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JSS Focus Issue on Chemical Mechanical Planarization: Advanced Material and Consumable Challenges

Shallow Trench Isolation Chemical Mechanical Planarization: A Review

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Electrical isolation of the billion or so active components in each integrated device is achieved using shallow trench isolation (STI) which requires chemical mechanical planarization (CMP) involving silicon dioxide removal at a high rate and stopping on an underlying silicon nitride film. Several colloidal slurries with various additives can yield the desired high rate selectivity between the oxide and nitride films during CMP while maintaining an acceptably low nitride rate. Here, many of such high selectivity STI CMP slurries described in the literature are reviewed along with the characteristics of the colloidal dispersions like the abrasives, additives, the interactions between them and with the films being planarized and the associated pH range in which the high selectivity is observed. The mechanisms proposed to explain the high reactivity of ceria with oxide, the role of additives in suppressing the nitride removal rate and resulting high selectivity are discussed. Reduction of a multitude of defects in post-CMP processed STI structures still remains an important challenge, especially as the feature sizes continue to shrink.

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Chemical mechanical planarization (CMP) is one of the important enabling processes in facilitating multilevel metallization (in some cases reaching up to 14 levels) and incorporation of novel gate and channel materials at the component level in modern semiconductor device manufacturing where its use has become widespread and ubiquitous.¹⁻⁶ Here, we review recent advances and remaining challenges in one specific application of CMP, the shallow trench isolation (STI) process. STI is a method of electrically isolating active areas using trenches created in the Si substrate around the active elements and filling it with an insulating dielectric, such as silicon dioxide or silicon oxy-nitride or silicon carbonitride.7-11 Process details of the STI structures are available in numerous publications. There are a multitude of techniques available for oxide deposition and even though the resulting oxides have very different properties, for simplicity we do not distinguish between them in this review. For completeness and ease of reference, a schematic representation of the STI process is given in Figure 1. While the trenches are being filled, silicon dioxide also deposits over unwanted areas on the entire wafer (since selective deposition in trenches only is not possible) creating an uneven topography. The excess and unwanted oxide has to be completely removed and CMP has proven to be the only viable and robust global and local planarization capable process technology.

Here, as shown in Figure 1, presence of a very thin silicon nitride stop layer (deposited on another thin pad oxide layer to control film stress) is an essential and integral part of the process. This nitride stop layer prevents any damage during planarization to the all-important epitaxially grown surface underneath and is itself removed by a wet etch process subsequent to the overburden oxide removal. Since the integrity of the nitride layer is crucial, thinning of the nitride should be minimized at all costs, implying that the oxide to nitride removal rate (RR) ratio, or selectivity, must be high. At the same time, a very high oxide film RR can lead to undesirable thinning of the field oxide in the trenches, making accurate end point control critical. Finally, if any of the oxide over the nitride is not removed, it interferes with the subsequent removal of the nitride itself. Indeed, while planarizing patterned STI features, metrics like the extent of nitride and field oxide loss across widely varying patterns, dishing, sensitivity to overpolish, defects, and within wafer (WIW) and die (WID) uniformity - and not just selectivity – become overarching for evaluating the performance of a slurry and we discuss them here only in a cursory manner and focus mostly on polish rates and the underlying mechanisms. As device dimensions continue to shrink, meeting these combined challenges has become even more difficult.

It is known that the rate selectivity can be altered by carefully choosing the components, viz. abrasives and additives, of the colloidal slurry used to achieve the planarization with more emphasis being placed now on their role on defects in the post-polished surfaces.¹ A low oxide polish rate even with complete suppression of nitride removal is not desirable, since the excess oxide has to be removed rapidly to ensure adequate throughput. As such, the STI planarization can sometimes be implemented in two steps, first with a high selectivity and high oxide polish rate slurry to remove most of the overburden oxide followed by a second step in which a low or 1:1 selectivity slurry is use. Normally, ceria or silica based slurries are employed in STI CMP, with a more recent emergence of core/shell type abrasives, again with the expectation of mitigating defects. In the absence of any additives, both the silica or ceria slurries tend to polish not only the oxide but also the nitride surface at rates that are not low enough. Compared to silica abrasives, ceria particles yield higher removal rates of both oxide and nitride surfaces.^{13,14} Certain chemicals, when added to the slurry, suppress the nitride removal without adversely affecting the oxide removal, thus enhancing the selectivity. In some applications such as damascene gate process, the nitride RR must be higher than oxide RR, i.e. reverse of the usual selectivity of the STI process.¹⁵

Since CMP uses abrasives, scratches can form on the surface and lead to yield loss. Other defects, such as residual particles, need to be removed in post-CMP cleaning step. The defect level and type of defects formed depend, as in any CMP process, on the slurry formulation as well as other parameters such as the shape and size of abrasives, type of pad used, conditioning, operating pressure etc. In this review, we focus our attention on high selectivity STI CMP slurries with very low nitride polish rates and slurries with reverse selectivity as well as the underlying mechanisms. The status of experimental results and analysis are compiled and the models proposed to explain them are summarized. The gaps in the literature are identified and directions for future work are outlined.

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(c) Deposition of dielectric **D** (SiO₂ or silicon oxy-nitride or silicon carbo-nitride)



(e) Subsequent processes lead to formation of transistors in the active areas

Figure 1. A schematic representation of the STI Process. Note that the dielectric, denoted by \mathbf{D} , may be pure or other forms of SiO₂.

Mechanisms

Silicon dioxide removal mechanism.— An early material polishing model was developed by Brown et al.¹⁶ who proposed that the abrasive particles penetrate into the work surface under the applied force and move with the pad, abrading the surface. This model was initially used on metals¹⁶ and later extended to the polishing of glass surfaces.¹⁷ Based on the polishing rates of glass in ethylene glycol and water mixture, Silvernail and Goetzinger¹⁸ identified the necessity for the presence of water for glass polishing. Later, Iler¹⁹ proposed that the Si-O-Si bonds present on the surface of silica react with water, given by a reversible polymerization and depolymerization reaction, shown below.

$$(SiO_2)_x + 2H_2O \leftrightarrow (SiO_2)_{x-1} + Si(OH)_4$$

Silicon dioxide surface can be polished by different metal oxide abrasives such as those of cerium oxide, zirconium oxide, titanium oxide and thorium oxide besides silicon dioxide itself. Due to its amphoteric nature, ceria was considered an excellent polishing agent compared to other metal oxides. Cook¹³ proposed that polishing particles such as ceria or zirconia possess a great affinity toward the oxide, which he called as "chemical-tooth", which helps in breaking the bonds on the silica surface. The surface of silicon dioxide, in water, is expected to be terminated with -Si-OH. At some of these sites, an OH⁻ ion in water can remove H⁺, resulting in -Si-O⁻ termination. According to the mechanism proposed by Cook¹³ cerium oxide, when dispersed in water, contains Ce-OH groups, which react with the surface sites Si-O⁻ forming Ce-O-Si and subsequently release Si(OH)₄ into the



Figure 2. Cartoons showing the mechanisms proposed in the literature and in this review, to visualize the interaction between ceria and silicon dioxide during polishing (a) model proposed by $Cook^{13}$ (b) model proposed by Hoshino et al.²² and (c) model proposed in this review in which Ce^{3+} species stabilized by an oxygen vacancy are the active species.

solution. The proposed reaction is written as

$$-Ce-OH + -Si-O^- \leftrightarrow -Si-O-Ce- + OH^-$$

Since the Ce-O-Si bonds are stronger than Si-O-Si bonds, this results in the polishing of the silicon dioxide surface by both chemical and mechanical actions (Figure 2a).¹³ Thus, SiO₂ is removed one molecule at a time, as Si(OH)₄.

A similar mechanism was proposed by Kelsall,²⁰ but he suggested that it is the Ce³⁺ species that are present on the surface of ceria abrasives that react with the hydrated silicon dioxide surface. Later, Sabia and Stevens²¹ proposed that the polishing between the ceria abrasives and silicon dioxide is due to the reaction between the particles and the work surface, promoted by the presence of Ce^{3+} on the abrasive surface. Later, Hoshino et al.,²² proposed a different model in which the Si-O-Si bonds react with hydroxylated ceria in water, forming Ce-O-Si bonds, and removing SiO_2 in the form of lumps (Figure 2b) rather than in the form of single molecules of Si(OH)₄ as proposed by Cook.¹³ They supported this hypothesis using Fourier transform infra-red spectroscopy and inductively coupled plasma atomic emission spectroscopy analysis of the post polish slurry containing the material removed. Wang et al.23 reported that the material RR increased from 250 nm/min to 675 nm/min when the concentration of ceria abrasives in the slurry was lowered from 1 wt% to 0.25 wt% at pH 4, which is counter intuitive since an increase in abrasive concentration may be expected to lead to an increase in RR in the initial stages and saturation at some higher abrasive concentrations. Based on the UV-VIS absorption spectra of solutions containing various quantities of ceria abrasives, they claimed that a decrease in the concentration of ceria in the slurry resulted in the conversion of Ce⁴⁺ to Ce³⁺, again suggesting an important role for Ce³⁺. However, there are no confirmatory reports in literature on the decrease in silicon dioxide RR with an increase in ceria concentration.

Using their own data and the results of Kelsall²¹ and Wang et al.,²³ Veera Dandu et al.²⁴ proposed specifically that Ce^{3+} (and not Ce^{4+}) present on the ceria abrasives enhance the oxide RR (Figure 2c). This hypothesis was supported by UV-visible spectroscopy data where the spectral peak height associated with the Ce^{3+} was monitored as well as thermogravimetric analysis that was used to measure the extent of additive adsorption on the ceria particles. They also showed that when the concentrations of the additives (used to suppress nitride but not oxide removal) were high enough, the oxide removal rates were also reduced, likely due to the blocking of the active Ce³⁺ surface sites by the additives. More recently, Seo et al.²⁵ proposed that the reactivity of ceria particles depends on the physicochemical conditions during their synthesis. Based on adsorption isotherms and theoretical analyses using density functional theory (DFT) calculations, they predicted that nitrate ions (source of nitrate is either the precursor or the pH adjusting agent or both) show a higher affinity than hydroxyl ions toward silicate groups. CMP results showed that the ceria functionalized with nitrate groups exhibit higher removal rates when compared to ceria functionalized with hydroxyl groups. We discuss the role of the Ce³⁺ surface species at some length later in the section on the reactivity of ceria abrasives.

Silicon nitride removal mechanism.— Suppression of the nitride film RR is essential to an acceptable STI process. An understanding of the nitride polishing mechanism will give an insight in choosing an additive which can enhance the selectivity. Silicon nitride is harder than silicon dioxide or ceria. When exposed to water or air, the nitride surface gets easily oxidized to silicon dioxide.²⁶ The overall oxidation reactions are given below.

$$Si_3N_4 + 3O_2 \rightarrow 3SiO_2 + 2N_2$$

 $Si_3N_4 + 6\,H_2O\,\rightarrow\,3\,SiO_2 + 4\,NH_3$

During the CMP of silicon nitride, it is believed that the nitride layer is not removed directly, but only the top layer consisting of silicon dioxide is removed. Hu et al.²⁷ proposed a sequence of hydrolysis reactions that convert the Si_3N on the nitride surface to -Si-O-Si-structures and NH₃.

During CMP, the chemically modified nitride surface layer may be further hydrated in the presence of water,

$$\equiv$$
 Si-O-Si \equiv +H₂O \rightarrow Si(OH)₄

with the hydrolyzed silica being removed by mechanical wear.²⁷ Note that this equation is not balanced. This suggests that if the conversion of silicon nitride to oxide is inhibited, then the nitride removal may be suppressed since the ceria particles are softer than the nitride film. Indeed, proline and other amino acids, when added to a ceria slurry, can preferentially adsorb on the surface of silicon nitride preventing its oxidation to silicon dioxide and suppress nitride removal.²⁸

Nitride rate suppression mechanism.— It is important to reiterate that in STI CMP, a low nitride RR (<1 nm/min) is a key requirement. Even a moderate nitride RR (e.g. ~few nm/min) will cause unacceptable thinning of the nitride stop layer. In order to understand how various additives suppress the nitride or, in some cases, oxide removal, various studies have been performed and the reports are summarized below. America and Babu²⁸ proposed that the nitride RR can be reduced to low values by adding a suitable chemical, an amino acid, which adsorbs on the nitride and inhibits its hydrolysis to silicon dioxide. The oxygen atoms present on the carboxylic group of the additives form a bidentate structure with the silanol groups present on the surface of silicon nitride along with simultaneous hydrogen bonding between the amino H and surface N atom (Figure 3). These bonds are strong enough to prevent exposure of the underlying nitride film to the abrasives. They also suggested that, for the additive to be effective, the hydrogen bonding group of the additive be in the alpha position relative to the acid group.

Carter and Johns²⁹ proposed that the nitride removal rates in high selective slurries are suppressed by a site blocking mechanism in which the additives block the active sites on silicon nitride, preventing them from forming SiO⁻ and inhibiting further polishing. They also suggested that, when a sufficiently high concentration of the additives is used in the slurry, the additives are likely to suppress silicon dioxide RR also. In another study with three different additives - pyridine



Figure 3. Cartoon showing the bond formation between proline and silicon nitride surface. Adapted from America and Babu.²⁸

HCl, imidazole and piperazine -with ceria slurries, it was reported the nitride RR was suppressed at pH 4 and 5 while the oxide removal rates remained high.³⁰ These authors reported that the additives cover the surface of silicon nitride more or less completely, but there is only a partial coverage on the surface of silicon dioxide with relatively weak coupling, which results in continued polishing of silicon dioxide.

Penta et al.³¹ investigated silicon dioxide and silicon nitride removal in ceria based slurries, in the presence of picolinic acid, nicotinic acid, proline and γ -amino butyric acid as a function of pH and additive concentration. These amino acids, based on pKa values, can exist in different forms in different pH ranges. The results were analyzed by comparing the polishing behavior with the additive species present at the respective slurry pH. The adsorption of amino acid onto the silicon dioxide and silicon nitride surfaces at various pH was evaulated by derivative thermograms. The results showed that the protonated amino group, present only in a specific pH range, can form a strong hydrogen bond with the nitrogen atom of the silicon nitride surface and the strength of this bond hinders nitride hydrolysis as well as subsequent polishing. This result was recently extended to other classes of additives, namley alcohols and carboxylic acids, see Penta et al in this focus issue.

However, for effective suppression of nitride removal, the amino acid must be available in sufficient quantity, which may not be the case if it is also strongly adsorbed on the high surface area abrasive particles. This can explain the results of Manivannan and Ramanathan,³² who found that in ceria based slurries, at pH 4, addition of glutamic acid lowered the oxide RR from ~40 nm/min to <1 nm/min, and the nitride RR from ~8 nm/min to <1 nm/min while at pH 5, 6 and 7, the oxide RR was ~60 nm/min while the nitride RR was <1 nm/min.However, glutamic acid did not lower the oxide and nitride rates in silica slurries. In this case, since the surface area of the particles in the 5 wt% silica dispersion is much larger than the surface area of the amino acids tend to adsorb well on the silica surface,^{30,33} it is likely that the amino acid remaining in the solution in the silica slurry is not sufficient to prevent nitride removal.³¹

Also, in some cases, the additive can adsorb on both oxide and nitride surfaces, but still lower only the nitride rate and not the oxide rate.^{30,33} In such cases, the strength of the coupling between the additive and the film being polished is important as was shown by Veera Dandu et al.³⁰ In this case, even though pyridine HCl adsorbed on both oxide and nitride surfaces, it lowered only the nitride rate. Based on contact angle and polishing rate data, they concluded that the additive was easily removed by the polishing process from the oxide but not from the nitride, presumably due to stronger coupling. Similar argument can be used to explain the results of Nagendra Prasad and Ramanathan³³ who found that, even though both L-proline and L-arginine adsorb to a similar extent on the surface of silicon dioxide at pH 9, 10 and 11 and to a smaller but again similar extent on silicon nitride, proline suppressed only nitride RR while arginine suppressed both oxide and nitride removal rates.

High Selectivity Slurries

Ceria-based slurries.— The published literature, especially patent literature, on high selectivity STI CMP slurries is replete with additives that can enhance the oxide to nitride RR selectivity. These include potassium hydrogen phthalate (KHP) along with Zonyl FSP,^{34–37} silane coupling agent (3-(aminoethylamino propyl) trimethoxysilane)),³⁸ ammonium polyacrylate,³⁹ organic polyols,⁴ acrylic acid,⁴¹ L-proline and other α amino acids,^{28,42–46} or nucleic acids,^{47,48} glutamic acid, picolinic acid, 4-hydroxybenzoic acid and Imidazole, anthranilic acid, pyrrole-2-carboxylic acid and 3hydroxypicolinic acid,^{29,49} lactic acid and poly acrylic acid,⁵⁰ ammonium poly carboxylate,⁵¹ poly acrylic acid,⁵² triethanol amine,⁵³ glutamic acid,³² aspartic acid,⁵⁴ pyridine HCl, piperazine, and imidazole,³⁰ picolonic acid,⁵⁵ nicotinic acid, proline and γ amino butyric acid.³¹ A partial, but still lengthy, combination of abrasives and additives employed, the pH range in which high selectivity was reported and the corresponding selectivity values are summarized in Table I for reference. This list is incomplete and the patents catalogue many more additives as selectivity enhancement agents. The selectivity values should not be considered precise since they can vary significantly even with only small changes, even if caused by experimental error, in the nitride polish rates.

The actual selectivity depends on the abrasive and additive concentrations and the pH of the slurry as well as the characteristics of the ceria used. Some slurries exhibit high selectivity only in a narrow pH range^{34–37} while others exhibit high selectivity in a wider pH range.^{42–46} While some of the patents mention the particle size and the method of synthesis of the ceria abrasive (colloidal, solid state displacement, etc.), such information was not provided in most cases. In a few patents, the possible mechanism of high selectivity was hinted at,^{29,42–46,49} for example, the adsorption of the additive on the nitride surface, but in most there was no explanation. In some cases, apparently contradictory results were observed. For example, Srinivasan et al.^{42–46} reported that slurries with L-proline yielded high selectivity while Carter and John²⁹ reported that a similar slurry yielded low se-

Table I Slurries exhibiting high selectivity

lectivity. This is likely due to differences in the method of synthesis, purity level and size of the ceria abrasives used, as discussed later in the section on the reactivity of ceria.

Slurries based on other abrasives.— Most of the reported studies on STI CMP dispersions used ceria or silica abrasives. Even though ceria particles are known to be prone to cause more defects, silica slurries are not the preferred choice in many cases due to high solids requirement (>10 wt%) to obtain reasonable oxide RRs and associated defects and post-CMP cleaning challenges. In contrast, ceria can yield high RRs with even ~0.25 wt% of particle loading which can result in significant cost savings for both high volume manufacturing and waste treatment. Also, it remains a challenge to enhance rate selectivity with silica slurries. Some of the additives reported to yield high selectivity, relatively speaking, in silica based slurries are: cerium nitrate and acetic acid,⁵⁶ triethanol amine,⁵⁷ surfactants such as ammonium lauryl sulfate, ammonium dodecylbenzenesulfonate, and dodecylbenzenesulfonic acid or triethanolamine dodecylbenzenesulfonate.⁵⁸

Penta et al.,⁵⁹ investigated the removal of oxide and nitride films in slurries with 10 wt% silica in the pH range of 2 to10 containing anionic surfactants such as sodium dodecyl sulfate (SDS), dodecyl benzene sulfonic acid (DBSA), dodecyl phosphate (DDP) and sodium lauryl sarcosine (SLS). When the pH was between 2 to 4, the nitride polishing rate was suppressed to <1 nm/min without affecting oxide removal rates. Beyond pH 4, silicon nitride removal was not suppressed. The authors proposed that when the slurry pH <IEP of the nitride surface, nitride rate suppression is caused by the adsorption of the anionic surfactants, validated by TGA results and zeta potential measurements.

Reverse Selectivity

During the fabrication sequence of metal gates, slurries with high nitride RR and low oxide RR are required.^{15,60,61} It is also possible to use such slurries to remove the nitride layer remaining

Table I.	iter i olurites exhibiting ingli seccertity.						
No	Abrasive	Additive	рН	Selectivity	Reference		
1	Ceria	Potassium hydrogen phthalate along with Zonyl FSP	6.5-7	68-246	34–37		
2	Ceria	3-aminoethylaminopropyl trimethoxysilane	7	54-233	38		
3	Ceria	Ammonium polyacrylate	7.2	66	39		
4	Ceria	Organic polyols	4 and 9.5	29-312	40		
5	Ceria	Acrylic acid	Not reported	~ 179	41		
6	Ceria	L-proline and other amino acids	6-11	42-306	42-46		
7	Ceria	Nucleic acids with poly acrylic acid	3.5-5	17-47	47,48		
8	Ceria	Glutamic acid, picolinic acid, 4-hydroxybenzoic acid and imidazole, anthranilic acid, pyrrole-2-carboxylic acid, and 3-hydxroxypicolinic acid	5	16-266	29,49		
9	Ceria	Poly acrylic acid with RE610 (phosphate ester based chemical)	7	31	50		
10	Ceria	Ammonium poly carboxylate	7-9	29-86	51		
11	Ceria	Poly acrylic acid	7	~ 50	52		
12	Ceria	Triethanolamine	6-8	~ 60	53		
13	Ceria	Glutamic acid	5-7	>100	32		
14	Ceria	Aspartic acid	4-5	~ 100	54		
15	Ceria	Pyridine HCl, Piperazine, Imidazole	4-5	>100	30		
16	Ceria	Picolinic acid	4-5	~ 38	55		
17	Ceria	Nicotinic acid,	4-5	>100	31		
18	Ceria	L-proline	4-10	>100	31		
19	Ceria	γ amino butyric acid	6-10	>100	31		
20	Silica	Cerium nitrate and acetic acid	4.2	28	56		
21	Silica	Triethanolamine	~11	28	57		
22	Silica	Ammonium lauryl sulfate, ammonium dodecylbenzenesulfonate, dodecylbenzenesulfonic acid, triethanolamine dodecylbenzenesulfonate	2.17-3.13	50-700	58		
23	Silica	SDS, DBSA, DDP and SLS	2-4	$\sim 20-60$	59		
24	Titania	L-Proline	10	73	42-46		

	Ū.				
No	Abrasive	Additive	pН	Reverse Selectivity	Reference
1	Ceria	polyethyleneimine	3.5	4	61
2	Ceria	Polyethyleneimine with polydiallyldimethylammonium chloride (pDADMAC), ethoxylate PEI, polyamidoamine and co polymers of acryl amide and DADMAC	4.9	~8 - 26	63
3	Ceria	poly (4-vinyl pyridine) (PVP), poly (4-vinlypyridine co-polystyrene) (PVP-PS)	~ 4	12-181	62
4	Ceria	poly (acrylicacid-co-diallyl dimethyl ammonium chloride) (PAD)	4	>200	64
5	Silica	Arginine	8	7	66
6	Zirconia	None	4	78	66
7	Phosphate functionalized silica	None	3-7	~10 - 30	67

after conventional STI CMP, replacing wet etching.⁶² The additives that were reported to enhance the reverse selectivity are mostly from the family of cationic polymers such as polyethylene imine (PEI),^{61,63} polydiallyldimethylammonium chloride (pDADMAC),⁶³ ethoxylate PEI,⁶³ polyamidoamine and co polymers of acryl amide and DADMAC,⁶³ poly (4-vinyl pyridine) (PVP),⁶² poly (4vinlypyridine co-polystyrene) (PVP-PS),⁶² and poly (acrylicacid-codiallyl dimethyl ammonium chloride) (PAD).⁶⁴ The reverse selectivity is achieved by the adsorption of these additives on the oxide and ceria surfaces, but not on the nitride surface. The combination of abrasives and additives employed, the pH range in which reverse selectivity was reported and the reverse selectivity values are summarized in Table II for reference.

Table II. Slurries exhibiting reverse selectivity.

Veera Dandu et al.⁶⁴ proposed that the negatively charged carboxylic groups of the PAD polymer strongly bind to the positively charged ceria surface, possibly by bi-dentate structure, while the cationic amine groups are on the unadsorbed side away from the ceria surface. These amine groups can bind to the negatively charged sub-oxide on the nitride surface and, hence, the oxide layer can be pulled away from the nitride surface by the relative motion of the wafer across the pad, presumably due to the weak nature of Si-Si present at the interface between sub-oxide and silicon nitride. Furthermore, it is very likely that the cationic amine groups of the polymer bind strongly to the negatively charged silicon dioxide surface while the anionic carboxylic acids are on the unadsorbed side. Similarly, Kim et al.⁶¹ showed that the adsorption of the cationic polymer, PEI on the surface of silicon dioxide is the key factor in the suppression of oxide RR. The adsorbed PEI presumably prevents the dissolution of silicon dioxide into the solution.

Ceria abrasive surfaces contains Ce^{3+} which is believed to be chemically active, as described later in the section on reactivity of ceria. It seems that the Ce^{3+} on the surface of ceria abrasivea interacts with the suboxide formed on the silicon nitride films forming a complex, which consists of Ce-O-Si structures, and pulls the suboxide during polishing, presumably since Ce-O-Si structures are much stronger that Si-O-Si structures (Fig. 2c). The suboxide is regenerated by hydrolysis and this removal process continues. The silicon nitride RR is suppressed when the reactivity of Ce^{3+} on the ceria abrasive surface is blocked and/or the hydrolysis reaction of the nitride conversion to silicon dioxide is hindered due to the adsorption of different additives.⁶⁵

Using zirconia- and silica-based dispersions, high silicon nitride and low silicon dioxide removal rates were reported by Natarajan et al.⁶⁶ Without any additives, zirconia gave a reverse selectivity of 78 at pH 4, while 2 wt% arginine in a 10 wt% silica slurry at pH 8 gave a reverse selectivity of 7.⁶⁶ The exact mechanism of silicon nitride polishing with these slurries was not explained. Veera Dandu et al.⁶⁷ showed that dispersions of silica particles functionalized with phosphate groups give higher nitride RR and low oxide RR, as may be expected from the use of hot phosphoric acid to etch nitride selectively over oxide. Using diethylphosphato-ethyltriethoxysilane (DPTS) as the precursor, the functionalized silica particles were synthesized in alcohol media to prevent hydrolysis and condensation of DPTS. The unreacted DPTS was removed from the dispersion by dialysis and then diluted with deionized water, while the isopropyl alcohol and ethanol formed during this process were removed using a rotovap. DPTS molecules have an ethanol group on one end and a phosphate group on the other end. During polishing, the phosphate end group of the DPTS molecule tethered to a silica abrasive reacts with the silicon nitride surface resulting in high RRs of silicon nitride film (Figure 4).

Characteristics of Ceria Abrasives

Nature and type of ceria abrasives.— As was mentioned earlier, the type of ceria abrasives used in formulating a slurry can have a profound effect on both rate selectivity and defectivity, as well as it colloidal properties.¹² For example, Kim et al.⁶⁸ prepared ceria abrasives by calcining cerium carbonate at 650°C for 4 h (sample A) and 6h (sample B), milled the particles and evaluated their performance. Slurry A yielded lower oxide RR, more number of scratches and a poorer within wafer non-uniformity. The XRD based grain size of particles A was smaller than that of B, but the agglomerate size of A in slurry was larger than that of B. They suggested that at the shorter duration (4 h), the conversion was incomplete and resulted in lower crystallinity which led to easy breakdown of the particles. The smaller particles agglomerated causing lower oxide RR and worse defectivity. In another report, Kim et al.⁶⁹ calcined cerium carbonate at 650°C for 4 h under controlled air flow conditions. The air flow conditions during synthesis were 35, 5 and 0 m³/h for samples A, B and C respectively. The particles were subsequently wet milled and dispersed in slurry at pH 8, with poly (methyl methacrylate) surfactant. Based on CMP experiments, they reported that particles synthesized at lower oxygen concentration included hexagonal structure (Ce₂O₃), broke down more easily during milling and agglomerated to larger sizes in slurries, and yielded lower oxide RR and higher defectivity (in terms of residual particles and number of scratches). The effect of two step calcination and milling with different sized beads (0.2 to 0.8 mm) on removal rate and defectivity was also investigated.⁷⁰ The two step calcination (680°C / 580°C) and milling with 0.3 mm beads resulted in a slurry with minimal defects and acceptable selectivity (\sim 37). These results suggest that synthesis method of the ceria particles has a strong effect on polishing performance.

Earlier, Carter and Johns^{29,49} measured the removal rates of silicon dioxide and silicon nitride in 0.5 wt% ceria (mean particle size of ~120 nm) based slurries with many organic additives, at pH 5. Among the additives, glutamic acid, picolinic acid, 4-hydroxybenxoic acid and Imidazole showed a selectivity of more than 100 while slurries with proline showed a selectivity of only 3. This contrasts sharply with the earlier reports by Srinivasan et al.^{42–46} and America and Babu²⁸ that showed much higher selectivity at pH 6 and higher. They used calcined ceria particles (avg. size ~180 nm, Ferro corp.) while Carter and Johns did not report the synthesis method. The difference between these results suggests that the synthesis method and/or the purity of the abrasives may have played a role.

Praveen et al.⁷¹ also showed that the calcination temperature of synthesized ceria particles and the associated crystallite size impact



Figure 4. Possible binding of DPTS on (a) silica and (b) silicon nitride surfaces. Adapted from Veera Dandu et al.⁶⁷

oxide RR (Figure 5). XRD analyses of the abrasives suggest that the crystallite size is positively correlated to the calcination temperature. Similarly, Kim et al.⁷² found that the oxide RRs obtained using calcined ceria abrasives (crystallite size \sim 46 nm) were higher than those with precipitated particles (average size \sim 34 nm) and assigned the enhanced RR to the larger crystallite size of the calcined ceria.

Recently, Doi et al.⁷³ observed that the addition of picolonic acid to colloidal ceria (mean dia ~69 nm) enhanced the removal rates from ~150 nm/min to 370 nm/min at pH 4.5, but lower than the ~400 nm/min obtained with almost the same size calcined ceria (Figure 6). Since the particle sizes were the same for both colloidal and calcined ceria, the synthesis method appears to strongly influence the oxide removal behavior. Their XPS data showed that the Ce³⁺ to Ce⁴⁺ ratio



Figure 5. Silicon dioxide RR in slurries containing 0.25 wt% ceria abrasives synthesized at different calcination temperatures. Adapted from Praveen et al.⁷¹

on the polished silicon dioxide films increased when picolinic acid was added. They speculated that picolinic acid might assist the chemical reaction between Ce^{3+} and silicon dioxide rather than increase the number of Ce^{3+} on the ceria particles or in the slurry.

Not only the method of preparation but also the associated impurities in the ceria particles seem to play a role on STI performance. For example, Praveen et al.⁷¹ compared the selectivity obtained in slurries containing either L-proline or L-glutamic acid with ceria abrasives from three different sources: Sigma Aldrich (ceria-SA), Sodiff, Korea (ceria-S) and ceria prepared by calcination of $Ce_2(CO_3)_3$ followed by milling (ceria-CM). The ceria-SA and ceria-S abrasives, but not ceria-CM, were found to contain La as an impurity. The results showed that with L-glutamic acid as the additive, all the slurries yielded high selectivity, while with L-proline, only slurries with pure ceria abrasives yielded high selectivity.

La doping in CeO₂ is expected to increase the oxygen vacancies and also 'pin' them, restraining the vacancies from migrating.⁷⁴ Gillis et al.⁷⁵ reported that La atoms doped in CeO₂ tend to migrate to the surface. Taken together, these findings suggest that La doping will increase the oxygen vacancies at the surface and those vacancies would not migrate, thus permanently changing the surface state. The increase in oxygen vacancies on the particle surface would tend to increase the fraction of Ce³⁺ on the surface. Thus it appears that both the synthesis method and purity level of ceria abrasive can strongly influence its polishing characteristics.

Reactivity of ceria.— Ceria based slurries are believed to chemically interact with SiO₂ and yield high RR, and the initially, Ce^{4+} was proposed as the reactive species.¹³ Subsequent investigations suggest that Ce^{3+} is likely to be the reactive species. The relevant reports are summarized below. Based on UV-visible absorption spectra, Veera Dandu et al.¹⁵ identified that the primary species on the ceria surface responsible for the high reactivity with silica are likely to be Ce^{3+}



Colloidal ceria

with picolinic

acid

Colloidal ceria

with Additive A

Figure 6. Silicon dioxide RR of slurries with calcined ceria and colloidal ceria (with and without additives). Adapted from Dio et al.⁷³

species. The absorption spectra of Ce^{3+} and Ce^{4+} show clearly different signatures and are dependent on pH. They analyzed the filtrates prepared from ceria dispersions and showed that the ions present in solution are Ce^{3+} . In addition, when additives such as PVP or PAD (which suppress oxide RR in ceria slurries) are present in the slurry, the spectra showed that the filtrate did not contain Ce^{3+} . This shows that Ce^{3+} is the species likely to interact with oxide film, and that PVP and PAD block the Ce^{3+} sites, thereby inhibiting oxide removal.

Colloidal ceria

w/o additive

Removal Rate, Å/min

0

Calcined Ceria

Recently, Veera Dandu et al.⁷⁶ measured the oxide and nitride RRs in ceria slurries with controlled dissolved oxygen content (DOC) in the pH range of 2 to 12 (Figures 7a and 7b). At pH <4, the oxide and nitride RRs were low, regardless of DOC. In the pH range of 4-12, the oxide and nitride RRs were high and more or less independent of pH, for a given DOC. In this pH range, the oxide and nitride RRs decreased with an increase in DOC. In another report, Manivannan and Ramanathan⁷⁷ showed that the addition of H_2O_2 to ceria slurries caused a drastic reduction in oxide and nitride RRs in the pH range of 7–10. Both these sets of results could be explained if Ce^{3+} is the active site, which would be converted to Ce^{4+} (assumed to be less active) at higher DOC or by the addition of H₂O₂. They also showed that if the ceria treated with H₂O₂ is filtered and redispersed in water (without adding H₂O₂), then the oxide and nitride RR were not suppressed, indicating that the conversion of Ce^{3+} to Ce^{4+} in an oxidizing environment is reversible.

Several published reports about the role of oxygen vacancies support this proposition. Deshpande et al.⁷⁸ and Dutta et al.⁷⁹ among others, have shown that ceria nanoparticles have Ce^{3+} on the surface and that oxygen vacancies drive the formation of Ce^{3+} from Ce^{4+} . Based on DFT calculations, Preda et al.⁸⁰ proposed that, on the surface of a ceria particle, a Ce^{3+} site with an oxygen vacancy can interact

with molecular oxygen and can possibly form two species, a Ce⁴⁺ superoxo species or a Ce^{3+} peroxo species (Figure 8). With increasing DOC in the slurry, it is likely that the Ce^{3+} sites with oxygen vacancies are converted to one of these two forms, leading to a reduction in the RR since only the Ce³⁺ with an oxygen vacancy, and not the superoxo and peroxo species, is the reactive site. Using DFT corrected for onsite coulomb interactions, Yeriskin and Nolan⁸¹ studied the effect of La doping on ceria surface. They showed that La³⁺ substitution of Ce⁴⁺ results in an oxygen vacancy, which results in the production of one Ce^{3+} . Patil et al.⁸² synthesized ceria nanoparticles (~3 to 5 nm) with controlled La and Nd doping by a microemulsion process. The particles were analyzed using XRD and Raman spectroscopy and they showed that the lattice parameter and defect concentration increased with La doping. They proposed that substitution of Ce⁴⁺ by La3+ causes introduction of oxygen vacancies and partial reduction of neighboring Ce⁴⁺ to Ce³⁺. These results are similar to those of Gillis et al.⁷⁵ with larger ceria particles.

Modification of ceria particles.— Even though ceria abrasives are prone to generate more post-CMP defects compared to colloidal silica,⁸³ they have certain inherent advantages such as higher throughput, lower particle loading, initial cost, and perhaps lower post-CMP waste disposal costs. Hence, novel design concepts that can minimize the challenges without sacrificing the advantages are continually being developed and evaluated. One example, though for silica particles, is the phosphate functionalized particles described earlier.⁶⁷ A more important example is the usage of slurries containing a mixture of ceria and other abrasives as well as core/shell type particles made of an external ceria coating. Some examples are described below to demonstrate the potential of such an approach.



Figure 7. (a) Silicon dioxide and (b) silicon nitride RR as a function of pH and DOC. Adapted from Veera Dandu et al.⁷⁶



Figure 8. Possible reaction pathways showing the formation of peroxo and superoxo complexes of Ce^{3+} at higher DOC values. The concentration of Ce^{3+} species with the oxygen vacancy, the reactive sites, drops in the presence of O₂. Hence oxide and nitride RR decrease when DOC is increased.

Jindal et al.⁸⁴ showed that the RRs of oxide increased with ceria coated alumina-based slurries when compared to RRs obtained with either ceria- or silica-based dispersions, but defectivity data were not reported. Lee et al.⁸⁵ synthesized silica particles coated with ceria and found that the oxide RR obtained using a ceria coated silica slurry was significantly higher than that in the pure abrasive slurries. Lu et al.⁸⁶ evaluated the polishing performance of silica, ceria and hematite abrasives, in single abrasive mode, (binary) mixed abrasive mode and in nano-particle coated abrasive mode. The ceria particles were relatively small (\sim 20 nm), while the silica particles were spherical (\sim 400 nm). Hematite particles were synthesized in two shapes, viz. ellipsoidal (\sim 400 nm) and cubic (\sim 750 nm). Nanosized ceria and silica (\sim 20 nm) abrasives yielded negligible oxide RRs and slurries with only silica or hematite showed very low (17-18 nm/min) oxide RRs. Hematite based mixed abrasives, on the other hand, showed higher oxide RRs. Silica or hematite abrasives coated with ceria produced even higher oxide RRs. They also showed that adding ceria abrasives to a fixed abrasive pad can dramatically increase the oxide RR. The authors suggested that the mixed abrasives and the coated abrasives synergistically utilize the reactivity of the ceria and the increased contact area between the wafer and the abrasive to enhance the oxide RRs.

Park et al.⁸⁷ investigated the oxide RR in zirconia and silica mixed abrasive slurries. Dilution of pure silica slurry resulted in lowering of oxide RR but addition of zirconia increased the oxide RR to original values. The WIW uniformity of the RR was also comparable to the original silica slurry results. The main advantage of this mixed abrasive system was the lower cost compared to the original silica slurry cost.

Armini et al.⁸³ synthesized two types of composite abrasives with a 300 nm polymer core coated \sim 14 nm ceria particles, one achieved with a silane coupling agents and the other with electrostatic interactions between the core and the shell. They reported that the two composite abrasive-based slurries exhibit different RRs, probably due to the difference in morphology and surface composition. More importantly, they showed that these composite particles exhibit lower defects when compared to conventional slurries, probably due to spring like effect of the softer elastic core during polishing. Lee et al.⁸⁸ evaluated a slurry with ceria and silica abrasives and showed that it gave reasonable oxide RRs, acceptable RR selectivity, good slurry stability, and low surface defects. While the reduction in defect level is important, other factors such as slurry stability, shelf-life and performance consistency also need to be evaluated before these mixed or composite abrasives are employed in production. There are several other reports of using mixed abrasive or core/shell particles in slurry formulation, for STI CMP as well as metal and barrier CMP.89

CMP of Patterned STI Structures

While planarization of patterned structures is all important, most of the published data are from blanket wafer film polishing and, as is widely known, these rates do not carry over to patterned structures. This poses a real challenge for developing in a cost-effective manner slurries for planarizing STI structures. Also, the results of polishing pattern wafers using different slurries, while available to most practicing engineers in the industry, are not widely available in the public domain, undoubtedly due to the associated intellectual property rights. As stated earlier, extent of nitride and field oxide loss, dishing, response to almost always required overpolish, WIW and WID uniformity, and defects - and not just selectivity - are some of the critical metrics for evaluating the performance of a slurry in conjunction with several other associate process variables. A few publications do address some of these issues and are summarized below.

Kim et al.⁹⁹ polished both blanket and patterned wafers using silica based slurries and reported that the oxide removal rates in both are strongly correlated. Later Kim et al.¹⁰⁰ employed a high selectivity silica based slurry, developed in house, to polish patterned structures and obtained significantly less variability in post CMP thickness values by using end point detection based on monitoring the motor current instead of polishing for a predetermined time and found that there is a strong correlation between the two RRs. In both cases, the selectivity data were not reported.

Lim et al.¹⁰¹ evaluated the effect of ceria abrasive size on the dishing and step height reduction during STI CMP. Ceria abrasives of three different particles sizes (primary particle sizes of 45 nm, 175 nm and 225 nm) were dispersed in DI water at pH 6.7. The dishing and step height reduction in trenches of about 10 micron width were measured using atomic force microscopy. The step height reduction was less initially but it increased at longer polishing times. This was attributed to the abrasives particles trapped in the trenches. The slurry with larger particles yielded quicker step height reduction and larger removal rates. At sufficiently long times, all the slurries resulted in complete step height reduction. However, the extent of dishing increased with over polishing time, as expected, and it also increased slightly with the size of the abrasive.

Merricks et al.¹⁰² compared the removal rates of silicon dioxide and silicon nitride as a function of time in ceria based slurries with two different additives, an unspecified amino acid and poly acrylic acid (PAA). In both case, the selectivity on pattern wafers was lower than what would be predicted from blanket film data. They found that, in their case, after the initial nitride film exposure, another 30s overpolish was needed to clear the oxide from the rest of the wafer during which time oxide loss continued with the PAA slurry but not with the amino acid slurry. Hence, the dishing was considerably higher and WIW and WID considerably worse for the PAA containing slurry. With the amino acid based slurry, removal of the silicon nitride film occurred only in the initial \sim 6s or so, supposedly the time required for the amino acid functional groups to equilibrate on the nitride surface. There was very little oxide as well as nitride loss afterwards, leading to a 1:1 RR ratio and, hence, no increase in dishing and no detrimental effects from overpolishing on WIW an WID uniformity, characteristics that are highly desirable in a slurry for pattern structure planarization.

Yang et al.¹⁰³ compared the polishing performance of three kinds of ceria and four kinds of silica slurries. The effect of particle size and shape on the step height reduction of rectangular (~100 nm size) and saw tooth (~500 nm pitch) patterns was studied. Based on the analysis of the results, they concluded that smaller sized and spherically shaped ceria particles are more effective in step height reduction. Euvrard et al.⁶⁰ evaluated the effect of selectivity on dishing, but using slurries with low selectivity (\sim 1). They compared the results from blanket wafers with those from patterned wafers and concluded that the selectivity is higher for the patterned wafers. However, since the mechanism of film removal in a high selectivity slurry differs vastly from that of a low selectivity slurry, this conclusions may not apply to high selectivity slurries. Kim et al.¹⁰⁴ showed that step height reduction, or planarization, was better with ceria-based slurries containing proline and serine over that obtained with glutamine and amino butyric acid. They proposed that a stronger interaction between the oxide and proline or serine, which they calculated from standard DLVO theory, is the cause of improved step height reduction.

Liao et al.¹⁰⁵ investigated the importance of pad surface topography in STI CMP using patterned wafers with varying pattern densities (10% to 90%), all with 100 micron pitch. They employed two conditioners and a mixture of commercial slurries from Hitachi. All yielded roughly similar RRs but vastly different dishing and erosion values. They suggested that the conditioners that generate more and sharper pad asperities can increase dishing and erosion by more than 100% in most features, presumably due to the direct contact of the down features with the sharp asperities.

Seo et al.¹⁰⁶ found that the step height changes can be tuned by controlling the adhesive force between ceria abrasives and the polyurethane pad when they used picolinic acid based ceria dispersions at pH 4.5 to polish 500 nm wide patterns. The step height reduction, measured as a function of polish time in slurries with and without picolinic acid, was significantly better in slurries with picolinic acid. They proposed that picolinic acid covers the ceria abrasive surface and helps with the attachment of ceria particles to the pad, which helps in the reduction of step height. Later, Seo et al.¹⁰⁷ investigated the effect of adding both PAA and poly (ethylene glycol) (PEG) to ceria based slurries at pH 5 to polish patterned wafers with 100 micron wide lines at various pattern densities (37.5% to 75%) and showed that the combination enhanced selectivity and reduced dishing. Without the additives, the selectivity was moderate (\sim 56) and the dishing was approximately 800 Å and 200 Å, respectively, for lines with a pattern density of 37.5% and 75%, and were reduced to about 600 Å and 100 Å, respectively, in the presence of 0.8 wt% PAA and 0.3 wt% PEG. They suggested that hydrogen bonding facilitates the adsorption of PAA on silicon nitride which suppresses nitride removal and enhances selectivity as well as the formation of PAA-PEG "interpolymer complexes" that reduce dishing by preventing oxide abrasion.

Clearly, the data needed to evaluate the performance of an STI slurry, indeed, any CMP process slurry for that matter, are more extensive and differ in many ways from those that can be obtained from blanket wafer film polishing. They also depend critically on the nature and morphology of the polishing pad, the polishing tool and the associated tool parameters. As such, enormous resources, including those needed to cover the cost of expensive patterned wafers, have to be allocated to validate and accept a slurry for large volume manufacturing and can indeed act as a barrier to entry for newer candidate slurries.

Current Challenges

While enormous progress has been achieved as described above and continues, several challenges remain. Only a couple of these – defect reduction and new dielectric materials - are addressed below.

Defect reduction .- CMP (dielectric or metal) process-induced defects can be classified broadly as micro scratches, gouges and pits, dishing, residual particles and organic residues. Any of these defects in STI CMP can result in yield loss and, hence, their reduction, and preferably elimination, is a key challenge.¹⁰⁸ Indeed, this is an overarching and overriding concern for maintaining yields and remains at the top of the list of performance metrics. An effective CMP process is one that minimizes defects and facilitates post-CMP processing to remove all contaminants from the post-polished surfaces. A typical commercial ceria-based slurry may contain large and/or irregular shaped particles which are more likely to cause many defects. Point of use filtration can prevent "large particles" from reaching the polish tool or the wafer surface and help in defect reduction^{109,110} and, consequently, online real time particle monitoring and feedback has gained considerable importance. Since it is known that slurries based on small and relatively narrow size-dispersed spherical ceria particles can lower defects, a judicious selection of ceria particle size and/or perhaps using a "mixture" of narrow sized silica and ceria can also help in reducing the defect levels without sacrificing oxide RR and selectivity.83,111

High selectivity or nitride rate suppression is, in principle, needed only at the last stage of removing the oxide overburden when silicon nitride surface is first exposed and overpolishing is used to remove residual oxide. In Cu CMP, the process is usually carried out in two steps: the first stage CMP when the bulk of the Cu is removed and the second stage soft landing step to remove the residual Cu followed by or concurrently removing the barrier layer. Similarly, it may be possible to remove the bulk of the silicon dioxide using a ceria based slurry with high oxide rate irrespective of the nitride rate and the final polish may be performed with a slurry with moderate or high selectivity that can minimize dishing, result in a good WIW and WID uniformity, low defect levels and a facile post CMP clean process. In any case, since any residual oxide will prevent the etching of the underlying nitride and hence interfere with the exposure of the active silicon region, some degree of overpolishing is commonly used, but at the cost of increased film thickness nonuniformity. Another option is to remove the residual oxide using a dilute HF etch but, as is well known, this will grow and expand/decorate even the smallest of the scratches that may be present in the oxide – a critical concern.

The drive toward 'green chemicals' leads to utilization of biocompatible additives in the slurry but this can simultaneously lead to bio-contamination in the slurry storage or transport channels and/or polishing equipment and hence on the wafer. This challenge is usually overcome by including biocides in the slurry. Additionally, as the use of smaller and smaller abrasive particles is gaining importance, their potential environmental importance must be investigated and all risks must be eliminated.¹¹² Since slurry formulations remain proprietary and dynamic, there is a need to collaboratively develop new approaches to properly dispose the used slurry to eliminate any risk in the work place or the environment.¹¹² The potential toxicity of the abrasives by themselves and in their modified form in the post-CMP dispersions, especially when they are at the nanoscale, is a serious concern and mandates stringent safe handling procedures that must become an integral part of their use.

Dielectrics other than silicon dioxide.— Silicon carbonitride has been evaluated as a dielectric diffusion barrier¹¹³ and its incorporation requires a CMP step with a high silicon carbontride RR and a low silicon dioxide RR. It is possible that similar materials such as silicon oxynitride or silicon oxycarbide may also be used as the dielectric in different STI integration schemes.¹¹³ Introduction of these or other new materials will require new slurries as well as reoptimization of the entire process recipe. For example, these new materials complicate the end point detection methodology,¹¹⁴ especially if the optical properties of the materials or the coefficient of friction are very different. Also, for materials such as silicon oxynitride used with an underlying silicon nitride stop layer, the difference in optical properties may not be sufficiently large for the optical method to identify the end point. One may have to rely on fluorescence¹¹⁵ or temperature¹¹⁶ as a parameter to identify the end point.

The challenges discussed here represent only the tip of the iceberg. Many more challenges exist but given the historical evolution of the CMP processes, the industry has been efficient and highly innovative in overcoming many such challenges at earlier nodes and there is no reason to believe that the trend will not persist.

Conclusions

CMP is ubiquitous in the semiconductor industry and has become increasingly integral to an ever growing number of process integration schemes involving novel materials. Specifically, STI process integration employs the CMP process to planarize the trench dielectric using usually a ceria based slurry and process combinations that generate a relatively high oxide rate polish rate with minimal nitride loss or high rate selectivity, as well as reduced dishing, erosion, WIW and WID nonuniformity and other defects.

The desired high selectivity is achieved mostly with ceria based slurries admixed with suitable additives. The additives are essential to suppress the nitride RRs while maintaining the oxide RRs at acceptable levels. The results presented in patents and published articles reviewed here have brought some clarity to the understanding of the nitride rate suppression mechanism. Additives such as amino acids, if available in sufficient quantities, and at the correct pH range where they remain protonated, can adsorb on the silicon nitride surface and prevent the hydrolysis of the silicon nitride surface and reduce its removal rate.

Ceria chemically interacts with the SiO₂ surface, and although the reactivity of ceria toward the silicon dioxide has been well known, the actual mechanism is only now emerging. Based on many recent experiments as well several first principle calculations, it appears that Ce³⁺ stabilized by an oxygen vacancy on the surface of ceria particles is the primary reactive species that interacts and polishes the oxide film. Among other results, the reduction in silicon dioxide and silicon nitride RR at various pH levels, with increasing dissolved oxygen content of ceria slurries suggests a role for molecular oxygen to transform these Ce3+ species into less reactive ones. The ceria abrasive synthesis process conditions that impact crystallite size, morphology and purity have a strong effect on the polishing characteristics. Also, precipitated and calcined ceria behave differently. The abrasive purity also appears to be important in determining the selectivity. Impurities such as La in the abrasive can drastically change the polishing behavior, at least in case of some additives such as proline. All these parameters seem to impact the concentration of the surface Ce³ species and, because of it, the oxide polish rate.

Ceria based slurries can generate more defects than silica based slurries, but they also yield higher selectivity and removal rates that enable high wafer throughputs. Innovations such as cost-effective monodispersed and/or smaller and spherical ceria abrasives, or the usage of mixed, composite, core/shell or other functional abrasive slurries with appropriate additive/s can assist in reducing the defect levels while maintaining throughput and selectivity. Introduction of new materials such as silicon oxynitride, silicon carbonitride or silicon oxycarbide in the STI structure complicates slurry and process development as well as end point detection. A high silicon nitride RR with a low silicon dioxide RR (i.e. reverse selectivity) is useful in certain process steps, for example, during the front end 3D-gate processing. Such reverse selectivity can be achieved by adding suitable chemicals such as PEI, PDADMAC, PVP and PAD. The additives such as PVP or PAD can block the active Ce³⁺ sites on the abrasive and suppress the removal of silicon dioxide. Also, silica abrasives can be modified by grafting phosphate functional groups and the resulting abrasives

selectivity polish nitride over oxide, mainly because of the interaction of the phosphate group with the nitride surface, bust cost is a barrier.

Other major challenges facing the industry in the usage of high selectivity STI CMP slurries include the ability to predict performance of patterned structures with different pattern densities and feature sizes from blanket wafer film rate data and reduction in defect levels including WIW and WID non-uniformity, end point detection and treatment and disposal of used slurry. The effect of nanoparticles in the slurry on the environment is an emerging and growing concern requiring effective treatment and disposal of the effluent from the CMP process.

In conclusion, CMP technology, in general, has undergone remarkable evolution in sophistication, complexity and utilization over the years while remaining far ahead of the understanding of the underlying fundamental principles - something that is not likely to change in the near future.

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