Chemical mechanical polishing of thermal oxide films using silica particles coated with ceria

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Thermal oxide covered silicon wafers were polished with slurries containing either nano-sized ceria (CeO_2) or newly prepared uniform colloidal silica particles coated with ceria. The polish rate of the latter was significantly higher than that of pure ceria. The experiments were carried out using different concentrations of the abrasives at pH 4 and 10. Little effect on the polishing rates was noted when the conditions of the slurries were varied, which was explained by the compensation of two opposite polishing mechanisms.

I. INTRODUCTION

Ceria slurries have been commonly used in polishing silicon oxide films. The CeO_2 particles offer certain advantages, such as high polish rates due to their chemical reactivity with the silica substrate. In spite of these advantages, ceria-based slurries have not yet gained widespread commercial acceptance. The reasons include their cost, as well as the broad size distribution and irregular shape of the particles. In addition, the commercial ceria abrasives contain several contaminants that influence negatively their polishing performance, since they can alter the surface morphology, the charge characteristics, and the roughness of the particles, resulting in the excessive scratches and defects of the polished films. Finally, the stability of the slurries can also be affected. So far, limited information has been given on the properties of ceria used in chemical mechanical polishing (CMP). Indeed, in the reported studies data on the characterization of the slurries are either nonexistent or incomplete.[1–4] More recently, America[5] employed two commercial particles of approximately 440 and 140 nm in diameter and Jindal[6] used mixed abrasives of nano-sized ceria and alumina in polishing silicon oxide wafers.

Depending on the size and the structural properties of the abrasives, different mechanisms may be operational in the CMP processes. Thus, it is important to carry out experiments with slurries of well-defined morphological characteristics. In this study experiments were carried out with uniform ceria particles. For this purpose, two different dispersions were prepared, one consisting of nano-sized ceria particles of narrow size distribution and the other of monodispersed colloidal silica coated with ceria. The latter dispersion was chosen because methods for the preparation of uniform larger ceria yielded only very low concentrations of solids,[7] insufficient for polishing experiments. In contrast, uniform silica cores are available in large amounts and could be coated with ceria by a process described in this work. This approach makes it possible to control the size of the dispersed abrasives, yet having the desired surface and other characteristics, in this case of ceria. The actual CMP experiments were conducted at two pH values with different concentrations of the slurries to examine the physical and chemical effects on the polishing of silicon oxide films.

Thus, the particles described here are superior in terms of purity and size uniformity over those available commercially. It is also shown that the surface roughness of the thermal oxide films polished with these particles is reasonably low.

II. EXPERIMENTAL

A. Preparation of nano-sized CeO_2 particles

Stock solutions of 2 mol dm^{-3} $Ce(NO_3)_3$ and 2 mol dm^{-3} NH_4OH were prepared from reagents and were diluted before use as needed.

Nano-sized CeO_2 particles were obtained by modifying a process described in a patent.[8] The procedure consists of adding NH_4OH solutions into a reactor containing a preheated $Ce(NO_3)_3$ solution. Systematic experiments were carried out to optimize the conditions (temperature, concentration of reactants, final pH, etc.) that would yield uniform, highly crystalline particles. It was observed that with increasing temperature the reaction was faster and that the resulting particles were

larger, if higher concentrations of $Ce(NO_3)_3$ solutions were used. Furthermore, the crystallinity of CeO_2 was poorer when the pH of the reacting solutions was higher.

The most uniform stable dispersions of nano-sized ceria (CeO_2) particles were obtained by adding 300 cm^3 of a 0.2 mol dm^{-3} NH_4OH solution into a reactor containing 200 cm^3 of a 0.2 mol dm^{-3} $Ce(NO_3)_3$ solution preheated to 93 °C. The mixture was kept at this temperature for 6 h, while stirred, and then the resulting dispersion was cooled to room temperature. To purify the particles, the supernatant solution over settled, aggregated particles (due to the high ionic strength) was decanted, and the remaining solids were redispersed in water and centrifuged. The process was repeated until the conductivity of the washing liquid was approximately 100 μmoh or until the pH of the suspension was approximately 4.0. The purified samples were kept in an aqueous suspension at room temperature.

The formation of CeO_2 particles proceeded through several stages. After the mixing of $Ce(NO_3)_3$ and NH_4OH solutions, a gel-like phase was formed in which, on aging at the elevated temperature, the Ce^{3+} ion was oxidized to Ce^{4+} and H_2 gas was released. It was shown that under these conditions hydrated cerium hydroxide complexes were generated,[9,10] and dehydrated during the described process, resulting in CeO_2 crystallites. This mechanism was corroborated in this work by the drop of the pH from approximately 7.0 to approximately 2.5, while the color of the suspensions changed from purple to light yellow.

Sugimoto[11] has demonstrated that such a "gel-sol" transformation can be used to produce a number of uniform inorganic dispersions.

B. Silica particles coated with CeO_2

Monodispersed silicas in modal diameters of 300 and 400 nm (MP3040 and MP4050, supplied by Nissan Chemical Industries, Ltd., Houston, TX) were employed as core materials in the coating process. Before use, these particles were washed with de-ionized water to remove excess NaOH present in the dispersions.

The procedure to coat the colloidal silica with cerium oxide (CeO_2) involved essentially the same conditions as those described in the previous section, except for the cores being present in the reactant mixtures. Thus, 300 cm^3 of a 0.2 mol dm^{-3} NH_4OH solution was added into the reactor containing 200 cm^3 of a 0.2 mol dm^{-3} $Ce(NO_3)_3$ solution preheated to 93 °C, followed by admixing 10 g of silica in 20 cm^3 of water. The entire system was then kept at this temperature for 6 h under stirring. The resulting dispersions contained both coated silica and nano-sized ceria particles. The latter were separated through several decantation and redispersion cycles.

The process of the formation of the coating seemed to follow the same stages as observed in the preparation of nano-sized CeO_2. First, a gel-like layer encases the cores, which on aging crystallizes into CeO_2 particles that adhere to silica, mostly in an incomplete monolayer. It is noteworthy, that the independent ceria particles and those comprising the shell are of the same size.

C. Particle characterization

The crystal structure of the particles was determined by x-ray diffraction using CuK_α radiation, and the crystallite size of ceria was evaluated by the Scherrer method. The particle size and morphology were assessed by scanning and transmission electron microscopies. The composition of the coated particles was estimated by energy dispersive x-ray spectrometry (EDX). The electrophoretic mobilities of the samples were determined with the Zetapuls instrument as a function of the pH, adjusted either with HNO_3 or KOH.

D. Polishing of wafers

Polishing experiments were carried out with thermally grown silicon oxide film on 4-in. silicon wafers (Noel Technologies, Campbell, CA) in a Buehler Phoenix-beta polisher using IC-1400 K Groove pads made of polyurethane (Rodel Inc., Phoenix, AZ). The rotation speed of the pad was set at 90 rpm, while the disk holder was held stationary. The applied pressure was approximately 4.0 psi. The feed-in slurry flow rate was 120 cm^3 min^{-1}. Before each experiment, the pad was hand-conditioned for 1 min with a diamond grit conditioner using de-ionized water. The polishing slurry was agitated continuously with a magnetic stirrer to maintain a good dispersion.

The polish rates for wafers were determined from the differences of the film thicknesses measured by means of optical interferometry using a Filmetrics instrument. The surface roughness of the polished wafers was estimated by a Horizon noncontact optical profilometer.

III. RESULTS
A. Nano-sized ceria

The transmission electron micrograph in Fig. 1(a) illustrates the nano-sized CeO_2, prepared as described in Sec. II.A. The size of the well-dispersed particles of nearly cubic shape is approximately 10–15 nm, evaluated from transmission electron microscopy (TEM) pictures. The x-ray diffractogram [Fig. 2(a)] is characteristic of the cubic phase ceria.[12] The crystallite size determined by the Scherrer method is approximately 10 nm. Thus, it would appear that these nanoparticles are single crystals.

The weight loss of the solids heated to 700 °C was 2.3%, as determined by the thermogravimetric analysis method. This result supports the crystalline nature of the particles which are, therefore, expected to be of high
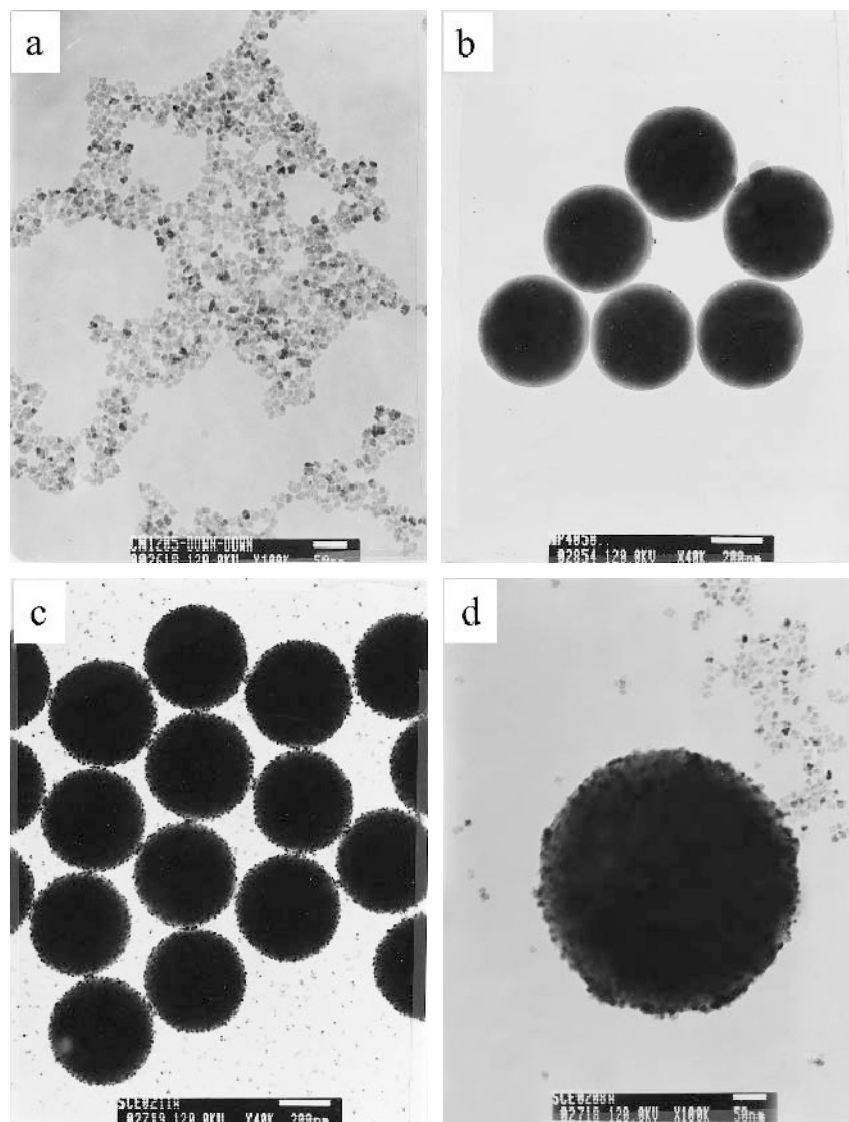
FIG. 1. Transmission electron micrographs of (a) ceria particles, (b) core silica particles, and (c, d) silica particles coated with ceria nanoparticles.

hardness. The latter is an important property with respect to their application in polishing. It should be noted that the commercial samples of nano-sized ceria (Nyacol) showed a weight loss of 6–8%.

B. Silica coated with ceria

TEM Fig. 1(b) displays silica cores used in this study, while Fig. 1(c) is the TEM of the same particles covered with ceria by the process described in Sec. II.B. To better visualize the nature of the shell a single coated particle is shown in Fig. 1(d). The XRD peaks of coated particles [Fig. 2(b)] are characteristic of CeO_2, the presence of which is also confirmed by the EDX analysis.

Electrokinetic mobilities (Fig. 3) of silica cores, of nano-sized CeO_2, and of the coated particles clearly display a significant shift of the isoelectric point from the

cores toward pure ceria. These data indicate that either the shell is incomplete or that silica may still exert an effect on the electrokinetic properties of the very small ceria particles in the shell.

C. Polishing of SiO_2 films on wafer

Thermal oxide films were polished with slurries containing nano-sized ceria, silica cores, a mixture of both, and silica particles coated with ceria, at different solid contents, and at pH 4 and pH 10, respectively. Data summarized in Table I show that the polishing rates were quite low with either of the single systems (SI-B and CE) or with their mixtures of different weight ratios (M-1, -2, -3).

In contrast, considerably higher removal rates were observed with slurries containing silica particles coated with ceria (Table II). It is noteworthy that varying the

solid contents of abrasives or of the pH had only modest influence on the rate of the process. Furthermore, the roughness of the films after polishing was essentially the same using these slurries under different conditions.

IV. DISCUSSION

A. Abrasive particles

Most of the preparation methods of nano-sized ceria were based on hydrothermal reactions in the absence[7,10,13–15] or in the presence of stabilizers.[16] The
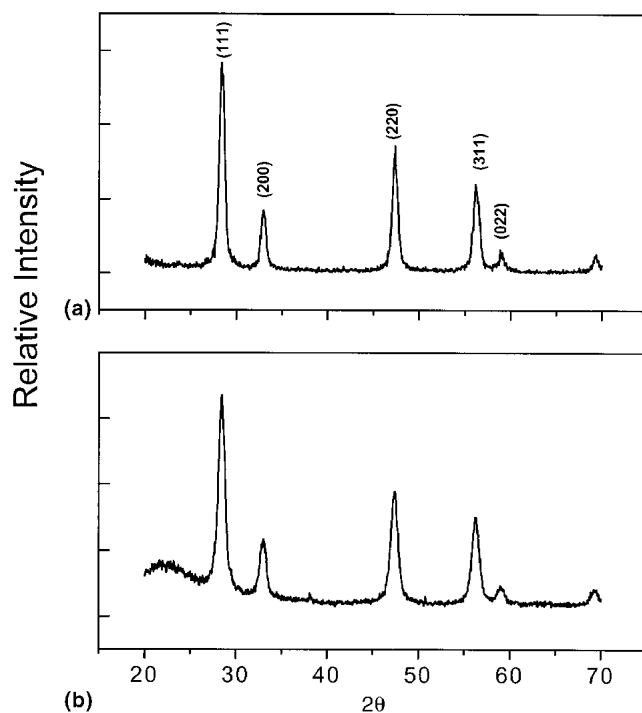

FIG. 2. X-ray diffractograms of (a) nano-sized ceria particles and (b) silica particles coated with ceria prepared as described in Sec. II.A. and II.B.
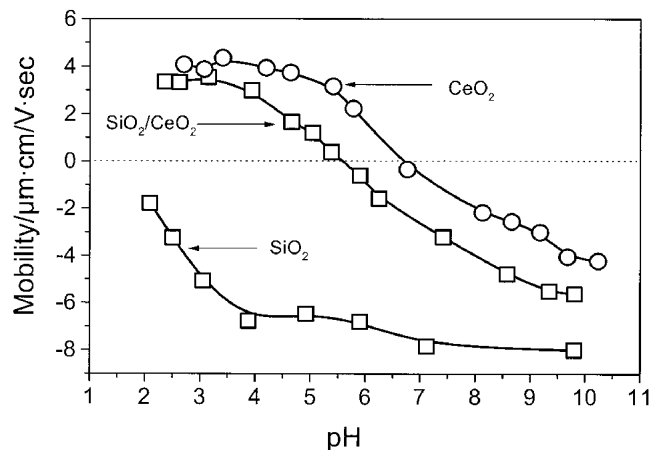

FIG. 3. Electrophoretic mobilities of SiO_2/CeO_2 (silica particles coated with ceria), CeO_2 (ceria particles), and SiO_2 (silica particles) suspended in 1×10^{-3} mol dm^{-3} KCl solution as a function of the pH.

synthesis employed in this work, which is a modification of a patent,[8] is characterized by a low-temperature process, without requiring pressurization or additives. The resulting dispersions remain stable, or they can be easily peptized by ultrasound. These properties are in part affected by the hydration envelope on the very small particles and by their charge. As noted earlier, the adopted procedure can be best described as a gel-sol process.[11]

The coating of silica cores with ceria may follow two different paths. One involves the precipitation of nano-sized ceria particles, which then adsorb on silica, while in the other case the gel is formed on the cores followed by crystallization of ceria in this layer. The experimental evidence supports the latter process. The actual attachment involves a bond formation between basic ≡CeOH groups on the particles and acidic ≡SiOH groups on the cores.[17]

B. Polishing

In discussing the polishing rate results, it is necessary to consider chemical and physical parameters. Any evaluation of chemical effects should involve the interactions due to the solvent, i.e., the effect of the pH, and of the possible bond formation between the abrasive particles and the wafer.

The very low polish rates of either nano-sized ceria or pure colloidal silica (CE, SI-B in Table I and SI-A in Table II) were observed before.[5,6,18] On the other hand,

TABLE I. Polish rates for thermal SiO_2 wafers using different mixture of silica particles of 400 nm in diameter and of nano-sized ceria particles at pH 10.

Sample	SiO_2 wt%	CeO_2 wt%	Polish rates (nm/min)
SI-B	3	0	11 ± 1
M-1	2.85	0.15	19 ± 5
M-2	2.55	0.45	28 ± 2
M-3	2	1	25 ± 0
CE	0	3	18 ± 6

TABLE II. Polish rates for thermal SiO_2 wafers using different solid concentrations of silica particles coated with ceria.

Sample	SiO_2/CeO_2 wt%	SiO_2 wt%	Particle size (nm)	pH	Polish rates (nm/min)	Roughness (nm)
SC-1	1	0	300	4	110 ± 8	0.7–0.9
SC-2	3	0	300	4	106 ± 1	1.2–1.4
SI-A	0	3	400	4	15 ± 0	0.9–1.1
SC-A	0.3	0	400	4	105 ± 5	1.5–1.7
SC-B	1	0	400	4	95 ± 5	1.1–1.4
SC-C	3	0	400	4	93 ± 9	1.0–1.4
SI-B	0	3	400	10	11 ± 1	0.8–1.0
SC-D	1	0	400	10	115 ± 14	1.3–1.5
SC-E	3	0	400	10	91 ± 10	0.9–1.2
M-4	1.5	1.5	400	10	57 ± 11	0.8–1.0

the great enhancement in the material removal rate with coated silica particles needs to be addressed. It is also important to note that the polish rates were not affected by the experimental conditions, which requires some explanation.

As mentioned in Sect. I, uniform colloidal ceria is difficult to produce, especially in large quantities needed in CMP studies; thus, the coated particles developed in this work are a useful substitute for this application.

The two pH values used in the experiments were chosen to alter surface charge characteristics of the interacting surfaces and to evaluate possible chemical reactions that may influence the process. Figure 3 shows that at the low pH the interacting surfaces are of opposite sign of charge, resulting in attraction, while at the higher pH the effect will be opposite. Consequently, at pH 4 the conditions are favorable for chemical bond formation between the sites on ceria and on the wafer, which should decrease the distance between the particles and the film. This condition facilitates the removal of the oxide film from the wafer by ceria, while decreasing the amount of abrasives sticking to the pad rather than to the wafer. At pH 10, some dissolution of the silica film can also take place, which would cause the formation of a gel-like layer and enhance the effect of the pressure on the impact of abrasive particles.

It should be mentioned here that the acidified slurry produced a distinct noise during polishing, while at pH 10 hardly any sound was heard. Obviously, at pH 4 the higher friction must be involved in the polishing process, most likely due to the electrostatic attraction between the particles and the wafer, as well as to the existence of bonds and to the indentation of the film surface by the abrasives.

The effect of the surface charges on the particle/wafer interface can also be seen in Fig. 4. The samples were prepared by dipping the oxide film wafers in 3 wt% slurries containing silica particles coated with ceria, followed by drying in air. At pH 4 silica particles coated with ceria form a nearly complete monolayer evenly distributed on the surface of the wafer [Fig. 4(a)], which means that they were immobilized by the electrostatic attraction.

In contrast, at pH 10 one observes patchwise distribution of the abrasives [Fig. 4(b)]. The particles are mobile due to the electrostatic repulsion, and on drying they rearrange. Either the repulsion between the particles and the surface layer is stronger than that between particles themselves or the capillary force brings the particles closer, resulting in separate close-packed patches on the wafer surface.

Table II shows that the polish rate was essentially independent on the concentration of coated particles (SC-1,-2, SC-A, -B, -C, -D, -E) and on the two pH values. In earlier studies it was demonstrated that, depending on the particle size of silica, the rates either increased or
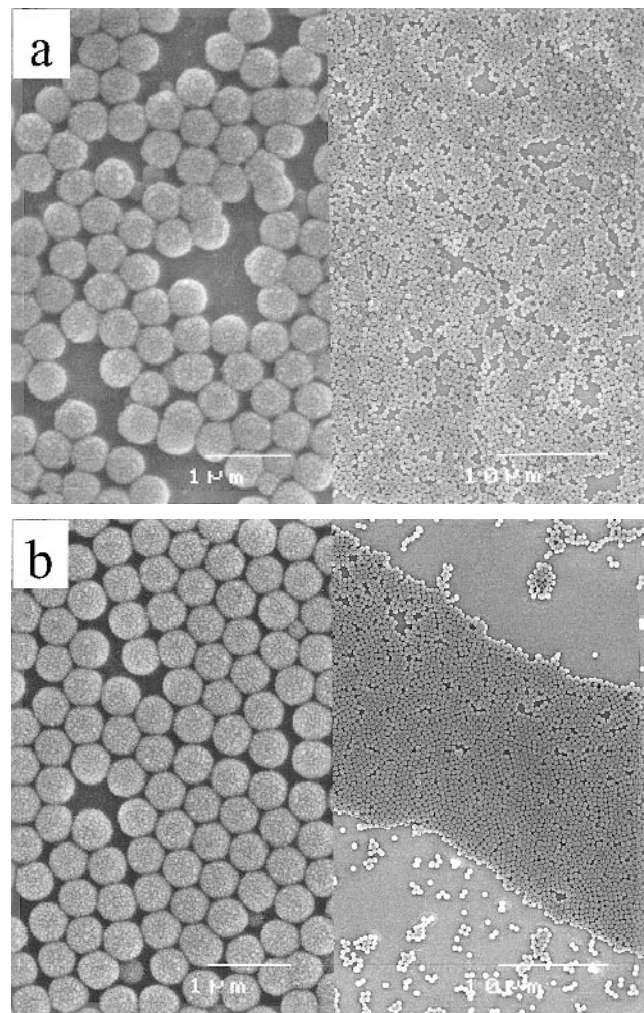

FIG. 4. Scanning electron micrographs of SiO_2 wafers dipped in 3 wt% slurries of silica particles coated with ceria at (a) pH 4 and (b) pH 10.

decreased with the slurry concentrations.[19,20] To explain the present finding, it is necessary to consider the possible mechanisms operational in the polishing process, which are based either on the effect of the surface area of the abrasive solids or on the indentation of the particles into silica film on the wafer surface. The polish rates for the two cases can be given in terms of parameter relationships as follows:[19]

$$\text{surface area based mechanism: } R \propto A \propto C_0^{1/3} d^{-1/3} \quad , \tag{1}$$

$$\text{indentation based mechanism: } R \propto V \propto C_0^{-1/3} d^{4/3} \quad . \tag{2}$$

Here R is the polish rate, A and V are the contact area and indentation volume, respectively, C_0 is the abrasive concentration, and d is the particle diameter.

These two relationships clearly show that for a given particle size the polish rate should decrease as the slurry concentration increases, if the indentation mechanism were dominant, while the opposite effect is expected on the basis of the surface area controlled process.

The independence of the polish rate on the solid content could indicate both mechanisms to be operational in the system described in this study. To understand the latter, it is necessary to take into consideration the individual pressure on the particles and the contact surface area during polishing. While at higher concentration of abrasives the contact area with the surface of the wafer is larger, the distributed pressure on each particle is lower and vice versa. Thus, over the range of the conditions in the reported experiments, the effects of these two parameters, i.e., the individual pressure and the contact surface area, may compensate each other, resulting in nearly the same polish rates.

In the specific case of polishing with silica coated with ceria, one must also consider the configuration at the surface of these particles; i.e., the surface is not smooth as of pure silica but studded with ceria "spikes." The latter would probably cause a sharper indentation and higher contact area per overall particle.

An indirect test of the concepts described above was attempted by carrying out the polishing with a slurry comprised of a mixture of pure silica and silica coated with ceria in an equal weight ratio (M-4 in Table II). The polishing rate was essentially halved, because the pressure was distributed over all particles, but pure silica had little effect by itself on the planarization of the wafer.

The fact that there is not much difference in the rates of removal at pH 4 and 10 may be coincidental, because in alkali medium the SiO_2 layer could partially dissolve, changing the nature of interfaces (bond formation and indentation) in the system. Similar independence on the pH was reported for the polishing rates with the mixture of ceria and alumina using the same kind of wafers.[6]

Finally, the roughness of the polished oxide films (Table II) is quite low, making the slurries prepared from these ceria-coated silica particles very attractive for commercial applications. A paper by K. S. Choi et al.[21] also shows that the polishing of silica glass with porous silica particles coated with ceria is considerably more efficient than when CMP was carried out with only nanosized ceria.

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J. Mater. Res., Vol. 17, No. 10, Oct 2002

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