). The friction on the polishing pad was produced when the mechanical wear accelerated by chemical reaction. The polishing slurry contain the abrasive particles that help to remove the unwanted materials on the surface of the wafer and get the high quality of the wafer. The process or mechanism of the CMP process is done by applied the known force is on the wafer carrier to the polishing pad and at the same time the polishing slurry also let to be flow on the surface of the polishing pad. The known force is in the range of 1-10 psi (Oliver, 2004). The wafer carrier is rotating on its own radial axis and same goes to the polishing pad. This movement help to increase the rate of removal of the unwanted layer on the surface of wafer.

The mechanism on how the materials on the surface of wafer is removed have been studied. According to Xin et al., (2010), the materials on the surface of wafer is clean off by the strong shear stress that is promoted by the non-Newtonian slurry that is flows on the surface of the polishing pad. The first action that taken by the polishing slurry is to start the chemical reaction on the surface of the wafer by chemical that contain in the slurry. The reaction of the atom or molecules on the surface of wafer with the polishing slurry will form a layer or weakened or passivated protective layer on the surface of the wafer. This layer then will be removed by the shear of the polishing slurry. With the help of the strong shear stress the layer can be remove easily from the surface of the wafer. The flowing of the slurry help to transport the materials or the atom/molecules away from the wafer surface (Xin et al., 2010). The process will be repeated until the surface of wafer is clean from the unwanted atom/molecules. Figure 2.1 show the schematic diagram for the removal of the atom/molecules from the wafer surface.

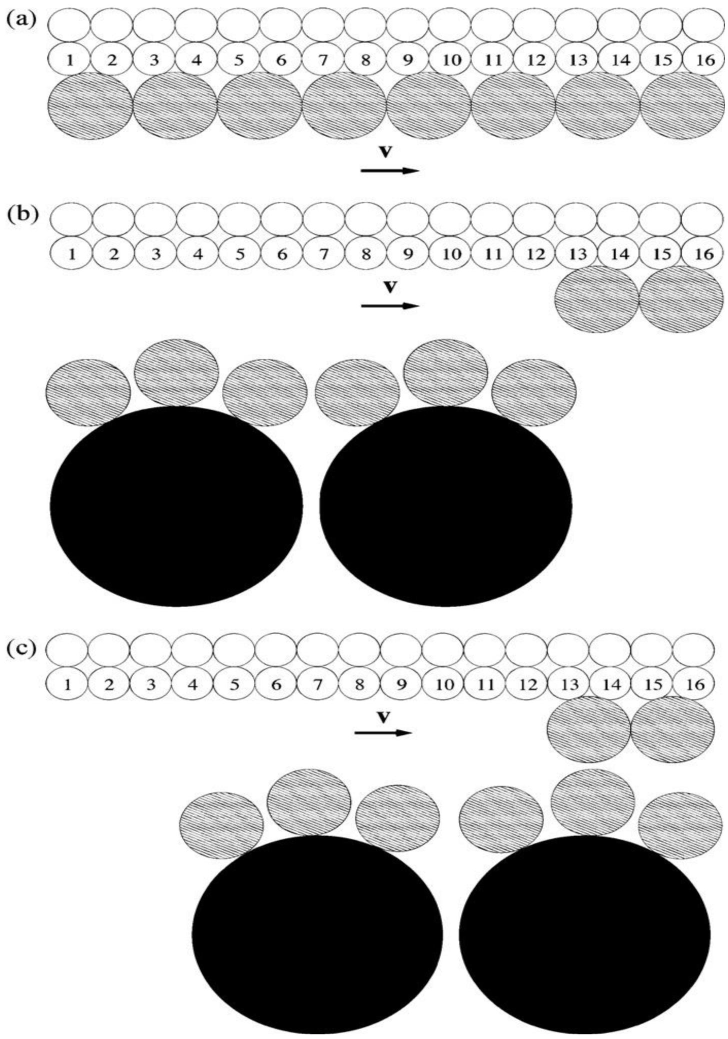

Figure 2.1: A schematic diagram for the removal of the atom/molecules from the wafer surface (Xin et al., 2010)

The mathematical model for this process also been studied to make sure that the materials removal rate can be calculated and determined. Preston's Law was the first mathematical model presented that can use to describe the material removal rate (MMR). The equation 2.1 (Chen et al., 2012) below shown the material removal rate of the CMP process.

$\rho = C_p PV$ ……………………………………………………………..………… (2.1)

The equation showed that the MMR is directly proportional to the applied pressure on the polishing pad and the velocity of the rotation between two surfaces. The C_p on the equation does not give advance effect to the calculation because the C_p is the Preston constant coefficient that is constant in the equation. According to the Oliver (2004), the relationship of the material removal rate and the pressure and velocity is empirical where the materials on the surface of the wafer is remove by grinding but it give the reasonable data that can be used in the wafer polishing process.

2.3 Tungsten polishing

Tungsten is one of the metals that been used in the fabrication of the integrated circuit (IC). Tungsten have great filling in the formation of the holes, contact and via for the connecting the inter-layer metal line for IC manufacturing (Kang et al., 2010). This process is done via the Chemical Vapor Deposition (CVD). In the earlier used of tungsten in the IC fabrication, the tungsten is removed from the IC by the isotropic plasma etch process (Oliver, 2004) and the tungsten was deposited in very thick form to avoid uncontrolled of etching process that can damage the surface of the IC. To overcome this problem, the tungsten plug technology is developed with deposition in the range of 0.5-0.8 μm. This technology help to reduce the thickness layer of the tungsten deposited on the surface of IC. Figure 2.2 show that the illustration of the fabrication tungsten plugs in contact holes.

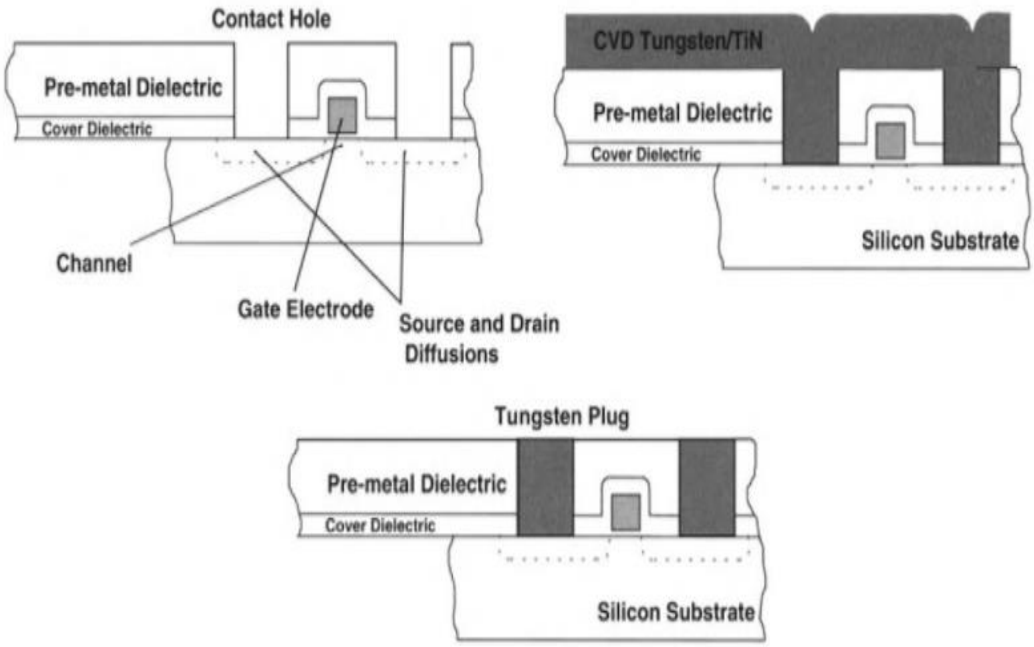

Figure 2.2: An illustration of the tungsten plug in contact holes (Oliver, 2004)

The endpoint for the removal of tungsten on the surface of IC is crucial to make sure that the surface of IC is not damage or overpolishing. The method for determining the endpoint for removing the tungsten is developed by using the spindle and platen motor driven current. By using this method, it help to determine the endpoint for the polishing of the tungsten on the surface of IC.

The removal of tungsten from the surface can be done in two different ways; firstly by passivation and the other way is by static etch dissolution, but static etch dissolution can lead to corrosion and also damage the planarization process (Coetsier et al., 2011). However, the tungsten CMP give adverse effect to the manufacturing field where it give cost effective and retrofit.

2.4 Chemical Mechanical Polishing slurry

A slurry contain abrasive materials such as silica, alumina or ceria and aqueous solution that help in the facilitating the suspension of the materials and also some slurry have an oxidizing agent (Testa et al., 2011). The slurry is the main component in the CMP process because of the characteristic of their own that help in the process of polishing. The slurry is different for every CMP process. Abrasive materials that contained in the slurry is the main character for the mechanical part of the CMP process. The abrasive materials in the slurry plays a role to abrade the chemically treated surface on the wafer of IC that want to polish from the surface in the aid of force on the wafer or IC surface. The table 2.1 below showed the particle properties of the abrasive materials in the slurry.

Table 2.1: Particle properties for abrasive materials in the slurry

Property	**Silica**	**Alumina**	**Ceria**
Particle structure	Amorphous	Poly-crystalline	Poly-crystalline
Crystal structure		Orthorhombic (corundum)	Cubic
Density (g/cc)	2.2-2.6	3.97 (alpha)	7.13
Hardness (Mohs)	6-7	9	
pH	2.2	9	7

In the slurry composition, there also have the aqueous media that help in the CMP process. Besides the function of the aqueous media to provide a suspension for other materials in the slurry, it also give the chemical agents that is used to attack the surface of the wafer that need to be polished. The chemical agents that contain in the slurry acts as pH adjusters, oxidizers, catalyst and inhibitor (Oliver, 2004). There are another functions of the aqueous media in the slurry like provide the electrostatics that help in stabilize the suspension of the abrasive and as a lubricant for the wafer and the polishing pad.

The stability of the slurry also can be measured by looking at the rate of settling. The slower the rate of settling the suspension materials in the slurry, the longer the feature of the slurry remain consistent. The understanding of the viscosity of the slurry is crucial due to the viscosity can affect the whole stability of the CMP removal rate and also the flow on the polishing pad. As stated by the Oliver (2004), the shear rate for the CMP slurry is higher than 10^6 s^{-1}. The slurry is the Newtonian, but it can change to non-Newtonian when the pH is vary due to the changes of the shear rate in the slurry that also lead to the change of the viscosity (Cruz and Peng, 2016).

2.5 Ion exchange technology

Nowadays, the used of ion exchange as one of the separating agent or adsorbing agent is increase due to the retrofit of its technology. The ion exchange is the materials that composed of the hydrophobic substrates, immobilized ion functionalized group and the movable counter ions (Ran et al., 2017). The usage of the ion exchange is widen because it is used in the wastewater treatment, water quality industry, electrodialysis, water desalination, removal of heavy metals and many other fields.

The dissociation of the ion-functionalized group will occur when the water molecules is penetrate and the cation or anion will be release (Ran et al., 2017). This showed that there are two types of the ion exchange and this can be classified into two; cation exchange and anion exchange. The different between these two types of ion exchange is cation will exchange with the positive ion and the anion will exchange with the negative ion. In the cation exchange, the most components are sulfonic acid, phosphoric acid and also carboxylic acid group. Those are the components that help in build the cation exchange. Besides the cation exchange, the anion also have their own identity that made up its backbones. The backbones of the anion is quaternary ammonium cation, imidazole cation and guanidinium cation (Ran et al., 2017).

Water softening is one of the example of the mechanism of the ion exchange. The mechanism involve the cation exchanger, which a reaction replaces calcium ions with sodium ions. The reaction below showed the replacement of the cation in water softening.

$Ca^{2+}_{(aq)} + 2NaR_{(s)} \leftrightarrow CaR_{2(s)} + 2Na^{+}_{(aq)}$……………………………………………….(2.2)

R in the reaction is the ion exchanger. The reaction is reversible and does not cause the changes to the solid ion structure (Seader et al, 2011).

The cation exchange have the sulfonic group that determined whether the cation is strong cation or weak cation. The sulfonic group in the cation exchanger can be completely dissociate from the $–SO_3^-$ groups and freely move within the particles. This controlled the overall requirement of the electrical neutrality of the solution.

2.6 Properties of Ion Exchange Resin

The ion exchange resin have a few properties that differentiate it’s from other method in adsorption process. The properties is swelling, capacity, stability, particle size (Kopeliovich, 2013) and selectivity. The swelling of the ion exchange resin is different for every type of resin and it’s depends on the moisture content of the resin in different solvent (Bodamer and Kunin, 1953). However, many types of resin is porous so that it can permit the accessed of solvent and ions without swelling. There are some condition where swelling of the resin can occur which is when the low cross-linking gel resin and the functional group of the resin contain large amount of water that cause the swelling of the resin to be happen (Kopeliovich, 2013).

The capacity of the ion exchange resin is the amount of the chemical equivalent that can be taken up by the unit amount of resin (Kopeliovich, 2013). The higher capacity of the resin will give higher amount of the chemical that be adsorbed by the resin. Another properties of ion exchange resin is stability. The toughness polymer structure of the resin give the mechanical stability of the resin and the chemical resin stability decrease when the resin degrade due to some fouling on the pores of the resin by the precipitation of some chemicals.

The other properties of the ion exchange resin is the particle size. The resin usually in the sphere form or granules that comes with specific size. In the industry, the resin is in spherical or beads form that have particle size around 0.3 mm to 1.2 mm. The smaller the resin will cause the pressure drop in when it is used in column and also cause decreasing in flow rate. The selectivity of the ion exchange resin is one of the crucial properties that determined the efficiency of the adsorption of the particle in the solution. The reaction for the ion exchange is reversible so that the selectivity of the ion exchange is depends on the excess of electrolyte in the solution. Resin selectivity coefficients in the reaction is regulate for range of ionic species either for cation (H^+) or anion (OH^-) and the selectivity value are assigned at 1.00 (Gregor and Bregman, 1951).

2.7 Strongly Acidic Cation Exchange Resin

Strongly acidic cation exchange resin is the resin with sulfonic acids as functional group and its chemical behaviour that similar to strong acid. The strong acid cation exchange resin is available in two form which are hydrogen form ($R\text{-}SO_3H$) and sodium form ($R\text{-}SO_3Na$) (Kopeliovich, 2013). The different of these form are the ion in the functional group which are one carry hydrogen ion (H^+) and the other carry sodium ion

(Na^+). The functional group of the strong acid cation exchange resin is extremely ionized and the hydrogen ions and sodium ions also extremely dissociated and exchangeable in the solution. The strong acid cation exchange resin can exchange their ions in any pH of solution from 0 to 14. Therefore, the strong acid cation resin is showed properties that is independent to the pH of the solution. The common processes that can use strong acid cation exchange resin is water softening and demineralization (Kopeliovich, 2013) which are the water treatment.

CHAPTER THREE

METHODOLOGY

3.1 Introduction

This chapter will cover all the chemicals, equipment and the experimental procedure that have been used in the study. The first part which is 3.2 will discuss about the chemicals and materials used in the experiment. In the 3.3 section will go into the experimental work that presented in the flow diagram. In the third section (3.4) will review about the characterization of the spent tungsten slurry in terms of chemical and physical properties. The fourth section (3.5) will explore about the performance of the cation resin used in the term of pH and resin loading. The last section which is 3.6 will discuss about the behaviour of the resin before and after loading with the tungsten from the spent tungsten slurry.

3.2 Chemical and Material

The chemical and material that were used in the study of the removal of the tungsten from spent tungsten slurry were 1M of sodium hydroxide (NaOH) and Dowex Marathon C resin respectively. Table 3.1 showed the characteristic of NaOH that is used to adjust the pH of the slurry to study the removal of the tungsten from spent tungsten slurry with 98.99% purity.

Table 3.1: Chemical used in the experiment

Items	**Purity**	**Supplier**	**Molecular formula**	**Purpose of use**
Sodium hydroxide	98.99%	Malay-Sino Chemical Industries Sdn. Bhd.	NaOH	pH adjustment of slurry

The resin used in this experiment is Dowex Marathon C resin which is the cation resin that is in group of strong acid cation resin. The resin is used in the softening and demineralization application in the industries. The Table 3.2 and 3.3 below pictured the pyhsical and chemical properties of the resin used.

Table 3.2: Material used in the experiment

Items	Physical form	Functional group	pH	Supplier
Dowex Marathon C resin	Amber translucent spherical beads	Sulfonic acid	0-14	The Dow Chemical Company

Table 3.3: Physical and chemical properties of the Dowex Marathon C resin

Description	Dowex Marathon C resin
Physical form	Amber translucent spherical beads
Matrix	Styrene-DVB, gel
Functional group	Sulfonic acid
Ionic form	H^+ form
Total volume capacity, min (eq/L)	1.8
Particle density	1.20
pH range	0-14
Maximum operating temperature (°C)	120

3.3 Experimental Process Flow

The slurry was collected from the SilTerra Malaysia Sdn. Bhd. that was located in Kulim Hi-Tech Park, Malaysia. The company conducted a semiconductor industry in Malaysia. The sample was collected by manually where the raw slurry take directly from the operator tools after the polishing process.

The experiment was carried out in three parts where the first part was conducted to characterize the chemical and physical properties of spent tungsten slurry. The characterization involve the turbidity, metal content, conductivity, pH and the viscosity of the slurry. The second part about to analyse the removal of tungsten from spent tungsten slurry by mixed it cation resin. The experiment was carried out to analyse the amount of the tungsten that can be removed from the spent tungsten slurry by varying the pH and the resin loading using the Inductively Couple Plasma – Mass Spectroscopy (ICP-MS). The last part was carried out to analyse the cation resin before and after loading with tungsten.

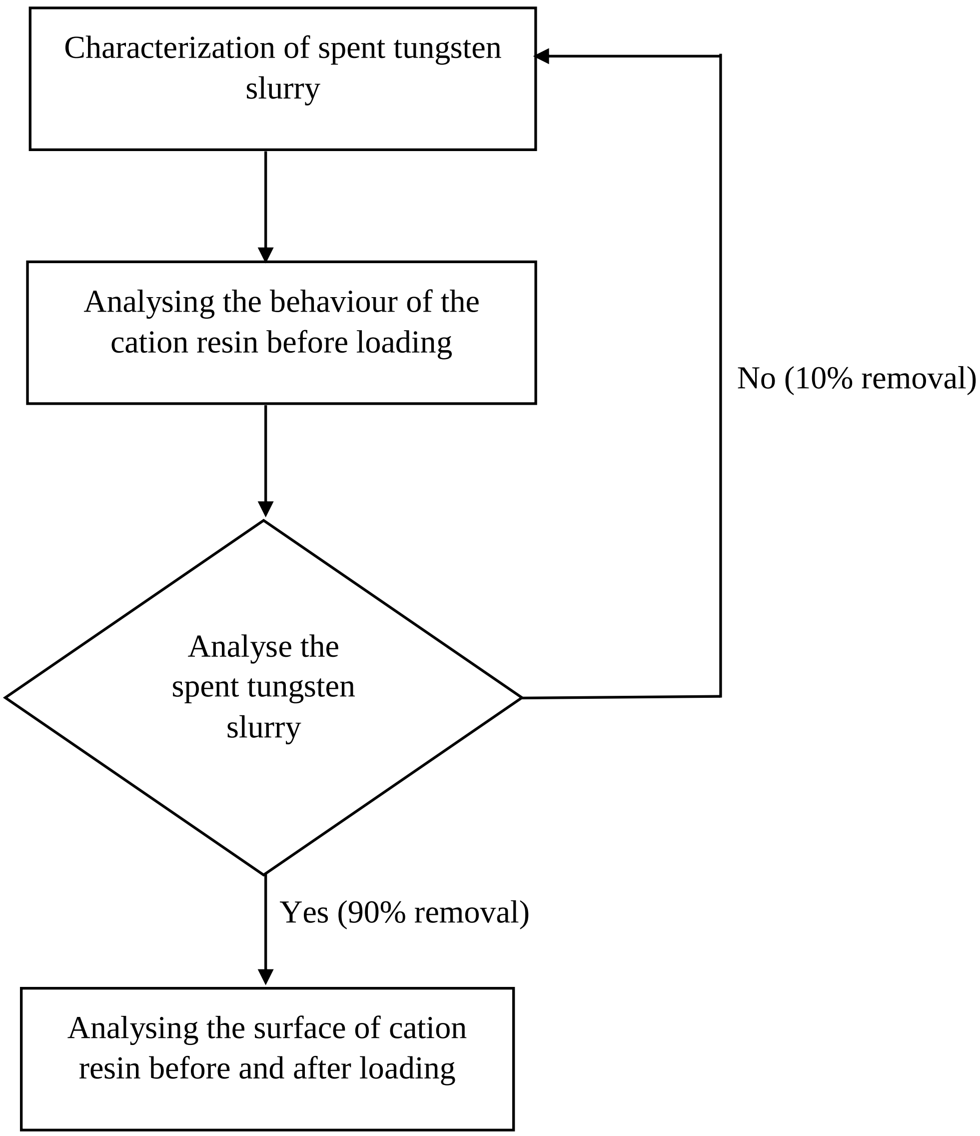

Figure 3.1: Process flow diagram for the overall experimental works involved

3.4 Characterization of the chemical and physical properties of the spent tungsten slurry

3.4.1 pH and conductivity

The pH and conductivity of the spent tungsten slurry was determined to know the actual value of pH and the conductivity that the spent tungsten slurry had after the polishing process was done. The conductivity was measured because to determine the amount of electrolyte in the sample. The electrolyte in the sample was effected by the amount of metal in the sample. This to make sure that the pH and the conductivity did not affected the entire experiment.

3.4.2 Turbidity (NTU)

Turbidity of the spent tungsten slurry was measure to know the total suspended solid that contain in the spent tungsten slurry. The total suspended solid pictured the percentage of silica in the spent tungsten slurry.

3.4.3 Metal content

Spent tungsten slurry was tested with the ICP-MS to determine the metal content in the sample. In this tested, the main aspect it to know the amount of the tungsten or initial amount of tungsten that contain in the spent tungsten slurry. This initial amount of tungsten can be used to determined how much of the tungsten that can be removed from the spent tungsten slurry by using ion exchange resin. The amount of the iron (Fe) also be measured using this equipment to determine the selectivity of the resin on the removal of metal from the spent chemical mechanical polishing slurry.

3.4.4 Viscosity

Viscosity was measured using the rheometer. The aim for determining the viscosity for spent tungsten slurry because of the particle content in the slurry will give effect to the shear stress and shear rate of the slurry. This help to study the changes of the shear rate and shear stress when the removal of the tungsten from the spent tungsten slurry.

3.4.5 Zeta Potential and Particle Size Distribution

Zeta potential and particle size distribution of the particle inside the slurry is determined by the Malvern Zetasizer Nanoseries. The sample about 1 mL is pour in the disposal cuvette to determine the size of particle in the sample. For the determining the zeta potential of the sample, the 1 mL of sample is poured in the dip cell which can convey the electricity through the cuvette. The temperature used in this test is 25°C and the solvent used is water. The measurement of the sample is done automatically by using the software on the computer that give the result automatically. The result is determined by the diffraction of light through a sample in the equipment that give the result on the zeta potential and also particle size distribution.

3.5 The Removal of Tungsten from the Spent Tungsten Slurry

3.5.1 Effect of Varying the pH

The sample was prepared with the different pH. The pH was varied for 5.26, 8.50 and 10.84. The sample with the initial pH 3.84 also been used as a control parameter. The pH of 100 ml of sample was adjusted by using 1M sodium hydroxide solution (NaOH). NaOH solution was prepared by diluting the 8 g of NaOH pellet in 200 ml of distilled water. Then, the sample was mixed with the cation resin (Dowex Marathon C resin) and stirred for 120 minutes at 25°C ± 1°C. The sample then filtered and analysed using ICP-MS to determine the amount of the tungsten that had been removed by using the cation resin.

3.5.2 Analysing the Samples

12 mL of sample was collected and analysed using ICP-MS to determine the amount of the tungsten after been adsorbed by the cation resin (Dowex Marathon C resin). The amount of the tungsten adsorbed was calculated by Equation 3.1 (Guikun Zheng; Hui Ye, 2015) below;

$$Q_{eq} = \frac{(C_0 - C_t) x\, V_f}{W} \quad \text{.......... (3.1)}$$

Where Q_{eq} = ion adsorption capacity (mg/g); C_0 = initial concentration of feed solution (mg/L); C_t = final concentration at time t (mg/L); V_f = volume of feed solution (ml) and W = dry membrane weight.

The percentage of sorption was calculated by using the Equation 3.2 (Bhatti et al., 2017),

$$\%\, Sorption = \frac{C_i - C_f}{C_i}\, x\, 100 \quad \text{.......... (3.2)}$$

Where C_i = initial concentration (mg/L); C_f = final concentration (mg/L)

3.6 Study the Surface of the Resin Before and After Loading with Tungsten and Iron

3.6.1 Scanning Electron Microscope (SEM) and (Energy-Dispersive X-ray spectroscopy) EDX Analysis

Scanning electron microscope (SEM) was used to observe the surface of the resin before and after loading. The SEM help to determine the chemical composition, crystalline structure and the orientation that making up the sample. In addition, the EDX was used for the elemental analysis and the chemical characterization of the sample. The magnification used in the range 500x to 20000x. For sample after loading, the samples were let to be dry first before the analysis can be done.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Analysis the Spent Tungsten Slurry

4.1.1 Characteristic of Spent Tungsten Slurry

A few analysis is conducted to determine the characteristic of the spent tungsten slurry in the wafer polishing process. The analysis conducted to determine the metal content which is the concentration of tungsten (W) and iron (Fe), pH, conductivity, turbidity, viscosity and the zeta potential and particle size distribution. The Table 4.1 below showed the characteristic of the spent tungsten slurry.

Table 4.1: Characteristic of spent tungsten slurry

Parameters	**Spent tungsten slurry**
pH	3.73±0.01
Conductivity (µS/cm)	539.67
Metal content (ppb)	
Tungsten (W)	15154.94
Iron (Fe)	480.08
Turbidity (NTU)	70.47
Zeta potential (ζ)	-11.3±0.2
Particle size (nm)	161.5
Poly-dispersion Index (PdI)	0.228
Viscosity (cp)	1.50