Particulate Science and Technology in the Engineering of Slurries for Chemical Mechanical Planarization

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Abstract

Chemical Mechanical Planarization (CMP) is a process that is now routinely used to planarize metal as well dielectric films during the fabrication of integrated circuits. This process uses slurries comprised of fine abrasive particles, such as silica, ceria or alumina. The stability and performance of the slurries are influenced by the size and properties of these particles, which in turn are influenced by their synthesis route. Stability is important to improve slurry lifetime and minimize defects such as microscratching caused by particle agglomerates or large particle counts (LPC) during polishing. The rheological behavior of slurry affects the friction at the pad-particle-wafer interface and alters the material removal rate. It is, thus, necessary to carefully engineer the slurry characteristics to achieve good removal rate and planarity without causing defects. This paper reviews the published literature on the synthesis of abrasive particles used in the preparation of CMP slurries as well as stability and rheological characteristics of slurries made from these particles. A brief account of particle-film interactions and importance of LPC in wafer scratching is also provided.

Keywords: chemical mechanical planarization, CMP, fumed silica, colloidal silica, ceria, alumina, slurry stability, coefficient of friction, COF, large particle count, LPC

1. Introduction

The fabrication of integrated circuits involves many steps in which topography in deposited dielectric and metal films is removed in order to create complex patterns of interconnects. The removal of topography is often referred to as planarization and a process known as Chemical Mechanical Planarization or CMP is routinely used to achieve this. In a CMP process, a wafer is held in a rotating carrier, which is pressed against a rotating polymeric pad on to which an aqueous slurry is dispensed [1]. A schematic of first generation CMP tool is shown in Fig.1.

The abrasive particles in the slurry along with the applied load (force) on the wafer and rotation provides the mechanical action for the removal of mate-

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The chemicals in the slurry provide the synergistic chemical action to improve selectivity between different types of films. The removal rate of a film is proportional to the applied pressure on the wafer and the relative velocity between the pad and the wafer.

Slurry is one of the most important consumables in CMP. It consists of fine abrasive particles that are dispersed in an aqueous solution containing one or more of various chemicals such as oxidizers, pH stabilizers, metal ion complexants and corrosion inhibitors [2]. Silica, alumina or ceria particles in the size range of 50 to 150 nm are most commonly used for making the slurries. The pH of the slurry affects the surface charge on the particles, which in turn influences slurry stability. Agglomeration of slurry particles results in large particles, which tend to create defects such as scratches on films that are planarized. Choosing slurry which provides good removal rates without causing defects is of utmost importance in CMP.

A comparison of the characteristics of typical slurries used in CMP of metal and dielectric films is given in Table 1. Slurries used to planarize dielectric films such as SiO2 or fluorinated silicon dioxide (FSG) typically contain 10% by weight of silica particles at alkaline pH values, as the removal is mostly mechanical in nature. These slurries typically provide a removal rate of the order of 2500 Å/min. Slurries for copper CMP contain a smaller amount of abrasives (~ 3% by weight) and are maintained at slightly acidic pH (4-6) values. These slurries contain an oxidant such as hydrogen peroxide and a copper complexant to enhance the chemical component of CMP. The removal rates of copper in these slurries can be tuned to a value between 500 to 6000 Å/min by controlling oxidizer, complexant and inhibitor concentrations.

This paper reviews the published literature on the synthesis of abrasive particles used in the preparation of CMP slurries as well as stability and rheological characteristics of slurries made from these particles. A brief account of particle-film interactions and importance of particle agglomerates in wafer scratching is also provided.

### 2. Abrasives in CMP Slurries

Colloidal sized SiO2, CeO2 and Al2O3 particles are used in the manufacturing of CMP slurries. Today, silica particles are predominantly used in the preparation of slurries for dielectric as well as metal CMP. Alumina particles find limited used in the manufacturing of slurries for tungsten CMP; however, because of their hardness, they are slowly falling out of vogue. Ceria slurries find use in the removal of oxide dielectric during the formation of shallow trench isolation (STI) structures.

#### 2.1. Silica particles and slurries

Two types of silica particles, fumed and colloidal silica, are used in the preparation of slurries for dielectric and metal CMP.

##### 2.1.1. Fumed silica

**2.1.1.1. Synthesis of fumed silica**

Fumed silica is produced by the oxidation of chlorosilane in a flame at temperatures greater than 1000°C.

### Table 1 Comparison of the characteristics of typical slurries used in CMP

| SLURRIES FOR CMP OF SiO2 AND FLUORINATED SiO2 (aka FSG) FILMS | Solid Content (weight %) | pH | Additives |
|---|---|---|---|
| Fumed silica slurries | -10 | 11-11.2 | Biocide, surfactant |
| Colloidal Silica slurries | -30 | 10 | Biocide, surfactant |
| Ceria Slurries | 0.1 to 4 | 4-6 | Inorganic acids, amino acids to provide selectivity between nitride and oxide films |

| SLURRIES FOR TUNGSTEN CMP | Solid Content (weight %) | pH | Additives |
|---|---|---|---|
| Fumed silica slurries | 2-4 | 1.5-3.0 | Oxidant (hydrogen peroxide, ferric nitrate), catalyst (metal ions), complexant |
| Fumed alumina slurries | 2-4 | 2-4 | Oxidant (potassium iodate, hydrogen peroxide), complexant, slurry stabilizer |

| SLURRIES FOR COPPER CMP | Solid Content (weight %) | pH | Additives |
|---|---|---|---|
| Colloidal Silica slurries | 2-4 | 4-6 | Oxidant (hydrogen peroxide), complexant, corrosion inhibitor |

| SLURRIES FOR TANTALUM CMP | Solid Content (weight %) | pH | Additives |
|---|---|---|---|
| Colloidal Silica slurries | 8-10 | 9-10 | Oxidant (hydrogen peroxide) |
according to the following reaction [3].

\[
\text{SiCl}_4(v) + 2\text{H}_2(g) + \text{O}_2(g) \rightarrow \text{SiO}_2(s) + 4\text{HCl}(v) \quad (R1)
\]

The primary silica particles that are formed during the reaction are about 30 nm in diameter. However, they aggregate due to high temperatures that exist in the flame during synthesis, as illustrated in Fig. 2. Zones of different temperatures in the flame are represented by different colors in this Fig. The temperature zone, where primary particles are formed, is close to the fusion point of silica (1710 °C). As the particles move outside this zone, they cool below the fusion point and form aggregates. The aggregates are roughly 140-160 nm in size and have a very irregular shape. These aggregates tend to agglomerate during the cooling of the particles and need to be dispersed during the preparation of slurries. The aggregate size is technically the primary particle size in these slurries.

Silica slurries used for planarization of SiO2 as well as fluorinated SiO2 (FSG) films are typically made from fumed silica particles. The weight percent of silica particles in these slurries is about 10%, with pH adjusted to 11.0 using potassium hydroxide (Table 1). Because of the high pH, there is a significant amount of dissolved silica in the slurries. It is believed that these soluble silicates provide electrosteric stabilization to the slurries. Additionally, these slurries often contain a biocide such as isothiazolin to prevent the growth of bacteria during storage. One of the advantages of fumed silica slurries is that it does not contain any sodium ions as impurity. However, because of the use of chlorosilane as a starting material in the manufacturing, chloride ions are invariably present in fumed silica slurries. Chloride ions are undesirable since they can cause metal corrosion.

2.1.2. Colloidal silica

The use of colloidal silica particles in CMP slurries has increased significantly over the last decade since it is possible to synthesize particles that are very uniform in shape and size using solution techniques. Unlike fumed silica, these particles are present in their primary size and not as aggregates. The size of these particles can be controlled anywhere between 5 nm and 200 nm by optimization of concentration of reactants and process conditions.

2.1.2.1. Synthesis of colloidal silica

There are many methods available to prepare colloidal silica particles, which include peptization, acid neutralization, dialysis, electrodialysis, ion exchange and hydrolysis and condensation of organosiloxanes (Stober method). The ion exchange and Stober method are the dominant methods used in the production of colloidal silica particles for CMP slurries.

In the ion exchange process, a solution of sodium silicate is passed through a strong acid cation exchange resin producing silicic acid, which is then converted to silica using an alkali such as ammonium hydroxide [5]. Alternatively, the sodium silicate solution and steam can be passed through a weak acid ion exchange resin at temperatures to produce finer particles of silica that can be subsequently enlarged [6]. The colloidal dispersion is then concentrated by ultrafiltration. Sodium ions greatly deteriorate integrated circuit device performance, and hence semiconductor industries are constantly looking for slurries that contain lower than 1 ppm of total sodium (solid + solution). Since, the ion exchange process uses sodium silicate as a starting material, it is important to purify the synthesized silica slurry to remove sodium ions. This is typically done by a deionization process.

One method to produce colloidal silica with very low sodium content is the Stober method that was patented in 1972. In this method, an organosiloxane, such as tetraethoxyorthosilicate, dissolved in alcohol is hydrolyzed using ammonium hydroxide as a catalyst [7]. The particle size depends on the catalyst and water concentration. Similar to the ion-exchange method, Stober method also yields particles which are spherical and uniform in size but with negligible sodium content. However, production of silica using this method is quite expensive compared to the ion exchange methodology. Integrated Circuit manufacturing industries have to decide between high purity and high cost of Stober silica versus lower cost and less pure ion exchange silica. A compromise product made from potassium silicate with low levels of sodium can perhaps bridge the gap.

2.1.3. Stability of aqueous silica dispersions

Agglomeration of abrasive particles is inevitable
in slurries but the kinetics of the process is of relevance. Unstable slurries with a wide particle size distribution can lead to wafer scratching and defects. In order to achieve effective planarization, with very few defects, it is essential to ensure long term stability.

Surfactants have been used in silica slurries to prevent particle agglomeration. Basim et al. evaluated the stability of slurries containing 12 weight percent of 0.2 μm sol-gel silica particles in the presence of cationic surfactants (CnTAB). They found that stability of silica particles increased with the carbon chain length of the CnTAB surfactant [8]. However, the disadvantage with use of surfactants in slurries is that they reduce the friction between the wafer and the pad during polishing which lowers the material removal rate. **Fig.3** shows that frictional force, measured by AFM, increases linearly with normal force for baseline silica slurry in the absence of surfactant and a salt. Addition of 68 mM of C10TAB to baseline slurry drastically reduces the frictional force which begins to increase slowly beyond a critical loading force in the presence of 0.6 M NaCl. This increase of friction force in NaCl has been attributed to partial desorption of cationic surfactant from negatively charged silica.

An interesting approach to preventing scratches on the wafer surface while maintaining the stability and activity of abrasives is the use of porous particles in CMP slurries [9]. The effective Hamaker constant of silica particles has been found to decrease from $0.67 \times 10^{-20}$ J to $0.23 \times 10^{-20}$ J with increase in porosity from 2% to 60%. Lower Hamaker constant is likely to reduce interaction between the particles and therefore expected to improve their stability.

The dependence of stability of silica slurries on pH and electrolyte concentration is ‘anomalous’ and does not follow the pattern predicted by conventional DLVO theory [10]. Iler found that silica sols were colloidally stable at isoelectric point pH and at high electrolyte concentration near neutral pH [11]. Allen and Matijevic noted an increased stability of silica sols with decrease in pH from 11.0 to 6.0 for 0.15 M of Na+ in solution [12]. It was proposed that protective silicate ologomeric and polymeric barrier layer is formed on the silica surface at pH lower than 10.5, and extends upto 2 nm at pH of 8.0 in 0.15 M of salt. This polymer layer usually comes from soluble silicates, such as sodium silicates, that are universal dispersants of many electrostatic colloids. The barrier layer can be viewed as M+-polysilicic coating that increases in thickness as Na+ (or salt) is added to dispersion providing greater stability. Similarly, decreasing pH 11.0 to 6.0 reduces the –SiOH ionization and reduces the binding of cation-silanol groups according to reaction R2.

$$M^{n+} + x(\equiv SiOH) \leftrightarrow M(\equiv SiO_x^{-(n-x)+}) + xH^+$$

(R2)

The reduced cation-silanol binding allows more sites to be available for binding of cation-polymer species to the silanol group, which improves the silica sols stability. However, since the desired levels of sodium in CMP slurries are very low, stabilization by this mechanism is not very useful. Hydration stabilization mechanism has provided insight on differences in stability observed with different types of ions [13].

### 2.1.4. Rheology of aqueous silica dispersions

Viscosity of CMP slurries is an important parameter that influences the slurry film thickness between the pad and the wafer and affects the drag force due to three body (pad-abrasives-wafer) interactions. The removal rate of material in CMP can vary depending on the friction between the pad and the wafer. The coefficient of friction (COF), defined as the ratio of shear force to the normal force, is a good indicator of frictional forces that exist during polishing. A plot of COF versus the Sommerfeld number ($S_0$), known as Striebeck-Gumbel curve, is often used to determine the extent of wafer-slurry-pad contact [14]). The $S_0$ is a dimensionless grouping of CMP specific parameters defined according to equation 1.
In the above equation, \( V \) is the relative velocity between the pad and the wafer, \( \mu \) is viscosity of the slurry, \( P \) is the applied downforce divided by the actual contact area between the pad and the wafer, \( \delta \) is the effective slurry film thickness. The contact area depends on the groove pattern in a polishing pad.

As can be discerned from equation 1, \( S_0 \) increases with slurry viscosity for specified values of \( V \), \( P \) and \( \delta \). Since COF depends on \( S_0 \), variation in slurry viscosity can significantly affect frictional forces between the wafer and the pad during polishing.

The different modes of lubrication exhibited during polishing are represented by the Stribeck-Gumbel curve as presented in Fig. 4. In boundary lubrication, where abrasives, pad and wafer are in intimate contact, the COF is constant and independent of \( S_0 \). The lubricant film thickness between the pad and the wafer is approximately zero and excessive wear can occur in this mode of polishing. The second mode of lubrication is partial lubrication where partial contact occurs between the wafer, pad and abrasives. Under this condition, the slurry film thickness between the wafer and the pad is approximately equal to mean surface roughness of the pad. Finally, at large values of \( S_0 \), hydrodynamic lubrication occurs where the liquid film totally separates the pad and the wafer and the COF becomes a weak function of \( S_0 \). The film thickness, in this case, is much larger than the mean surface roughness of the pad.

Assuming values of \( V \), \( P \) and \( \mu \) to be 0.5 m/s, 2 psi and 2 mPa-s during polishing, the effective lubricant film thickness, \( \delta \), is approximately 50 \( \mu \)m for concave shape of the wafer [15]. The Sommerfeld number for these conditions can be computed as 0.0015. The Stribeck-Gumbel curve suggests the existence of boundary lubrication mechanism, in which case the COF should be constant and stable.

Comparison of frictional characteristics of fumed (12.5 weight % of 110 nm particles at pH of ~ 11) and colloidal silica slurries (30 weight % of 50 nm particles at pH of ~ 10) used for oxide CMP shows that fumed silica slurries exhibit higher COF than colloidal silica slurries. As indicated in Fig. 5, the average values of COF for fumed silica and colloidal silica slurries are 0.3 and 0.22 respectively. Both slurries display boundary lubrication, in the Sommerfeld number range of \( 10^{-4} \) to \( 10^{3} \).

In a CMP process, shearing of the slurry can occur during various stages of polishing such as pumping, mixing of ingredients or sedimentation of abrasives. The shear rates during these processes are lower than 1000 s\(^{-1}\) and hence viscosity of slurries under these conditions can be easily measured using conventional viscometers based on rotating concentric cylinders or plates.

Much higher shearing occurs during the actual polishing process when the wafer, pad and abrasives are in contact. The resulting shear rate between the wafer and the pad can be calculated by determining...
the relative pad wafer velocity and the lubricant film thickness. Typical values of average relative velocity between the wafer and the pad range from 0.5 m/s to 1.0 m/s. Assuming a slurry film thickness between 35 $\mu$m and 60 $\mu$m at a downforce of 2 to 6 psi [15], shear rates of 8000 s$^{-1}$ to 30000 s$^{-1}$ can be calculated to exist during actual polishing conditions. High pressure capillary or slit viscometers are typically used to measure viscosity at such shear rates.

Lortz et al. studied the rheology of commercially available colloidal and fumed silica CMP slurries containing 30 % and 12.5 % abrasives respectively [16]. It was found that at shear rates lower than 1000 s$^{-1}$, the slurries behaved as Newtonian fluids with nearly constant viscosities of 2 mPa-s, as shown in Fig.6. When the shear rates were increased from 100,000 to 1000,000 s$^{-1}$, the viscosity for both slurries increased from approximately 2 to 10 mPa-s.

The rheological properties of aqueous silica dispersions, synthesized by Stober process, have been investigated as a function of particle size (0.1 – 1 µm) at pH values of about 9 and 3 (IEP). Measurements were carried out for particle volume fractions of 0.05 to 0.5 at shear rates of 0.1-1000 s$^{-1}$ [17]. The suspension, at pH value close to 9.0, behaved as newtonian fluid when the volume fraction of particles was equal to or less than 0.3. At higher volume fraction, shear thinning behavior was observed. These results are displayed in Fig.7.

The shear thinning effect was attributed to breaking of agglomerates formed at higher volume fraction, causing reduction in viscosity as the particles become free. The effect was more pronounced for smaller particles (0.1 µm) and at smaller shear rates (1-10 s$^{-1}$). The viscosity for dispersions made from 0.1 µm particles at a volume fraction of 0.45 reduced from about 10 mPa-s to 0.2 mPa-s with increase in shear rates from 1 to 1000 s$^{-1}$. In the case of slurries made from larger particles of 1 µm in size, similar increase in shear rates reduced the viscosity from 0.05 mPa-s to 0.02 mPa-s. At a given volume fraction, higher viscosity observed for smaller particles was attributed to lower interparticle distance resulting in stronger interactions between particles. Depending on the particle size, the viscosity of the silica suspension started to increase significantly at volume fraction of about 0.4. The transition from viscoelastic liquid like properties to elastic solid like behavior was observed at this volume fraction.

Mooney’s correlation, expressed in equation 2, is often used to obtain the relationship between relative viscosity (viscosity of suspension to that of suspending fluid) and particle volume fraction for silica dispersion [17, 18]).

$$\eta = \eta_0 \text{Exp} \left( \frac{\alpha \phi}{1 - \frac{\phi}{\phi_m}} \right)$$

(2)

where $\eta$ and $\eta_0$ are the viscosity of suspension and
suspended fluid respectively, $\alpha$ is the fitting parameter, $\phi$ and $\phi*$ are the particle volume fraction and maximum packing fraction respectively. The values of $\alpha$ and $\phi*$ have been estimated to vary between 2.78 and 4.9 and 0.7 and 0.74 respectively for colloidal silica dispersions.

### 2.2. Ceria particles and slurries

#### 2.2.1. Synthesis of ceria

Two most common routes for the synthesis of CeO$_2$ particles are solid-state displacement and wet chemical precipitation method [19]-21]. In the solid-state displacement method, cerium salt such as cerium chloride or cerium carbonate in its anhydrous form is milled with a base such as NaOH to induce a chemical displacement reaction to form cerium (+3) hydroxide. This mechanochemical reaction is followed by calcination in air at temperatures in excess of 500 $^\circ$C. In the wet chemical precipitation method, an aqueous solution containing a cerium salt, typically cerium nitrate is hydrolyzed with a base and then calcined. There is at least one report in the literature which describes the formation of cerium (+3) hydroxyl carbonate by aqueous phase precipitation followed by calcination to produce CeO$_2$. More recently, vapor phase techniques have been used to synthesize fine ceria particles. In a technique known as Physical Vapor Synthesis (PVS), a solid precursor of Ce is vaporized, reacted with a gas and cooled at a controlled rate to form nano particles. A modified version of this process known as Nano-Arc Synthesis (NAS) is capable of working with a wide variety of precursors to form nano-particles. It is claimed that the NAS process is capable of providing in situ surface modification to create very stable dispersions in water, which can be used for CMP.

Literature values of iso-electric point (IEP) of ceria particles fall in the range 6 to 10.3. There is at least one commercial product (AdNanco Ceria) that has a thin carbonate coating to increase the IEP to 10 [22]). The dependence of IEP value on synthesis method and calcination temperature is yet to be established.

The use of ceria particles in slurries for dielectric polishing is due to the strong chemical interaction between ceria and silica. In this context, a detailed understanding of surface chemistry of ceria and silica is essential. The acid-base behavior of surface hydroxyls in aqueous dispersions of ceria particles has been predicted based on multi-site complexation or ‘MUSIC’ model developed by Van Riemsdijk [23], 24)]. Ceria crystallites are expected to exhibit three types of surface hydroxyls, monodentate, bidentate and tridentate, depending on site coordination. The estimated values of equilibrium constant for deprotonation reactions, corresponding to ceria surface sites Ce$_2$-OH, Ce$_3$-OH and Ce$_7$-OH, are summarized in Table 2. The calculated point of zero charge (PZC) of ceria from these pKa values occurs at a pH of 7.9.

#### 2.2.2. Stability of aqueous ceria dispersions

Ceria slurries have been increasingly used for STI CMP as they offer better selectivity of removal rates between SiO$_2$ and Si$_3$N$_4$ compared to slurries with other abrasives. However, ceria slurries have the major disadvantage of inducing defects on the wafer surface due to agglomeration of abrasives [25]). Further, ceria particles due to higher density (~ 7000 Kg/m$^3$) or silica (~ 2000 Kg/m$^3$) or alumina (~ 4000 Kg/m$^3$) or silica (~ 2000 Kg/m$^3$) or silica (~ 2000 Kg/m$^3$) are prone to faster sedimentation. Thus, stabilization of ceria slurries is critical for its successful implementation in STI CMP.

Ceria slurries are commonly stabilized by water soluble polymers such as poly methylacrylate acid (PMMA) and poly acrylic acid (PAA) for dielectric CMP [26]. The adsorption of these polymers is believed to increase the zeta potential of ceria abrasives in neutral and alkaline pH range from 6 to 9 [27]). This increase in the zeta potential of ceria abrasives is understood to be due to ionization of the polymeric molecules to form negatively charged macromolecules with increase in pH of the solution. Kim et al. found that ceria slurries, containing 1 % abrasives and 1 % PMMA, were very well dispersed in neutral and alkaline conditions with narrow particle size distribution from 0.01 to 1 $\mu$m [27]). By contrast, the same dispersion in acidic pH condition was observed to be unstable with a large agglomeration of particles and a wide size distribution ranging from 0.02 to 100 $\mu$m. Lower zeta potential of ceria abrasives in acidic pH regions was considered to be the cause for decrease in the slurry stability. The IEP of ceria shifted from pH of 7 to 2.5 with addition of PMMA.

### Table 2: Equilibrium constants for deprotonation reactions for aqueous dispersions of ceria particles [24]

| Deprotonation Reaction | pKa Value |
|------------------------|-----------|
| -Ce$_2$-OH$_{2+}$ $\leftrightarrow$ -Ce$_2$-OH$^+$ + H$^+$ | 10.4 |
| -Ce$_3$-OH$^+$ $\leftrightarrow$ -Ce$_3$-OH$^+$ + H$^+$ | 24.2 |
| -Ce$_2$-OH$^+$ $\leftrightarrow$ -Ce$_2$-OH$^+$ | 1.0 |
| -Ce$_3$-OH$^+$ $\leftrightarrow$ -Ce$_3$-OH$^+$ | 14.8 |
| -Ce$_7$-OH$^+$ $\leftrightarrow$ -Ce$_7$-OH$^+$ | -8.3 |
| -Ce$_3$-OH$_{3+}$ $\leftrightarrow$ -Ce$_3$-OH$_{3+}$ | 5.5 |
2.2.3. Rheology of aqueous ceria dispersions

The rheological properties of aqueous ceria dispersions were investigated by Hsu and Nacu [28]. For ceria volume fractions less than 2%, the slurries exhibited Newtonian behavior and at higher volume fractions shear-thinning behavior was observed. In the absence of any added electrolyte, a maximum in viscosity was measured at the IEP (~ 6.0) of the ceria particles. Interestingly, they found the IEP to increase with increase in NaCl concentration.

In another study by Kim et al., the rheological behavior of ceria slurries with 1 % solid content was examined as a function of pH for shear rates between 10 and 1000 s⁻¹ [27]. These slurries contained polymethylacrylate acid as an additive, which shifted the IEP of ceria particles from 7 to 2.5. In the basic and neutral pH regions, the slurry showed newtonian behavior with a constant viscosity of less than 1 mPa-s. In the acidic pH region, the particles were found to agglomerate and the viscosity dropped from 2.5 mPa-s to 0.5 mPa-s with increase in shear rate from 10 to 1000 s⁻¹. The shear thinning behavior in acidic pH suggested breaking of agglomerated particle structure with increasing shear rates.

2.3. Alumina particles and slurries

2.3.1. Synthesis of alumina

Sol-gel method is the most common method for synthesis of alumina particles in aqueous solution [29]. In sol gel process, aluminium alkoxide is used as a precursor which undergoes hydrolysis reaction in excess water under vigorous stirring followed by peptization of the hydroxide to a sol and eventually a gel. Peptization requires that a critical concentration (0.03 to 0.1 mole of acid per mole of alkoxide) of certain acids (nitric acid, perchloric acid and hydrochloric acid) be introduced in the slurry, which must be maintained at 80 °C for sufficient time [30]. The pyrolysis of dried gel forms alumina particles [31]. Since the reactivity of aluminium alkoxide is very high, a chelating agent is normally used to control the hydrolysis rate. The sol gel route for synthesis of alumina provides advantages such as high surface area, better purity, narrow size and pore distribution, [32].

Fumed alumina is manufactured by hydrolysis of gas precursors such as aluminum chloride in hydrogen/oxygen flame at about 1800 °C [33]). The high pressure gas precursor is mixed with oxygen or air and introduced in the reaction chamber along with a fuel such as methane. The water vapor that is formed as an intermediate reacts with vapors of AlCl₃ to produce fumed alumina (Al₂O₃). The overall reaction for the formation of oxide can be represented as:

\[ 2AlCl₃ + 6H₂ + 3O₂ \rightarrow Al₂O₃ + 3H₂O + 6HCl \]  

(R3)

Reaction R3 is exothermic and therefore super-saturation of gaseous oxide occurs rapidly in the reaction chamber. The oxide molecules start to condense into small liquid droplets after they leave the flame or reaction zone. The mixture of gaseous and liquid Al₂O₃ is then passed through a series of tubes or the coagulation zone, where temperature gradients exist that result in formation of primary alumina particles. Aggregation of primary particles occurs in the aggregation zone and is controlled by temperature, concentration of primary particles and time spent by the particles in the aggregation zone. Hot steam may be used to remove hydrochloric acid from the surface of particles. The primary particles of fumed alumina synthesized by this process are about 13 nm with a specific area of 100 m²/gram.

2.3.2. Stability of aqueous alumina dispersions

Alumina dispersions are commonly stabilized under acidic conditions for use in CMP [34), 35]). In contrast to the commercially available silica slurries that are normally stable, alumina slurries have been found to require continuous stirring to maintain the particles in suspension [36]). Alumina slurries are often stabilized by additives including amphiphilic polymeric surfactants such as DAPRAL (a maleic anhydride α-olefin copolymer) or polyacrylic acid [37), 38]).

A commercial alumina slurry for metal CMP would contain an oxidant such as hydrogen peroxide, ferric nitrate or potassium iodate. Luo et al. investigated the effect of Fe³⁺ ions and BTA, a corrosion inhibitor, on the stability of two weight percent alumina (0.3 μm) slurry [36]). They found that at pH values less than 2.0, ferric ion concentrations higher than 0.01 M decreased slurry stability. At pH values higher than 2.2, Fe²⁺ precipitated out as Fe(OH)₃, which increased coagulation of alumina particles causing instability. In the case of BTA, the stability of alumina particles, at pH of 1.3, was affected only for BTA concentrations greater than 0.01 M. The settling rate of alumina particles increased by about eight times when BTA concentration was increased from 0.01 M to 0.1 M. The adsorption of BTA anion on positive alumina surface was concluded to be responsible for slurry instability.
2.3.3 Rheology of aqueous alumina dispersions
The rheological properties of colloidal alumina (0.2 μm) dispersions of 1-40 volume percent solid in the pH range 2.0 – 10.0 were studied by Wang et al. [39]. Dispersions containing 20 % solids in the pH range from 2.0 to 6.8 behaved as Newtonian fluid whereas under conditions of similar concentration but higher pH values between 8.2 and 10.0, they exhibited pseudoplastic behavior. In addition, basic dispersions were characterized by a higher viscosity than acidic dispersions. The apparent viscosity in the pH range of 2.0 – 7.0 for particle concentration equal to or lower than 20 % was found to be between 10^2 and 10^3 Pa-s. This viscosity range increased to 10^3 – 1.0 Pa-s for dispersions with higher pH between 7.0 and 10.0.

2.4. Particle–film interactions in CMP
2.4.1. CeO₂ particle - SiO₂ film interactions
Ceria based slurries have been used in glass polishing for many decades and are finding increased use in the formation of shallow trench isolation (STI) structures by the polishing of silicon dioxide films with a high selectivity over nitride. A mechanism commonly known as “Chemical Tooth Model” has been proposed to explain the interaction of ceria particles with silica surface during CMP [40]. This model proposes that ceria particles temporarily bind to silica surface during polishing via condensation reactions of the form.

\[-\text{Si-O} + \text{Ce-OH} \rightarrow \text{-Si-O}^–\text{Ce-OH} \rightarrow \text{-Si-O-Ce}^+ + \text{OH}^–\]  \hspace{2cm} (R4)

During shearing actions that prevail during polishing, the –Si-O-Si – bonds that are bound to the surface – Si-O-Ce- bonds are strained and removed as shown in R5. The net result is the removal of a certain amount of SiO₂ film.

\[-\text{Si-O-Si-O-Ce} \rightarrow \text{-Si-O}^+\text{Si-O-Ce} \rightarrow \text{-Si-O} \quad \text{(film)} \]
\[+ \text{-Si-O-Ce}^- \quad \text{(particle)}\]  \hspace{2cm} (R5)

Under slightly acidic (~ pH 4) and near neutral conditions, high removal (polishing) rate of silica films can be achieved at solid contents lower than a few weight percent. This is in contrast to silica slurries which have to be used at much higher percent (~10%) solids for providing the same rate.

Ceria slurries that provide very high selectivity between oxide and nitride contain additives that interact with nitride surface. Various amino and carboxylic acids have been found to be useful for improving selectivity [41, 42]).

2.4.2. SiO₂ particle - SiO₂ film interactions
The hydration of silica films as well as attack of Si-O bond by OH ions play a key role in SiO₂ CMP. At alkaline pH of about 11, even though both silica particle and silica films are characterized by negative zeta potential, removal rates as high as 2000 Å/min can be achieved. This precludes any type of interactions similar to those between ceria and silica. Dissolution and softening of silica by OH most likely contributes to removal mechanism.

2.4.3. SiO₂ particle - ta film interactions
In the case of tantalum polishing, rapid oxidation of tantalum films to tantalum oxide (Ta₂O₅) is observed. The binding of silica particle to Ta₂O₅ is similar to binding of ceria particles and has been postulated to be responsible for high removal rates. The tantalum removal rate is known to increases with increase in weight percent of silica in slurries.

Vijayakumar et al. investigated the removal of tantalum in silica slurry at pH of 6.0 [43]. Formation and mechanical tearing of Ti-O-Si bonds was considered as the primary removal mechanism. The Ta-O-H and Si-O-H react to form Ti-O-Si bonds according to reaction R6.

\[\text{Ta} – \text{O} – \text{H} + \text{Si} – \text{O} – \text{H} \rightarrow \text{Ta} – \text{O} – \text{Si} + \text{H}_2\text{O} \]  \hspace{2cm} (R6)

It was proposed that first multiple contact points are formed between silica particles and Ta₂O₅ on tantalum surface. The movement of silica particles away from the surface causes straining and removal of Ta₂O₅ lump.

2.5. Large particle counts (LPC) in CMP slurries
Filtration of slurries is done to remove large defect generating agglomerates, commonly referred to as large particle counts or LPC. Scratching of films due to a small number of large particles present in CMP slurries has been recognized as a critical problem in CMP. Large particles can be traced to two different sources; particle synthesis / milling procedure and slurry distribution loop in a fabrication plant. In fumed and colloidal silica slurries, particles with diameter of 0.5 μm or greater are considered to be large particles. Fumed silica slurries are more sensitive to shear agglomeration compared to colloidal silica slurries. Alumina and ceria slurries, on the other
hand, are least sensitive to shearing conditions. Proper choice of slurry handling and dispense systems can reduce the formation of LPC in CMP slurries. In a study by Johl et al., it was found that recirculation of slurries using diaphragm pump generated much lower LPC than that using bellows pump [44]. The effect was attributed to difference in the shearing action in these two pumps. Similarly, centrifugal pumps cause less flocculation of particles than bellows type pump [45].

Large particles in slurries can be characterized using several techniques including static light scattering (SLS), capillary hydrodynamic fractionation (CHDF), acoustic spectroscopy (AS), and single particle optical sensing (SPOS). Ramsen et al. obtained a correlation between LPC, measured by SPOS method, and surface defects generated during dielectric polishing by CMP slurries containing 9% fumed silica abrasives at pH of 3.0 [46]. The surface defects were characterized by measuring the number of scratches on wafers using dark field optical microscopy. As shown in Fig.8, the scratch counts on wafer increased approximately linearly with fraction of LPC (corresponding to particles with diameters ranging from 0.469 to 1.887 µm) in slurries. This suggested that scratch formation was predominantly due to large particles in the slurry that get trapped between the wafer and the pad during polishing. A size of 0.68 µm was estimated as the minimum particle diameter that contributed effectively to wafer scratching at the experimental polishing conditions.

2.6. Conclusions

The synthesis route for abrasives influences the primary particle size, their tendency to agglomerate and the type of ionic contamination they introduce into slurries. In order to ensure slurry stability and minimize surface defectivity, additives such as surfactants or polymers can be used. However, these stabilizers also tend to lubricate or reduce the friction between wafer and abrasive particles and lower the material removal rate. Use of functionalized particles with tailored surfaces is a viable option and needs to be explored. The rheological behavior of slurries should be ideally determined at shear rates of the order of 30,000 s⁻¹, which typically exists in CMP. Chemical interaction or binding between abrasives and the film followed by shearing action during polishing is critical to achieve selectivity and high material removal rates. Control of Large Particle Counts in CMP slurries is important to reduce scratching of films during polishing.

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