

# Evolution and Revolution of Cerium Oxide Slurries in CMP

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## Abstract

As the IC industry progresses through each successive technology node on the ITRS roadmap, to continually produce more demanding devices, new consumable materials are required to realize the high yields necessary for success. For the chemical mechanical planarization (CMP) process, silica-based slurries have traditionally been used at technology nodes of 90nm and higher, for both Shallow Trench Isolation (STI) and Inner Layer Dielectric (ILD) applications. However, at 65nm and below, cerium oxide-based slurries are being introduced, since these slurries address many of the issues resulting from the use of silica-based slurries. This paper presents the evolution of cerium oxide-based slurries from their introduction at the 130nm and 90nm nodes, through their current use in high volume manufacture at the 65nm node and also, the revolution necessary for these slurries to be effective at the 45nm node and below.

## 1. Introduction: CMP Applications for Ceria Particles

Cerium oxide (ceria) based slurries are becoming more widely used in a variety of chemical mechanical planarization (CMP) applications<sup>1</sup> for integrated circuit (IC) manufacture. However, this was not the case even a few years ago, when most facilities used silica-based slurries for virtually all IC applications, mainly to remove deposited oxide topography. At the 90nm technology node and at older nodes, fumed silica slurries and colloidal silica slurries were used for bulk oxide removal for Shallow Trench Isolation (STI) and Inner Layer Dielectric (ILD) applications. Additives were formulated with these abrasives in order to increase the oxide to nitride selectivity required in STI CMP<sup>2</sup>. Ceria-based slurries had made their appearance by this stage, mainly for the finishing step in STI CMP, wherever increasing performance and defectivity were required, but these were only used in small volumes. Ceria slurries have the capability of achieving higher removal rates than silica slurries and can more easily be controlled by additives in the slurry formulation. However, for cost reasons, two-step processes were utilized, with silica slurry in the first step (bulk oxide removal) and ceria slurry in the second step (finishing, stop on nitride). This process was found to be extendable to the 65nm node, although some processes were shown to be effective using the ceria slurry for both steps<sup>3</sup>.

At this stage, most of the ceria slurries used were two-component systems, in which an abrasive component was mixed with an additive component and then used fairly quickly before the particles agglomerated too much<sup>4</sup>. In these systems, the additive chemistry is adsorbed onto the abrasive causing the particle size to grow, limiting the pot-life of these slurries. One-component, high selectivity slurries began to make their appearance<sup>3</sup> and although these slurries were more stable than two-component slurries, the latter continued to be used as they were seen

as being more flexible, with the abrasive/additive ratio being adjusted to accommodate different wafer types. The ceria slurries contained abrasives made by traditional calcination/milling techniques and these have been shown to be extendable to the 45nm node and beyond.

As we reach the 45nm node and past it, down to the 32nm node, deposition of oxide into high aspect ratio features (>4:1) becomes necessary, meaning that HDP oxide may be replaced by oxide deposited by the HARP (High Aspect Ratio Process) from Applied Materials<sup>5</sup>. Silica slurries are less effective on this oxide<sup>6</sup> and the current process involves two-steps, with a high selectivity ceria slurry (preferably a one-component slurry) being used in the first step and a fixed abrasive (FA) pad used in the second step<sup>7</sup>. The advantage of a FA pad process is that excellent planarization and dishing can be achieved.

This paper shows the development of a one-component slurry that can be used for both steps, which gives equivalent dishing values and superior defectivity with respect to a FA pad process, at lower cost of ownership. Ferro have developed a viable, slurry-only alternative to FA pads.

## 2. CMP Processes

As already mentioned, currently the main IC application for ceria-based slurries is STI CMP and a three-platen process is most widely used. This uses silica slurry on platen 1 for bulk oxide removal, a high selectivity ceria-slurry on platen 2 and a buff step on platen 3, which helps clean off particles. Ceria slurry can be used on the first two platens<sup>3</sup>, but most IC fabs use silica on the first platen for cost (and familiarity) reasons. An advantage of using a ceria-only process is that one platen can be used for both steps and there is no possibility of cross-contamination with silica slurry.

At the 45nm and 32nm technology nodes, there will probably be some difference in the processes used at logic and memory fabs. A fixed abrasive pad process may be adopted by logic fabs, but memory fabs may continue to use the silica/ceria slurry process described above, or a variation of it, as FA pad processes have a higher cost of ownership (and still show higher defectivity than straight slurry processes. DRAM and Flash memory markets will drive STI in the future.

The Applied Materials best known method (BKM) is moving away from silica slurry at 45nm/32nm<sup>6</sup>, for performance and defectivity reasons on HARP oxide, which is believed to be necessary for void-free gapfill at these nodes, replacing HDP oxide. The current BKM utilizes a high selectivity ceria slurry in the first step and a FA pad with selective chemistry in step 2. Ceria particles are incorporated into FA pads<sup>8</sup> and up to now, these have been manufactured by solid state methods. Investigations are ongoing to develop pads containing round particles, with the intention of improving defectivity, but it is far from clear if these will be necessary (see section 4).

Another application for which ceria slurries have several advantages over silica slurries is self-stopping ILD CMP<sup>9</sup>. Ceria, unlike silica, can be formulated with chemical additives, which lead to the self-stopping mechanism. These additives protect the oxide surface leading to low blanket removal rates, but still produce high rates on topography. Therefore, as topography is removed, the removal rate decreases. When using optimum formulations, the polishing essentially stops, leading to a wide process window. Advantages of self-stopping slurries over standard silica-based ILD slurries include reduction in the incoming film thickness and elimination of the need for endpoint detection, due to the increased overpolish window. Planarization is more efficient, resulting in lower 'down' oxide loss.

Ceria slurries are now also being developed for tunable selectivity in front end processes, where the addition of optimized chemistry leads to the desired removal rates on silicon nitride, silicon dioxide and polysilicon<sup>1</sup>.

### 3. Ceria-Based Slurries for STI CMP

Although ceria abrasive can be manufactured by a variety of methods<sup>10</sup>, the high selectivity slurry market is dominated by slurries formulated from solid state (calcined, milled) cerium oxide. And of the slurries currently being used at all technology nodes, the vast majority are 2-component systems, which are comprised of separate abrasive and additive components, mixed together just prior to use<sup>4</sup>. The ratio of the components can be varied for flexibility on different wafer types. However, these systems suffer from limited pot-life. The additives interact with the surface of the ceria particle causing agglomeration and formulation instability. To address this downside, 1-component slurries have been developed which are stable, leading to a more robust process. The additives do not interact with the particle, as shown in the zeta potential curve in Figure 1. The plots for the particle with and without formulation are identical. The additives in these formulations interact with the wafer surface, which leads to better dishing control<sup>11</sup>. Such one-component systems are required for 45nm and 32nm polishing.

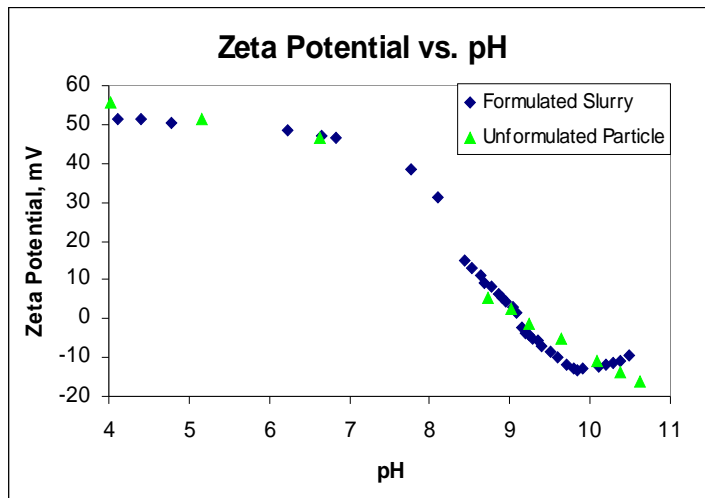


Figure 1: Zeta potential plots for fully formulated 1-component slurry and the ceria abrasive (no chemistry)

Most slurries used have an operating pH which is neutral or basic, although the newer acid-based slurries show some advantages. The acid-based slurries tend to exhibit higher stability (as seen in figure 1) and there is no induction period on polishing. Neutral/basic slurries show an induction period, in which the removal of the oxide surface is very slow at first and elimination of this increases the process time and therefore yield. Another advantage is at ceria loadings of up to 4%, the slurry behaves like a FA pad, giving low dishing and improved planarization, with the added advantage of giving lower defectivity (see section 5).

### 4. Particle Morphology Effects on Defectivity

There are many ways to make ceria particles<sup>10</sup> and most of these give rise to particles with irregular morphology possessing sharp edges, corners and apexes. Certain methods give rise to spherical particles and it is thought that slurries formulated using such particles will be required for future technology nodes in order to meet the ever more challenging defectivity

requirements<sup>12</sup>. However, only a few references address ceria particle morphology effects on defectivity<sup>13</sup>. Thus, there is not much convincing evidence that spherical particles are superior in effective CMP slurries. Of the slurries containing round particles being promoted, it has not been possible to convincingly tie in morphology with removal rate, or defectivity. In fact, two studies have shown that round particles lead to unacceptably low oxide removal rates and higher defects compared to particles with irregular morphology<sup>11,14</sup>. Surface chemistry appears to be more important than morphology, as ceria reacts with the oxide surface to remove it. Many references suggest that the dominant mechanism for material removal may not be the mechanical plowing of the slurry particles into the wafer surface<sup>15</sup>. Figure 2 shows a scratch defect comparison, showing superior defect performance for optimized solid state ceria particles versus flame synthesized and solution grown ceria.

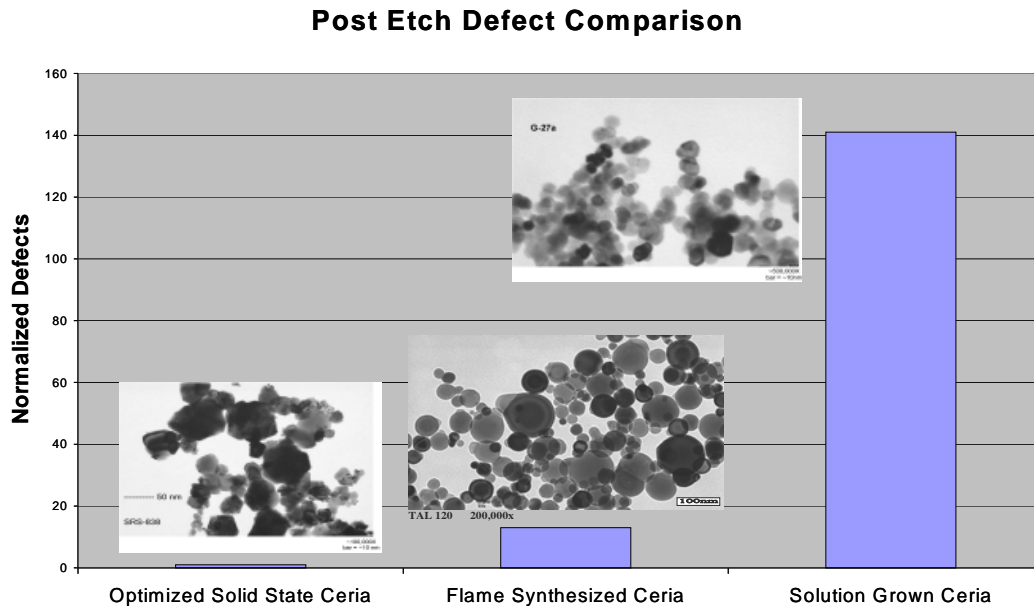


Figure 2: Ceria Morphology vs Defectivity (micro-scratches)

### 5. Low Defectivity/Low Dishing Slurry for STI CMP

It has already been mentioned that FA pad processes give excellent planarization and dishing, but both defectivity and cost of ownership are unacceptably high. Therefore, a slurry-only process for polishing HARP oxide at the 45nm and 32nm nodes would be desirable. This option is now available, with TruPlane™8272, a 1-component high selectivity slurry based on an optimized solid state ceria particle. This slurry has been shown to give equivalent performance (dishing) to a FA pad process, with the added advantage of giving lower defectivity<sup>16</sup>. Perhaps the most impressive feature of this slurry is its extremely wide overpolish window, with no loss of field oxide, or explosion of defects out to 100% overpolish (see Figure 3). This is a true revolution in ceria slurry technology.

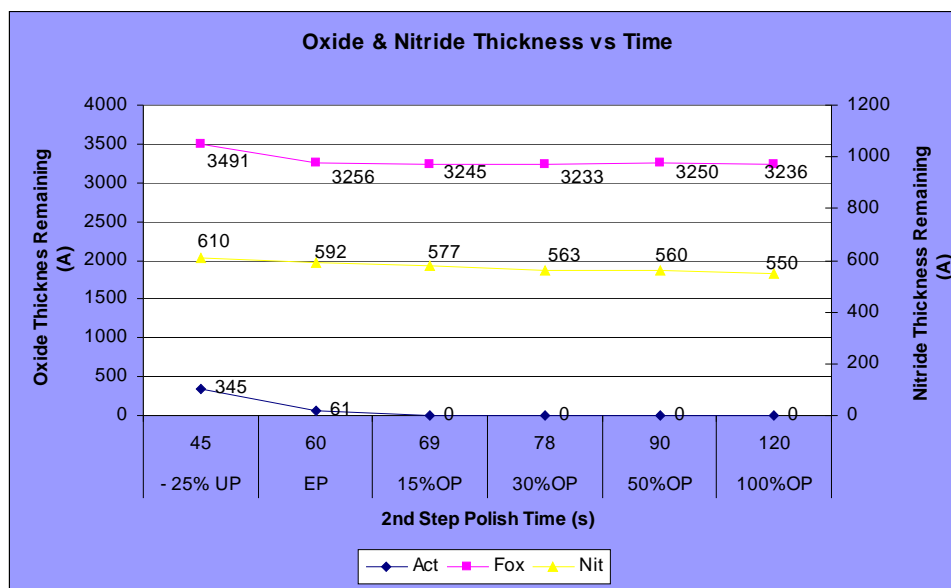


Figure 3: Flat Profiles for Field Oxide and Nitride During Extended Overpolish (OP)

## 6. Polishing Mechanisms

The mechanism of polishing of slurries with different zeta potentials (ZP) will be described in a subsequent paper and presented in the near future. It is believed that this difference in polishing mechanism of the acid-based slurries (positive ZP) is responsible for the 'FA pad-like' performance.

## 7. Future of Ceria Slurries in CMP

The volumes of ceria slurries for various applications are expected to increase out to 2011. Ceria-based slurries will continue to replace silica-based slurries for not only STI (HARP oxide), but also for ILD (self-stopping) applications, where ceria slurries are known to lead to better process control, performance and defectivity.

STI CMP will remain the main application with DRAM and NAND Flash dominating wafer starts (STI growth will be limited by the number of wafer starts).

HARP oxide will probably replace HDP oxide for STI gapfill at 45nm and/or 32nm, but the current problems with the FA pad processes may not be overcome. For that reason, a viable slurry alternative to FA pads has been developed, which gives equivalent performance and superior defectivity.

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