Origin of high oxide to nitride polishing selectivity of ceria-based slurry in the presence of picolinic acid*

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We report on the investigation of the origin of high oxide to nitride polishing selectivity of ceria-based slurry in the presence of picolinic acid. The oxide to nitride removal selectivity of the ceria slurry with picolinic acid is as high as 76.6 in the chemical mechanical polishing. By using zeta potential analyzer, particle size analyzer, horizon profilometer, thermogravimetric analysis and Fourier transform infrared spectroscopy, the pre- and the post-polished wafer surfaces as well as the pre- and the post-used ceria-based slurries are compared. Possible mechanism of high oxide to nitride selectivity with using ceria-based slurry with picolinic acid is discussed.

Keywords: chemical mechanical polishing, ceria, oxide over nitride selectivity, origin
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1. Introduction

In recent years, there has been increasing interest in the use of ceria-based slurries for the chemical mechanical polishing (CMP) of shallow trench isolation (STI). The STI has been the mainstream device isolation technology since the advent of 0.25 μm technology node.[1] In a typical STI CMP process, oxide is removed; nitride is left as a protective layer. To avoid the slurry contamination and to ensure the performance of underlying active area, a complete removal of oxide with a minimal loss of the nitride sublayer is required.[2] Ceria-based slurries can preferentially remove the overburden oxide layer with the minimal polishing of nitride in the presence of specific additives, which well meets the requirements for the STI CMP process. Many efforts have been made to search for suitable additives.[1] Meanwhile, a beneficial trial has also been made to explore the origin of the high electivity of ceria slurry, which is of vital importance for understanding the CMP process and also for finding the suitable additives.

The origin of the high selectivity of ceria slurry is related to the polishing mechanisms for both oxide and nitride. In a pioneer study on oxide polishing, Cook[3] proposed that CeO_2 possesses a chemical tooth that expedites both the bond shearing on the glass surface and the transport away of reaction products. In his chemical tooth model, he proposed that the chemical reactions between the siloxane (Si–O–Si) bonds and water determine the polishing behaviour and oxide film is removed in the form of $Si(OH)_4$. Kelsall[4] and Dandu *et al.*[5] further proposed that Ce^{3+} on ceria surface is chemically active and should be responsible for the oxide removal. Recently, Hoshino *et al.*[6] presented another model, in which Si–O–Ce bonds are formed due to the reaction of oxide surface with CeO_2 particles and then mechanical tearing of Si–O–Si bonds leads to the oxide removal as a lump.

As for nitride polishing mechanism, Hu *et al.*[7] proposed a two-step mechanism. In the first step, the nitride is hydrolyzed into suboxide and ammonia. In the second step, the suboxide is removed by the polishing action.

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Based on the polishing mechanisms for both oxide and nitride and the experimental results of different organic additives, Carter and Johns[8] claimed that nitride polishing could be influenced through additive basicity and site-blocking mechanism, the oxide removal would be decreased if molecules were likely adsorbed on either silica or ceria surface and prevented the direct interactions between Si–O^- and ceria. The variation of oxide to nitride removal selectivity with organic additive could be as high as three orders of magnitude. By using proline, America and Babu[9] achieved an oxide-nitride removal selectivity of 228. They argued that the proline could be adsorbed on the nitride surface through a combination of hydrogen boding and coupling of oxygen atoms, which suppresses the hydrolysis and the removal of the nitride. Recently, Kim *et al.*[10] confirmed that the preferential adsorption of anionic polyelectrolytes onto nitride surface is responsible for the high selectivity of SiO_2 over Si_3N_4. Many studies have been conducted to elucidate the origin of high oxide to nitride selectivity of ceria-based slurry, yet the mechanism remains unclear.

Some efforts in fields other than CMP have also been made to study the friction behaviour, which are good references for better understanding the CMP process. Lin *et al.*[11] found parameters like amplitude, frequency, direction of driving force to have a strong influence on static friction force. Meanwhile, Xiong *et al.*[12] investigated the interfacial adhesion of confined liquid thin film and found that the maximum interfacial adhesive force decreases with liquid volume and strongly depends on the film thickness in central area.

In the present study, the picolinic acid is used as a representative additive, which can lead to high oxide to nitride selectivity for the ceria-based slurries. The picolinic acid is chosen according to our experiments. No matter what kind of ceria abrasive is used, the picolinic acid could always suppress the removal of nitride. By using zeta potential analyzer, particle size analyzer, horizon profilometer, thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR), the pre- and the post-CMP wafer surfaces and the pre- and the post-used ceria-based slurries are compared. Based on the experiments, some insight into the origin of high oxide to nitride selectivity with using ceria-based slurry in the presence of picolinic acid is obtained.

2. Experiment

The preparation of polishing slurry started with dissolving the additive (Aldrich, without further purification) in deionized (DI) water under magnetic stirring. Ceria dispersions (Ferro Corp.) were 52 wt% and the mean particle size was around 140 nm measured by transmission electron microscope (TEM). The ceria was added with dynamic mixing. The last step of slurry preparation was to adjust the pH value to 5 by adding nitric acid or potassium hydroxide. The polishing slurry was composed of 0.5 wt% ceria, 0.1 wt% additive and DI water. All the chemicals were obtained from Sigma-Aldrich (USA).

Si wafers each with a diameter of 200 mm were obtained from Montco Silicon Technologies Inc. The wafer was covered with thermal silicon dioxide (grown at $\sim$900 °C) or silicon nitride (low pressure chemical vapour deposition at $\sim$790 °C), with an initial film thickness of $\sim$2000 or $\sim$500 nm. The silicon nitride wafer had a SiO_2 layer ($\sim$100 nm thick) between the nitride film and the Si substrate. Before polishing, the 20 cm wafers were all cut into 5 cm ones.

Polishing was performed using a CMP Tester (CETR CP-4). The polishing parameters were set as follows: pad rotation speed 75 rpm, wafer rotation speed 75 rpm, down force 4 psi, feed rate of the slurry 100 ml/min, polishing time 1 min. The polishing pad (IC 1010, Dow Electronics) was conditioned for 2 min before each polishing experiment. The removal rate was calculated from the difference in film thickness measured before and after polishing. The film thickness was measured using a Filmetrics F20 interferometer and averaged over 17 points distributed throughout the wafer surface. The wafer surfaces before and after polishing were characterized by a horizon profilometer in an area of 268.8 μm$\times$268.8 μm.

In order to compare the fresh slurry with the used slurry, the pre- and the post-CMP ceria-based slurries were collected. A zeta potential analyzer and a particle size analyzer (Brookhaven ZetaPlus) were used to measure the zeta potentials and particle sizes of the slurry samples, respectively. In addition, certain volumes of slurry samples were centrifuged and the sediments were dried in an oven at 100 °C for 2 d. The dried powders were tested by TGA and FTIR separately. Since there was too much noise in the direct FTIR tests of oxide and nitride wafers, instead SiO_2 (1–5 μm) and Si_3N_4 (< 50 nm) particles were used to mimic the oxide film and the nitride film respectively. The samples were prepared by dissolving

the additive in a certain volume of deionized water, followed by adding 10 wt% silicon dioxide (or silicon nitride) particles to make up the volume to 50 ml and adjusting the pH value to 5. After centrifugation, the sediment was dried in an oven at 100 °C for 2 d. The dried powders were used for FTIR tests.

3. Results and discussion

3.1. Removal of oxide and nitride

Figure 1 shows the structure of picolinic acid. The pKa values of the functional groups are also assigned. The picolinic acid possesses an aromatic group with one C substituted by N and a carboxyl group. The pKa values of carboxyl and aromatic N are 1.0 and 5.4, respectively.

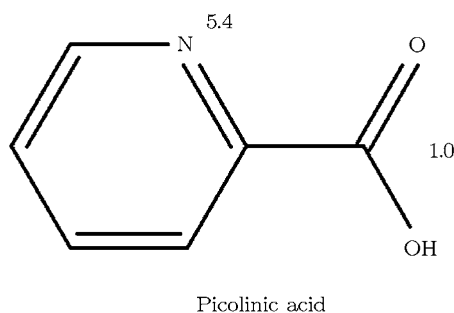

Fig. 1. Molecular structure of picolinic acid, where the pKa values of functional groups are also assigned.

Figure 2 shows the removal rates of oxide and nitride with and without the picolinic acid separately. As can be seen from Fig. 2, when using the 0.5 wt% ceria without piconilic acid (pH 5), the removal rates of oxide and nitride are 249 nm/min and 74 nm/min, respectively. While using the ceria slurry containing 0.1 wt% picolinic acid, the removal rates of oxide and nitride are 332 nm/min and 4 nm/min, respectively. With the picolinic acid, the enhancement of oxide removal and the suppression of nitride removal lead the oxide to nitride polishing selectivity to a sharp increase from 3.4 to 76.6.

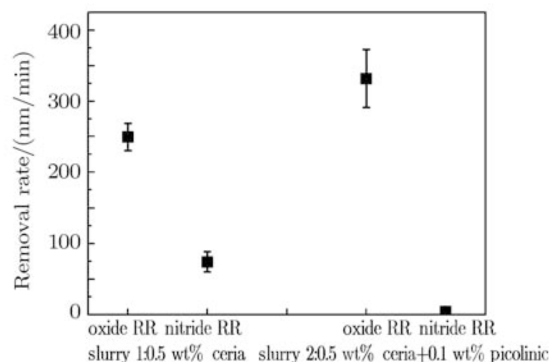

Fig. 2. Oxide and nitride removal rates using the ceria slurries with and without picolinic acid.

3.2. Pre- and post-CMP wafer surface

To find the origin of high oxide to nitride polishing selectivity with the picolinic acid, the wafer surfaces before and after polishing were compared.

The root mean squares (RMSs) of pre- and post-CMP wafer surface are shown in Table 1 separately. The RMSs of oxide pre- and post-CMP using ceria slurry without the picolinic acid are 1.1 nm and 1.3 nm respectively, and the corresponding values of nitride are 0.7 nm and 1.3 nm. With the picolinic acid added to the ceria slurry, the RMSs of oxide pre- and post-CMP are 0.9 nm and 1.4 nm respectively, while the RMSs of the nitride surface remain the same since the removal rate is almost zero. From the comparison between the pre-CMP and the post-CMP it follows that the increments of the RMS are less than 0.6 nm for both cases, implying that both the oxidized surface and the nitridized surface after polishing are degraded slightly in surface roughness. In general, their surface qualities could be taken as being almost the same as those of pre- and post-CMP for both cases with and without the picolinic acid.

Table 1. Root mean squares of wafer surface pre- and post-CMP using ceria slurries with and without the picolinic acid.

items	slurry 1: 0.5 wt%ceria	slurry 2: 0.5 wt% ceria + 0.1 wt% picolinic acid
pre oxide CMP	1.1 nm	0.9 nm
post oxide CMP	1.3 nm	1.4 nm
pre nitride CMP	0.7 nm	0.7 nm
post nitride CMP	1.3 nm	0.7 nm

3.3. FTIR of oxide and nitride particles

The interactions among the ceria particles, the organic additive and the film surface influence the final CMP performance. To check whether there is an interaction between the picolinic acid and the oxide/nitride film, FTIR was used to test the oxide particles and the nitride particles, which were adopted to mimic the corresponding films. The FTIR spectra of oxide particles with and without the picolinic acid are shown in Fig. 3. As can be seen in Fig. 3, the shapes of the spectra are exactly the same for the oxide particles with the picolinic acid as that without the picolinic acid, which shows there is definitely no interaction between the oxide particle and the picolinic acid. As for nitride, the scenario is different, which is shown in Fig. 4.

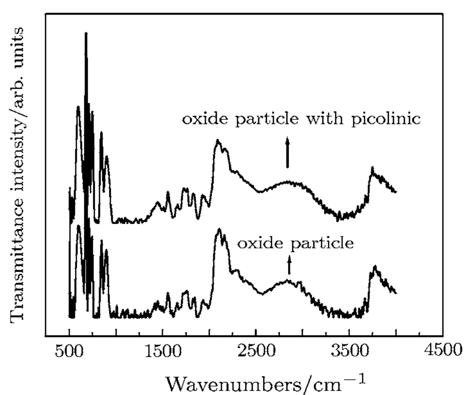

Fig. 3. FTIR spectra of oxide particles with and without the picolinic acid.

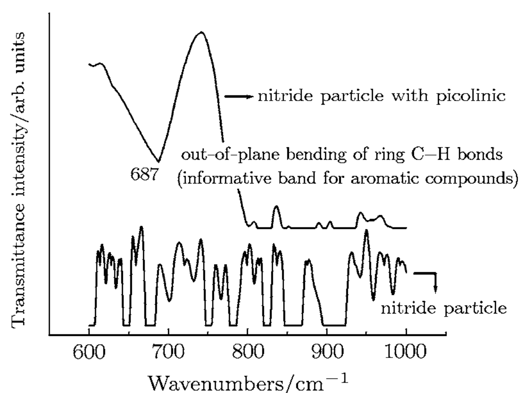

Fig. 4. FTIR spectra of nitride particles with and without the picolinic acid.

A peak at position 687 cm^{-1} appeared when the picolinic acid was added to the nitride particle solution. The new peak could be ascribed to out-of-plane bending of the ring C–H bonds, which is an informative band for aromatic compounds and indicates the existence of picolinic acid on the nitride surface. It means that the picolinic acid can be absorbed onto the nitride surface by either chemical or physical absorption. It should be mentioned that there was much more noise in the FTIR tests of nitride particles, thus the reliability of Fig. 4 is not as good as that of Fig. 3.

3.4. Zeta potential and particle size of the slurries

Table 2 shows the zeta potential values and the particle sizes for the pre- and the post-CMP ceria slurries. For both slurries, with and without the picolinic acid, there is a minor decrease of zeta potential value after being used in oxide polishing, while there is a large shift of zeta potential value towards the negative direction after being used in nitride CMP.

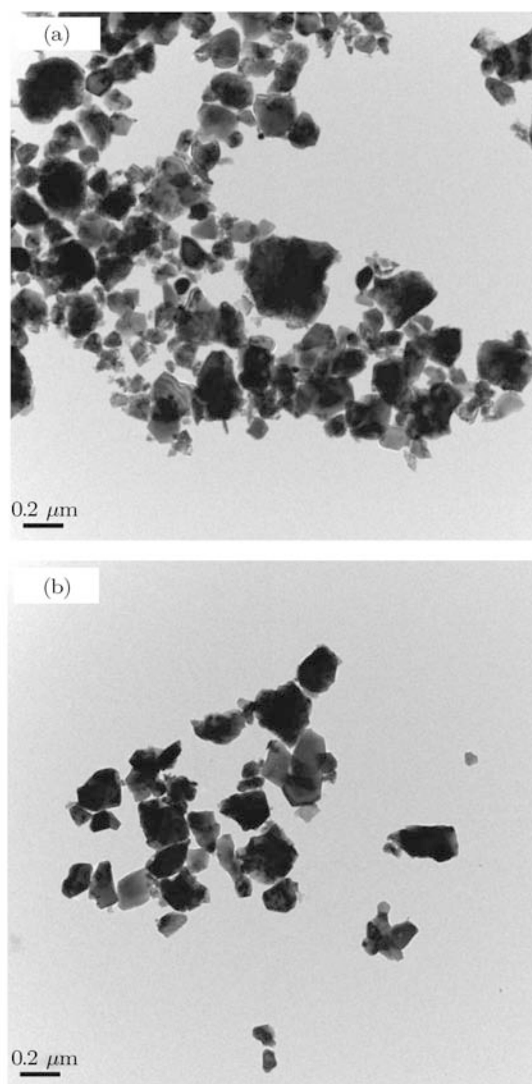

Fig. 5. TEM images of the ceria slurries (a)without and (b) with picolinic acid.

These potential value shifts are in accordance with the isoelectric point (IEP) data, which are

around 2–3 for SiO_2, 6.5–7.5 for Si_3N_4 and 7 for CeO_2.[13] No matter whether there is picolinic acid or not in the ceria slurries, the particle sizes in the pre- and the post-CMP slurries are almost the same for both the oxide polishing and the nitride polishing. The only change that occurs is the agglomeration of particles in the slurry with picolinic acid used in the oxide polishing. This might be due to the fact that the surface potential decreases by about 25 mV after the CMP, which leads the abrasives to be less stable.

TEM was used to characterize the morphology of ceria abrasive. As can be seen from Fig. 5, there is a large size distribution for both the slurries with and without the picolinic acid. The average particle size of ceria is around 140 nm, which is also the value supplied by the Ferro Corporation. There is a slight improvement on the slurry dispersion with the addition of picolinic acid, which is in line with the data shown in Table 2.

Table 2. Zeta potential values and particle sizes for pre- and post-CMP ceria slurries (a) without and (b) with picolinic acid.

(a)

items	Zeta potential/mV	particle size/mum	
		Num%	Vol%
pre-CMP	19±1	0.8	1.7
post oxide CMP	–11±16	0.9	1.9
post nitride CMP	12±3	0.8	1.8

(b)

items	Zeta potential/mV	particle size/mum	
		Num%	Vol%
pre-CMP	35±1	0.1	0.2
post oxide CMP	10±4	0.6	1.2
post nitride CMP	26±2	0.1	1.0

3.5. FTIR of the sediment of slurries

To find further evident revealing the origin of high oxide to nitride selectivity of ceria slurry, the sediments of the pre- and the post-CMP slurries were measured by the FTIR. The result is shown in Fig. 6.

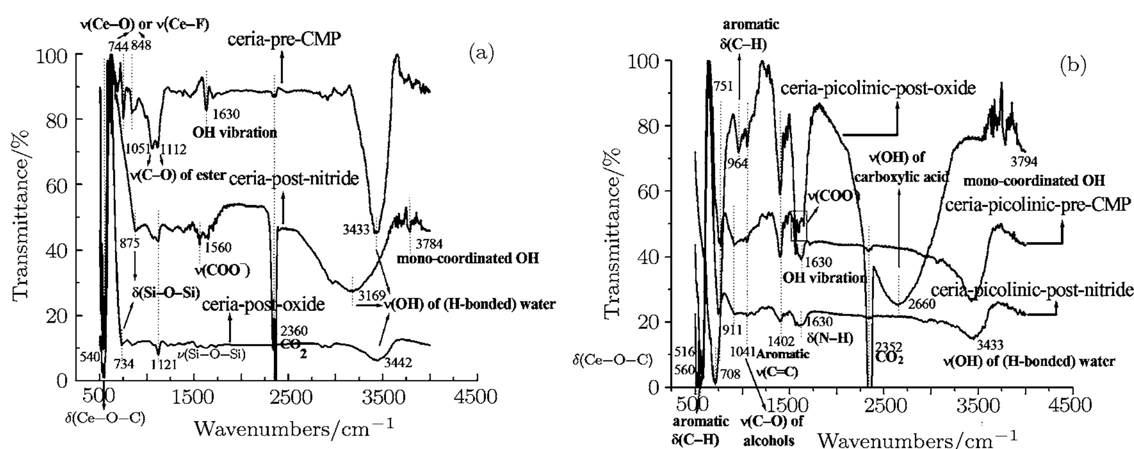

Fig. 6. FTIR spectra of sediments of pre- and post-CMP slurries (a) without and (b) with picolinic acid.

The peak assignments in Fig. 6 are summarized in Table 3.[14,15] As shown in Table 3, the surface OH bond sends strong signals for all the samples. The Ce–O bonds also exist in all the samples, which indicates that the

tested samples are of ceria. The Ce–F signals show F impurities in the ceria. The Ce–O–C signals might be due to the complex between the ceria and the dissolved CO_2 from the air. There are Si–O–Si bondings in post-oxide and post-nitride CMP samples when there is no additive in the ceria-based slurries, while no Si–O–Si peak is detected in the corresponding samples with the picolinic acid. As for nitride polishing, there is Si–O–Si bond in the slurry without picolinic aicd, while N–H bondings appear after the picolinic acid has been introduced into the ceria slurry. By comparing the spectra with and without the picolinic acid, there are corresponding peaks (aromatic C=C, C–H) for all the samples with the addtition of the picolinic acid, which indicates that there is an interaction between the ceria and the picolinic acid.

Table 3. FTIR peak assignments for sediments of pre- and post-CMP ceria slurries.

0.5 wt%slurry@ pH=5	pre-CMP	post-oxide CMP	post-nitride CMP
without additive	OH, Ce–O/Ce-F Ce–O–C, C–O	OH, Si–O–Si Ce–O/Ce–F, Ce–O–C	OH, CO2, Si–O–Si Ce–O/Ce–F, Ce–O–C
with 0.1 wt% picolinic	OH, aromatic C=C, C–H C–O, Ce–O–C	OH, CO_2, COO aromatic C=C, C–H, Ce–O–C	OH, N–H aromatic C=C,C–H Ce–O–C

3.6. TGA of the sediment of the slurries

The TGA was also performed to check the changes in the sediments for the pre- and the post-CMP ceria slurries. Figure 7 shows the TGA curves for the sediments of the pre- and the post-CMP slurries.

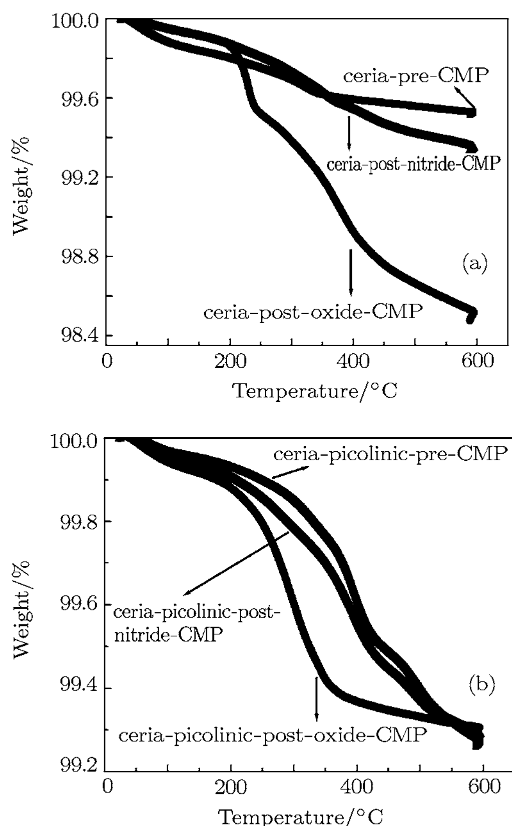

Fig. 7. TGA curves of the sediments of pre- and post-CMP slurry (a) without and (b) with picolinic acid.

As can be seen in Fig. 7, there is minor weight loss for the sediment sample used in the nitride polishing. There appears some decomposition at temperatures higher than 200 °C in the sample used in the oxide CMP, no matter whether the picolinic acid has been added to the ceria slurries.

3.7. Possible mechanism of high oxide to nitride selectivity

From the aforementioned results, the following points can be seen. (i) The oxide surface quality and the nitride surface quality remain almost the same before and after polishing (RMS deterioration $\leq$ 0.6 nm). (ii) The FTIR spectra of particles show that there is no interaction between the oxide and the picolinic acid, and that the picolinic acid can be absorbed onto the nitride surface. (iii) Particle size measurement shows that no change in slurry occurs during the polishing, especially during the oxide polishing. (iv) The FTIR spectra of the slurry sediments show that the picolinic acid can inhibit the hydrolysis of nitride and there is a strong interaction between the ceria and the picolinic acid. (v) The TGA results indicate there are some decompositions at temperatures higher than 200 °C in the samples used in the oxide CMP. The result is unrelated to the presence of the picolinic acid.

To explore the origin of high oxide to nitride selectivity, the polishing mechanism of oxide and the polishing mechanism of nitride are discussed separately.

According to the experimental results and the previous researches by Cook,[3] Hoshino *et al.*[6] and Kelsall,[4] we propose the following mechanism for the oxide polishing: highly active Ce^{3+} on the ceria surface is responsible for the fast removal of oxide; the oxide film is removed in the form of $Si(OH)_4$, which is supported especially by our experiments. The evidences include the following facts. 1) The surface quality remains almost unchanged after polishing by any slurry we used. If the oxide film was removed as lumps, there should be some deterioration in surface roughness and some scratches left on the surface. 2) The particle sizes in the slurries do not change during the polishing. 3) The TGA results show that there are some decompositions in the sediments of slurries used in the oxide CMP. The bulk ceria and the silica particles should be stable enough at the test temperatures. If the silica was torn in the form of $Si(OH)_4$, the decomposition of the less stable $Si(OH)_4$ gel on the sample surface could account for the weight lost found in our experiments. 4) The FTIR spectra of the slurry sediments show the presence of Si–O–Si bonds in the post-oxide CMP and the post-nitride CMP samples without the additive, and the absence of Si–O–Si peak in the corresponding samples with the picolinic acid. If the oxide film was removed in the lump form, there should be Si–O–Si bonds for all the post-oxide and the post-nitride samples, which is inconsistent with our experiment result. When $Si(OH)_4$ is removed from the oxide film, the silicic acid is quite unstable in near-neutral pH and can easily form silica gel, which can account for the Si–O–Si bonds in the post-oxide CMP sample and post-nitride CMP sample without the additive. The gel process for the silicic acid is catalyzed by the base. When the picolinic acid is present, this gel process is inhibited. The complex tendency between the picolinic acid and $Si(OH)_4$ can also stop the formation of silica gel. Then no Si–O–Si bond is formed in the sample with the picolinic acid, thereby explaining the Si–O–Si bonds observed in our experiments.

As for the nitride polishing, it is believed to be a two-step process including the hydrolysis of nitride to oxide and the removal of oxide.[7] Any parameter, which can influence either step, will affect the polishing process. The FTIR results show that there is Si–O–Si bond in the sediment of the slurry without the picolinic aicd, and N–H bonds appear only in the samples with the picolinic acid. It is well known that acidic silanol (SiOH) is the major surface group on silica, while silicon nitride surface consists of basic amine (Si_2NH) and acidic silanol (SiOH) groups.[16] Therefore the FTIR results indicate that the hydrolysis of nitride to oxide is inhibited by the picolinic acid, which leads to extremely low nitride removal rate. The suppression can be ascribed to the catalysis disruption by basicity or the site blocking of picolinic acid.

Thus, the origin of high oxide to nitride selectivity could be reasoned with following facts. 1) Mixed oxidation states of ceria. The bulk ceria (Ce^{4+}) ensures the necessary hardness and the density characteristics to serve as a fine abrasive to the softened oxide surface, while highly chemically active Ce^{3+} on the ceria surface can bond to the hydrated oxide surface aiding the fast oxide removal in the form of $Si(OH)_4$.[4] 2) The interaction between the additive and the oxide to nitride film. Taking the picolinic acid as an example of the additives, the picolinic acid does not interact with the oxide. On the contrary, the picolinic acid may form complex with the abraded $Si(OH)_4$ and promote the removal of oxide. These two factors result in a high oxide removal rate. As far as nitride is concerned, the FTIR result for the nitride particles shows that the picolinic acid can be absorbed onto the nitride surface. The FTIR spectra of the post-CMP slurry show that the picolinic acid can inhibit the hydrolysis of nitride to oxide, which leads to an extremely low nitride removal rate. Therefore, a high oxide to nitride selectivity can be obtained by using ceria-based slurry in the presence of picolinic acid.

It worth mentioning that the pads and the ceria abrasives themselves and their interactions with the additives can also influence the selectivity of oxide to nitride. They will be discussed elsewhere.

4. Conclusions

We report on the investigation of the origin of high oxide to nitride polishing selectivity using the ceria-based slurry in the presence of picolinic acid. The ceria slurry with the picolinic acid shows a removal selectivity of oxide to nitride as high as 76.6 in the chemical mechanical polishing. Comparisons between the pre- and the post-CMP wafer surfaces and between the pre- and the post-CMP ceria-based slurries show that oxide is fast removed in the form of $Si(OH)_4$ by the mixed oxidation states of ceria. No interaction is observed between the oxide and the picolinic acid, which keeps the removal rate of oxide at a high level. While the FTIR results show that there

is picolinic acid absorbed on the nitride surface and the picolinic acid inhibits the hydrolysis of nitride to oxide, resulting in a much lower nitride removal rate. Thus, high oxide to nitride selectivity can be obtained using ceria-based slurries in the presence of additive. Our future work will elucidate the interactions between the pad/ceria particles and the additives.

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