

Low Defect Ceria-Based Slurries: Novel Selectivity, Slurry Characterization, and Polishing Mechanisms

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Abstract

Using a low defect ceria dispersion as a base material, formulations having drastically different polishing performance have been developed. It is well known that ceria can exhibit high oxide:nitride selectivity for Shallow Trench Isolation. (STI) However, using formulation additives, novel selectivities can be obtained using the same ceria particles. Ceria-based formulations have been formulated showing extremely high oxide:nitride selectivity for STI, auto-stopping behavior for Inner Layer Dielectric (ILD), and tunable poly:oxide selectivity using the same particle system. The fundamental question is: How can the same base ceria dispersion give such different polishing performance? In order to answer this question, a suite of slurry characterization techniques were used, including light scattering techniques to determine PSD shifts, zeta potential and isoelectric point (IEP) determinations to probe surface-chemistry interactions, and solid state FT-IR to characterize the binding of chemical species to the ceria surface. Using this data, polishing mechanisms can be postulated to describe the unique polishing performance of the slurries.

1. Low Defectivity Ceria

Using proprietary methods for the synthesis and manufacturing of ceria, Ferro has been able to consistently manufacture low defect ceria particles for the 65nm technology node and beyond. The most common ceria process starts with a raw form of cerium – cerium hydrate, nitrate, carbonate, etc. – and converts it to cerium oxide through a solid-state calcination process, followed by particle size reduction. Other technologies being heavily developed involve solution-grown ceria or generating ceria powders through flame pyrolysis, each of which may or may not involve a further particle size reduction step. Although there is published work touting the theoretical advantages of these new particles¹ – especially because of their tendency toward a spherical morphology, recent defect data generated at Ferro indicates the scratch performance of slurries made with such particles does not exceed the scratch performance of optimized solid-state particles (Figure 1).

In addition to creating a particle that has the optimal properties for defectivity, the process of making the particles must be very robust. Ferro has been able to design a robust process for HVM particle manufacture leading to a repeatable, consistent performance of the ceria slurries developed from the base particle. All of the slurries described in this paper are based on the 2nd generation solid-state ceria particle (Figure 1).

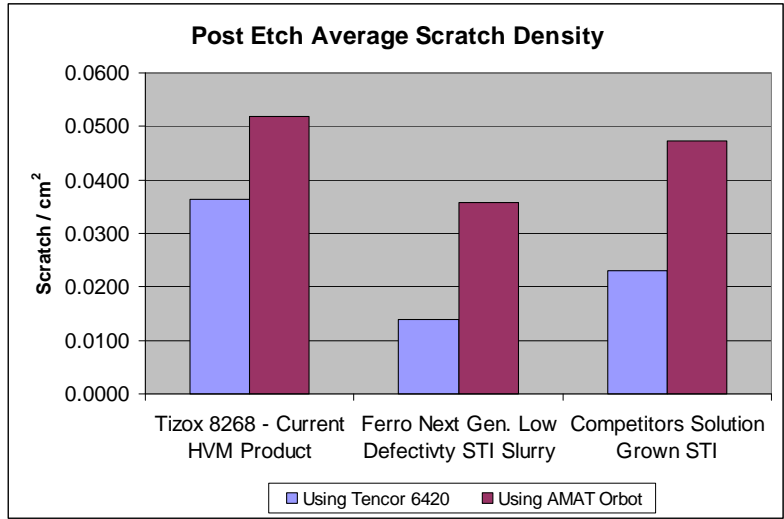


Figure 1. The differences between 1st and 2nd generation solid-state particles are many, but can all be included under the heading of process optimization. As this chart clearly shows, the post-etch defectivity level of the 2nd generation particle has 1.5X – 3X lower defects as compared to the 1st generation particle.

2. Extremely High Selectivity STI CMP Slurry

The low defect slurry for STI CMP shows extremely high oxide to nitride selectivity, low dishing and exhibits excellent within wafer (WIW) and within die (WID) performance. Typical blanket selectivities for this slurry platform exceeds 100:1.² The additives in this slurry platform can be easily tuned to give the desired selectivity and removal rates. The mode of action of the additives in this slurry is to bind with the wafer surface to protect the oxide and nitride layers.³ The ability of the suppressant to bind both the oxide and nitride layers during polishing allows for nitride suppression and dishing protection during overpolish. As can be seen in figure 2, the high selectivity STI slurry stops on nitride and protects the trench oxide during roughly 60 seconds of overpolishing! Because the additives do not bind with the ceria surface, there is no chance for additive-based agglomeration of the ceria particles. This is in contrast to other STI slurries on the market, where it is well known that the selectivity additives cause particle agglomeration, leading to shelf-life problems and performance degradation.⁴ Evidence for the absence of particle-additive interactions in our systems is illustrated by the absence of a change in ceria IEP (Figure 3) and the absence of peaks associated with the additive in the solid state infrared spectrum of ceria treated with additive (Figure 4). The absence of additive-particle chemical interaction leads to a slurry with an extremely long shelf life (>1 year) with low defectivity.

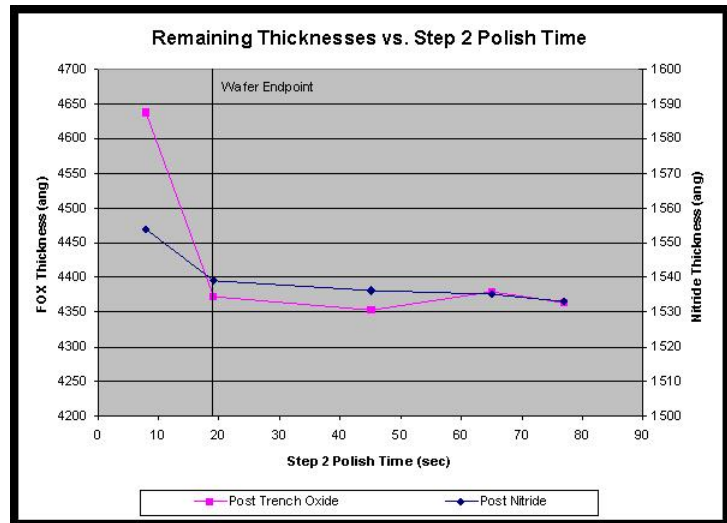
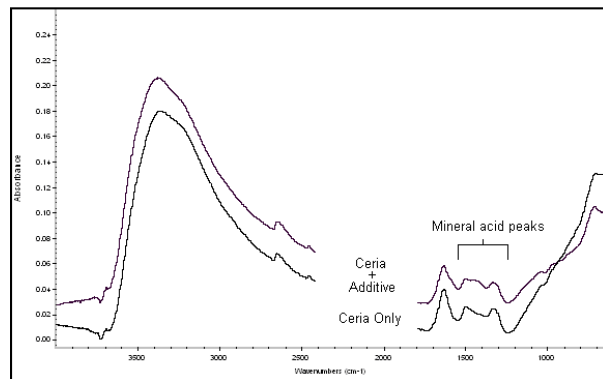
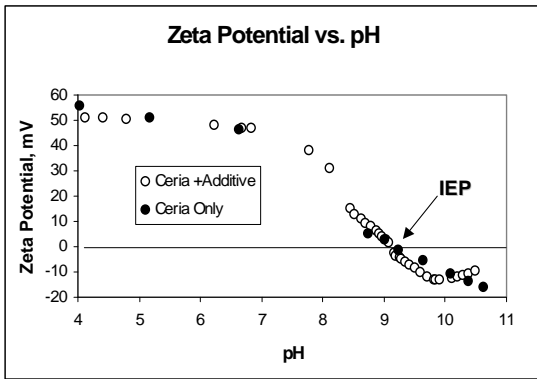


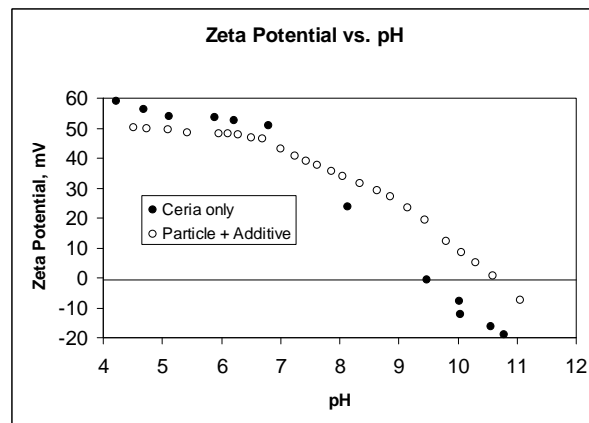
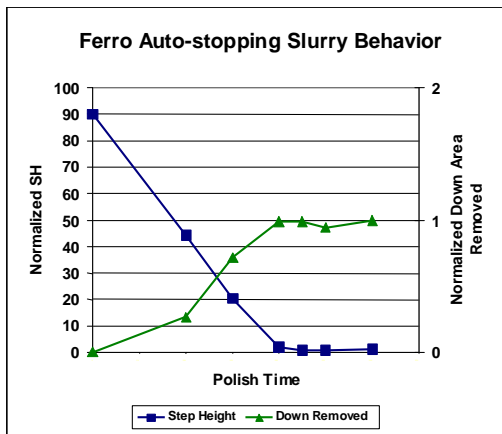
Figure 2. Extremely long overpolish window for Ferro’s high selectivity STI slurry.



Figures 3 and 4. IEP curves and infrared spectra indicate absence of significant chemical interactions between ceria particles and the selectivity additive in the high selectivity STI slurry.

3. Autostopping ILD Slurry

The slurries for ILD CMP give very fast step height removal rates (SHRR) and exhibit ‘auto-stopping’ behavior. When polishing wafers with a variety of pattern densities and feature sizes, the cerium oxide slurries show lower dependency on pattern density, as compared to silica slurries. Furthermore, once the topography is removed, polishing effectively stops (Figure 5). The additives in this slurry platform can be easily tuned for the desired SHRR, while keeping the same autostopping behavior. The additives in this slurry platform also bind with the wafer surface during polishing. Differing from the STI additive, there is evidence from the IEP titrations that the autostop additive also interacts with the ceria surface (Figure 6). In Figure 6, the IEP of the ceria particles has been shifted nearly +1.5 pH units. From the IEP curve, however, it can also be seen that there is a large pH window for slurry stability in the pH range 4-6 (i.e. >40mV in this regime). When properly formulated, this autostop slurry can also have a long shelf life (>6 months).



Figures 5 and 6. Characterization of the ILD polishing performance and IEP determination of Ferro’s autostopping slurry.

4. Poly:Oxide Tunable Selectivity

Using the same low defect ceria particles used for the STI and autostopping ILD slurries, Ferro has developed slurries with tunable selectivity for polysilicon and oxide films. By carefully choosing the additive and properly tuning the slurry components, slurries have been developed which can polish poly and stop oxide, give a 1:1 rate ratio of poly to oxide, or polish oxide and stop on poly (Table 1). Using mechanistic considerations, additives were identified which bind to the wafer surface in order to shut down polishing. Since the slurries are formulated to minimize

additive-particle interactions, these slurries also exhibit the low defectivity and long shelf life of the STI and autostopping ILD slurries.

	Polysilicon Rate (Ang./min.)	Oxide Rate (Ang./min.)
Formulation #1	> 2000	<25
Formulation #2	700-800	700-800
Formulation #3	<10	>2000

Table 1. Tunable low defect ceria slurries for different poly:oxide selectivity.

5. Experimental

5.1 General. All of the slurries described in this paper were manufactured and tested at the Penn Yan facility of Ferro Electronic Material Systems. The infrared spectra were measured at the Posnick Technology Center of Ferro Corporation in Independence, Ohio.

5.2 Slurry Analytical Techniques. Zeta potentials were measured using a Dispersion Technologies DT-300 probe. Particle size analysis of the ceria particles was measured on a Horiba LA-910 light scattering particle size distribution analyzer. Infrared spectra were obtained on a Nicolet Magna 560 FTIR equipped with a diamond ATR probe and were auto-baseline corrected. Distortions due to diamond in the region of 1800-2400 cm^{-1} were blanked out.

5.3 Polish Results. Polishing was done on an Applied Materials 200mm Mirra platform using IC1000 Suba IV polishing pads. Post-CMP cleaning was carried out using an Ontrak double-sided brush scrubber. Film thicknesses were measured using a ThermaWave 3290DUV Optiprobe. Defects were highlighted on oxide films using HF dip in a linear automated chemical transfer etch station from JST corporation. Optical defect inspection was carried out using an Applied Materials WF-736 Orbot tool and a KLA-Tencor Surfscan 6420 and defects were classified using an Applied Materials SEM-vision CX Plus.

6. Conclusions

Integration of new materials will become increasingly important for the 45nm and 32nm technology nodes and beyond. Using the slurry characterization techniques presented in this study, slurries can be rapidly developed with the ability to polish new materials. As integration schemes and materials become more complex, the fundamental understanding of slurry-additive-wafer interactions is needed in order to accelerate slurry development for future materials selection. We will continue to work to understand the fundamental materials properties of our slurries in order to design robust solutions for semiconductor manufacturers.

7. References

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4. B. A. Bonner et. al., CMP-MIC Conference **2001**, proceedings pp. 572-579.