CHARACTERIZATION AND BEHAVIOUR OF SILICON DIOXIDE NANOPARTICLES IN CHEMICAL MECHANICAL POLISHING WASTEWATER WITH THE PRESENCE OF FERROUS SULPHATE AND POLYALUMINIUM CHLORIDE

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ABSTRAK

Pada abad ke dua puluh satu, industri semikonduktor adalah salah satu industri pembuatan yang paling berdaya saing di seluruh seluruh dunia. Keadaan ini disebabkan permintaan semikonduktor yang tinggi daripada pembuatan alat-alat elektronik yang berteknologi tinggi. Walaupun terdapat banyak wafer dan cip yang dihasilkan setiap hari oleh pihak industri, namun kesedaran pentingnya menjaga alam sekitar menjadi semakin rendah dalam kalangan masyarakat. Oleh kerana pengeluaran semikonduktor semakin meningkat setiap tahun, sisa air semikonduktor yang dijana daripada pengeluaran juga meningkat. Untuk mengelakkan sisa air semikonduktor terus mengalir ke alam sekitar, banyak bahan pengental digunakan untuk merawat sisa air semikonduktor. Walau bagaimanapun, sisa air semikonduktor tidak dapat rawat sepenuhnya kerana masih ada sisa dalam skala nano tertinggal dalam sisa air. Dalam kajian ini, potensi zeta dan saiz zarah air sisa semikonduktor menjadi tumpuan untuk memerhati perubahan ciri-ciri ini dengan nilai pH yang berbeza. Tujuan kajian memerhati sikap potensi zeta dan saiz zarah adalah untuk menambah pemahaman yang lebih baik mengenai mekanisme penggumpalan. Tambahan pula, sulfat ferus dan poly-aluminium digunakan sebagai bahan pengental dalam kajian ini untuk menyiasat bagaimana potensial zeta dan zarah saiz sisa air sisa semikonduktor berubah semasa bahan pengental ditambah. Berdasarkan keputusan kajian, poly-aluminium adalah koagulan yang dapat meneutralkan potensial zeta untuk sisa air semikonduktor pada 30 mg/L. Bagi ferus sulfat, ia tidak berkesan seperti poly-aluminium di mana nilai potensi zeta lebih rendah dan saiz zarah tidak berubah. Kesimpulannya, poly-aluminium mempunyai potensi yang lebih baik untuk merawat sisa air semikonduktor berbanding dengan ferus sulfat.

ABSTRACT

In the twenty-first century, semiconductor industry is one of the most competitive manufacturing industries around worldwide. This is due to high demand of semiconductor for the manufacturing of electronic devices in this high technology era. While there are many wafers and chips produced daily from the industries, it seems the awareness of people to the environment become lesser among the society. As more semiconductors produced throughout every year, the chemical mechanical polishing (CMP) wastewater generated from the output also increased. In order to prevent the CMP wastewater directly flow into the environment, there are many coagulants and methods done to treat the CMP wastewater. However, the CMP wastewater is always to purify at the best condition as there are some residue in nano-scale still left in the wastewater. In this study, zeta potential and particle size of CMP wastewater are concerned to observe how these characteristics behave along different pH value. The purpose for study of behaviour of zeta potential and particle size is to have a better understanding on the coagulation mechanism. Furthermore, ferrous sulphate and poly-aluminium are used as coagulant in this study to investigate how zeta potential and particle size of CMP wastewater behave as coagulants are added. Based on the results, poly-aluminium is an effective coagulant which able to neutralize the zeta potential of CMP wastewater at 30 mg/L. However, ferrous sulphate does not as much effective as poly-aluminium where zeta potential is slightly lower while particle sizes are remained constant. In conclusion, poly-aluminium has better potential to treat CMP wastewater compare to ferrous sulphate.

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LIST OF ABBREVIATIONS

CMP	Chemical Mechanical Polishing
COD	Chemical Oxygen Demand
EDL	Electrical Double Layer
PZC	Point of Zero Charge
DLS	Dynamic Light Scattering
DAF	Dissolved Air Flotation
UF	Ultrafiltration

CHAPTER 1

INTRODUCTION

1.1 Semiconductor Manufacturing Industries

For the past few decades, semiconductor industry has well developed sector in Malaysia and many other countries around the world. In the next few years, this industry is expected to expend its growth to a wider prospect (Lee et al., 2011). The electric and electronic industry has assumed the role of a prime mover in the Malaysian economy securing foreign investment and creating employment. According to the Malaysia Investment Performance Report 2015, exports of electrical and electronic products accounted for RM277.9 billion and contributed 44.4 percent of total manufacturing goods in 2015 (Growth, 2015).

The semiconductors are used in various types of equipment such as computer devices, telecommunication devices, consumer electronic products, electronic control devices, scientific and also in medical test equipment. Water is fundamental to the manufacture of semiconductors. The semiconductors produced must be rinsed after produced, which require massive amount of water. According to (GWI, 2009), industry statistics indicate that creating an integrated circuit on a 300 mm wafer requires approximately 2200 gallons of water in total, of which 1500 gallons is ultra-pure water. Ultra-pure water which is defined as water of utmost purity and without presence of microorganisms, minerals, or trace organic or nonorganic chemicals (Lee and Choi, 2012). It is widely used in polishing the semiconductors and hence large amount of wastewater is produced from the effluents of semiconductor industry which is known as chemical mechanical polishing (CMP) wastewater.

The semiconductor industry not only consumes an ever-increasing amount of water but, as a consequence, also ends up discharging large volumes of wastewater. Lin et al. (2006) stated that exposure to silicon dioxide nanoparticles is associated with the development of several autoimmune diseases, including systemic sclerosis, rheumatoid arthritis, lupus, and chronic renal disease, while certain crystalline silica polymorphs may cause silicosis and lung cancer. Industrial water consumption, as well as environmental pollution, is being closely monitored by certain agencies are demanding that water consumption be reduced and that discharged wastewater have low levels of suspended solids (Mekonnen et al., 2015).

1.2 Problem Statements

The treatment of CMP is a burden to semiconductors industry as the operating cost is very high. The high treatment cost also due to the high amount of coagulants or chemicals required to treat CMP. The semiconductor industry spends approximately $1 billion on water and wastewater systems and services every year. Some semiconductor manufacturers were recycled the water to minimise the cost before reuse again to polish microchips. Through reduction, reuse and recycling water at semiconductor plants, the industry could save over $100 million per year. However, there is an inherent risk if water is containing impurities where short-circuiting and other defects may occur. Many types of treatment have been applied to chemical mechanical polishing wastewater to prevent the release of silicon dioxide nanoparticles into the environment. However, due to its minute size (100 – 200 nm), the silicon dioxide nanoparticles are still unattainable to be destabilized and aggregated to an appropriate size and molecular weight that induces precipitation via conventional coagulation. The ultrafiltration section in the wastewater process has a membrane with pore size in range of 1 – 100 nm requires high maintenance and operating cost. Should there be any inefficiency in the chemical precipitation reactor, this will lead to a high burden loading of silicon dioxide nanoparticles in ultrafiltration process, leading to clogging. Therefore, it is imperative to study the surface charge and particle size to reduce the loading of suspended solids from the early stages of the treatment process.

1.3 Research Objectives

The objectives for this research include:

1) To study the zeta potential and z-average particle size of silicon dioxide nanoparticles in CMP wastewater as a function of pH
2) To evaluate the zeta potential and z-average particle size of the applicable coagulants as a function of pH
3) To analyse the physicochemical interaction between silicon dioxide nanoparticles and coagulants in separate experiments to identify their behaviour

CHAPTER 2

LITERATURE REVIEW

2.1 Semiconductor Manufacturing Processes

Starting with an uniformly doped silicon wafer, the fabrication of integrated circuits needs many sequence of complex process steps. The most important process steps used in the semiconductor fabrication are lithography, etching, deposition, chemical mechanical polishing, oxidation, ion implantation and diffusion (Wong et al., 2013).

Lithography is used to transfer a pattern from a photomask to the surface of the wafer. The pattern defined by the mask is either removed or remained after development, depending if the type of resist is positive or negative. For example, the developed photoresist can act as an etching mask for the underlying layers.

Etching is used to remove material selectively in order to create patterns. The pattern is defined by the etching mask, because the parts of the material, which should remain, are protected by the mask. The unmasked material can be removed either by wet or dry etching. Wet etching is strongly isotropic which limits its application and the etching time can be controlled difficultly. On the other hand, dry etching is highly anisotropic but it is more capable for transfer small structures.

A multitude of layers of different materials have to be deposited during the integrated circuit fabrication process. The two most important deposition methods are the physical vapor deposition and the chemical vapor deposition. During physical vapor deposition, accelerated gas ions sputter particles from a sputter target in a low pressure plasma chamber. The principle of chemical vapor deposition is a chemical reaction of a gas mixture on the substrate surface at high temperatures.

Processes like etching, deposition, or oxidation, which modify the topography of the wafer surface lead to a non-planar surface. CMP is used to plane the wafer surface with the help of a chemical slurry. First, a planar surface is necessary for lithography due to a correct pattern transfer. Furthermore, CMP enables indirect pattering, because the material removal always starts on the highest areas of the wafer surface. This means that at defined lower lying regions like a trench the material can be left. Together with the deposition of non-planar layers, CMP is an effective method to build up IC structures.

Oxidation is a process which converts silicon on the wafer into silicon dioxide. The chemical reaction of silicon and oxygen already starts at room temperature but stops after a very thin native oxide film. For an effective oxidation rate, the wafer must be settled to a furnace with oxygen or water vapor at elevated temperatures. Silicon dioxide layers are used as high-quality insulators or masks for ion implantation

Ion implantation is the dominant technique to introduce dopant impurities into crystalline silicon. This is performed with an electric field which accelerates the ionized atoms or molecules so that these particles penetrate into the target material until they come to rest because of interactions with the silicon atoms. Ion implantation is able to control exactly the distribution and dose of the dopants in silicon. The dopant dose can be controlled by varying the ion source

Diffusion is the movement of impurity atoms in a semiconductor material at high temperatures. The driving force of diffusion is the concentration gradient. There is a wide range of diffusivities for the various dopant species, which depend on how easy the respective dopant impurity can move through the material. Diffusion is applied to anneal the crystal defects after ion implantation or to introduce dopant atoms into silicon from a chemical vapor source. In the last case, the diffusion time and temperature determine the depth of dopant penetration.

2.2 Characteristics of CMP Wastewater

Chemical mechanical polishing (CMP) is a highly used planarization technology in the manufacturing of semiconductors. Available studies estimates that CMP process consumes as much as 40% of the ultrapure water used in semiconductor manufacturing (Lai and Lin, 2003). Hence, treatment of CMP wastewater is important so it can be reuse to reduce the amount of water usage. The quality of semiconductor wastewater is concerned by researchers as it is important to understand the behaviour of wastewater before undergo any treatment.

The total solids in CMP are extremely high but the suspended solids have been reported to be very low (Hu et al., 2005; Yang and Yang, 2004). This is because the CMP contain many fine particles and contaminants. The wastewater had a diluted milky appearance due to oxide particles content in the solution (Chou et al., 2010). The wastewater also had high turbidity and pH range between 8 to 9. The CMP also has high chemical oxygen demand (COD) concentration (Wong et al., 2013).

Improper treatment of the CMP will cause river pollution as the CMP may contain heavy metal. Once the water flow into river, living organisms in aquatic environment will accumulate heavy metals in tissues and undergo bioaccumulation. Concentrations of these elements may increase as they may move up the food chain because of slow breakdown in the environment, food chain energetics, and biomagnification.

2.3 Previous Studies on CMP Wastewater Treatment

In order to solve the problems, many studies were conducted to treat the wastewater. There are several studies conducted to treat the CMP in several ways. Among the methods that were used in these studies are air flotation (Ghazy et al., 2010;

Chou, 2010), electrocoagulation (Chou et al., 2010; Kabdaşlı et al., 2012), and ultrafiltration (Chou et al., 2010). There are also certain studies that combined the methods to treat the semiconductor wastewater (Hu et al., 2005; de Luna et al., 2009). There are also some studies which separate the silica from the wastewater using different coagulant such as aluminium chloride (Liu and Tourbin, 2012), cetyltrimethylammonium bromide (Liu et al., 2013) and poly-aluminium chloride (Coagulation, 2010).

2.4 Semiconductor (CMP) Wastewater and its Properties

CMP wastewater treatment is one of major problems faced by semiconductor industry. The treatment of CMP wastewater is distinctly different with ordinary wastewater. This is due to the release of contaminants in CMP wastewater can cause some environmental issues.

CMP wastewater has the nature of high alkalinity, total solids content, and turbidity (Yang et al., 2003; Chou et al., 2009). The pH value of CMP normally is between 8 to 9. High total solid content is due to the presence of fine particles and chemicals such as oxidising agents (Lai and Lin, 2003). However, suspended solids is very low in CMP wastewater as the size of the fine particles are in nanoscale (Lin and Yang, 2004). High total solids content also cause the high turbidity of the water. The CMP wastewater is in milky colour due to the oxide presence in it (Chou et al., 2010).

The chemical oxygen demand (COD) value of CMP wastewater is very high due to high inorganic and organic content (Lin and Kiang, 2003; Lin and Jiang, 2003; Chou et al., 2009). CMP wastewater possesses highly negative surface charges that repel particles and contribute their suspension stability (Liu and Lien, 2006; Liu and Tourbin, 2012). This also prevents aggregation occur between particles. Thus, the zeta potential of CMP wastewater is also highly negative charge.

2.5 Nanoparticles Properties

2.5.1 Zeta Potential

Molecules surface interactions are composed of several complex mechanisms such as electrostatic interactions, van der Waal forces and hydrophilic interactions. Electrostatic interactions are the most important interaction forces among of them. Zeta potential is a parameter used to measure the electrostatic interactions on the surface charge of nanoparticles in a solution (Salg et al., 2012). Zeta potential also determines the electrical double layer (EDL) repulsive forces strength between particles and controls the stability of a colloidal system (Sabah et al., 2007). Understanding the concept of zeta potential is very important for conducting the wastewater treatment especially for coagulation process.

Zeta potential also able to determine the stability of suspension of colloids (Cosgrove, 2010). Despite the zeta potential affecting electrostatic repulsion between particles, the greater the zeta potential value, the stronger the repulsion the more stable the system of a solution. As the value of zeta potential is larger, many colloidal particles show good dispersion as the electrostatic repulsion becomes stronger (Ostolska and Wiśniewska, 2014). However, as the zeta potential registers close to zero, the particles become unstable and are likely to aggregate (Kłodzińska et al., 2010). Hence, the aim of the study is to adjust the zeta potential of CMP wastewater so that the charges between the nanoparticles surface are neutralised and no repulsion will occur between the nanoparticles.

2.5.2 Point of Zero Charge

The point of zero charge (PZC) or isoelectric point, defined as the pH value at which the net proton charge equals zero, is an important parameter for understanding the aggregation process between nanoparticles (Kosmulski and Saneluta, 2004). When nanoparticles are dispersed in solutions at PZC, the surface charge of nanoparticles approaches zero and the electrostatic force is depleted, followed by the formation of aggregation between nanoparticles.

It is familiar that when metal oxide surfaces exposed to either the ambient environment or immersed in aqueous solutions the outermost layer of hydroxyl groups will be terminate due to their interaction with water molecules (Dai and Song, 2016). The surface charge is positive when pH values below PZC and negative at pH values above PZC (Samad et al., 2014).

If $pH<PZC$:

$$-MOH(surface) + H^+(aq) \leftrightarrow -MOH_2^+ \text{ (surface)} \qquad (2.1)$$

If $pH>PZC$:

$$-MOH(surface) + OH^-(aq) \leftrightarrow -MO^- \text{ (surface)} + H_2O \qquad (2.2)$$

where M denote as metal ion.

Several research have conducted to find the behaviour of nanoparticles at PZC (Umh & Kim, 2013). The results found that as the solutions approach their PZC, the size distribution of nanoparticles within them are increasing. This prove that the particles are experience aggregation and the size of the aggregates are largest at PZC.

2.5.3 Electrical Double Layer

Electrical Double Layer (EDL) is a structure on the surface of particles which affects the dispersion of ions interface region, resulting in an increased concentration of opposite charged ions near to the surface. It consists of 2 elements where the inner element known as compact layer or “Stern layer” and outer element known as diffuse layer or zeta potential (Biswas, 2009).

Many models have been developed which explain the EDL behaviour since a decade ago. The models include Helmholtz double layer model, Guoy-Chapman double layer model, and Stern modification double layer. The Helmholtz double layer model states surface charge is neutralized by opposite charged ions placed at an increment of atomic distance away from the surface (Wang and Pilon, 2011). The model was later modified by Gouy and Chapman on the consideration thermal motion of ions near the charged surface, which is referred as a diffuse layer (Zhang and Zhao, 2009). Then, Stern combined two previous models and described the EDL as two layers namely Stern layer and diffuse layer (Wang and Pilon, 2011). Although these models describe the vital behaviour of the ions near the particle’s surface forming the double layer, they ignore some key factors caused the inconsistency with the experimental results (Gongadze et al., 2009).

Figure 2.1 shows the schematic representation of the EDL models. Based on the Figure 2.1, the electrical potential within the EDL or Stern layer on the particle surface has the highest value. The potential decreases while distance from the surface increases and reaches 0 at the boundary of the EDL. When a colloidal particle in dispersion motion, a layer of the surrounding liquid remains attached to the particle. The boundary of this layer is called slipping plane. The value of the electric potential at the slipping plane is called zeta potential, which is mentioned above.