

## Towards Understanding Smaller Ceria Particles (< 10 nm) for SiO<sub>2</sub> Removal Rates during Chemical Mechanical Planarization

Ravitej Venkataswamy<sup>1</sup>, Ngoc-Tram Le<sup>1</sup>, Kyungju Park<sup>2</sup>, Hyungoo Kang<sup>2</sup>,  
and Jihoon Seo<sup>1,\*</sup>

<sup>1</sup>Department of Chemical and Biomolecular Engineering, Clarkson University, Potsdam, New York, USA

<sup>2</sup>C&C Materials Development, SK Hynix Inc., Icheon-si, South Korea.

*jseo@clarkson.edu*

### ABSTRACT

Ceria abrasives play a crucial role in achieving many of our desired STI-CMP performance metrics. The current understanding is that the only way to move forward with obtaining defect-free surfaces is to use smaller and smaller abrasive particles. However, the challenge for using smaller colloidal ceria particles is the low SiO<sub>2</sub> removal rates.

In this study, we investigated the reaction and process parameters to make Ce(OH)<sub>4</sub> and CeO<sub>2</sub> particles (<10nm) to obtain reasonable removal rates of SiO<sub>2</sub> films with scratch and defect-free surfaces by optimizing the reaction environments such as temperature and pH. Ce(OH)<sub>4</sub> particles have higher surface reactivity than CeO<sub>2</sub> particles when particle size is less than 10 nm, which yielded high SiO<sub>2</sub> removal rates. The synthesis pH and temperature affect the surface reactivity of Ce(OH)<sub>4</sub> particles. We show how it is possible to influence removal rates by varying synthesis temperature and additives along and how to control the particle size distribution and morphology by tuning parameters during synthesis.

**Keywords:** *chemical mechanical planarization; ceria particle; ceria slurry; semiconductor; emerging technologies.*

### INTRODUCTION

Chemical Mechanical Planarization (CMP) is used to remove material from the surface of a wafer and to planarize the surface. The semiconductor industry has been able to keep up with the demands of Moore's Law by making constant improvements in chip manufacturing technology. The increasing demand for semiconductor chips due to the growth of modern technologies such as autonomous driving, artificial intelligence (AI), 5G communications, the Internet of Things (IoT), and large-scale data processing is putting pressure on the semiconductor industry to evolve rapidly and reliably. Semiconductor chips are getting smaller, faster, and cheaper at a rate that is nothing short of astounding. This rapid evolution of technology demands that chips keep up with this pace to remain relevant. As semiconductor fabrication technology has become more complex, CMP has also become more sophisticated, enabling the implementation of new integration schemes. Novel chemical additives and advanced particle technologies in CMP slurries enable smaller geometries and complex integration schemes. The abrasive particles in a CMP process are crucial to achieving many performance metrics.

In recent years, there has been a greater interest to reduce and mitigate the adverse effects of both calcined and colloidal ceria particles during the CMP process. These particles are developed with controlled size distribution and spherical shape, while still maintaining a high SiO<sub>2</sub> removal rate (RR). However, as feature sizes continue to shrink, it becomes more challenging to use calcined ceria particles without causing defects. Therefore, smaller ceria particles that can potentially meet the highly demanding requirements of defect-free CMP are receiving significant attention [1]. The main objective of this study is to understand the physicochemical properties of smaller ceria particles (< 10 nm) and make strategies to increase the RRs of SiO<sub>2</sub> films [2, 3]. The reaction and process parameters, such as precursors, feeding speed, reaction temperature, time, and pH, to make smaller ceria particles (< 10 nm) were optimized to get reasonable SiO<sub>2</sub> RRs while maintaining the scratch and defect-free wafer surface.

### EXPERIMENTAL METHODS

Cerium (III) nitrate hexahydrate Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, ammonium cerium (IV) nitrate (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub>, and

ammonium hydroxide  $\text{NH}_4\text{OH}$  were obtained from Sigma Aldrich. Poly (vinyl alcohol) (PVA) was purchased from Polysciences, Inc. Synthesized particles were dispersed at 0.2 wt.% in deionized water and 0.2 wt.% PVA as a stabilizing agent was added to the slurry, and then adjusted to pH 6 using either  $\text{HNO}_3$  or  $\text{KOH}$ . The average particle size and  $\zeta$ -potential of particles were measured using a Malvern Zetasizer instrument (Zetasizer Nano-ZS, Malvern).

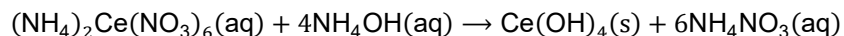
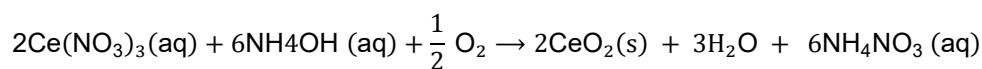
As shown in the flowchart (Fig. 1), many variables can affect the synthesis, including the oxidations state and concentration of metal ions, the type of solvent, precipitating agent, the pH of the solution, and the reaction temperature, reaction time, molar ratio of reactants. In this paper, the synthesis mechanism was using the precipitation method by adding  $\text{NH}_4\text{OH}$  to precursor solutions. Obtained precipitates have been centrifuged and washed two times to remove all the excess unreacted ions. Extracted abrasives were later dispersed in DI water. Based on our strategy, the particles are subjected to various additives to improve chemical reactivity and support stable dispersion. If there is no reasonable RR of  $\text{SiO}_2$  was achieved, variables in the synthesis of ceria nanoparticles were changed such as precursor ( $\text{Ce}^{4+}$  and  $\text{Ce}^{3+}$ ), molar ratio of precursor to the precipitating agent ( $\text{Ce}^{3+}$  or  $\text{Ce}^{4+}/\text{OH}^-$  1:1, 1:2, 1:3, 1:4, and 1:5), reaction pH, reaction temperature (RT and 80 °C). The synthesized ceria particles were characterized by XRD (Fig 2a and b), FTIR, DLS,  $\zeta$ -potential, SEM, TEM, UV-Vis. The ceria-based CMP slurries were prepared from synthesized ceria particles with different additives (polymers (PVA) and amino acids) and were performed by CMP test.

During the synthesis, the growth rate of these superfine ceria particles was controlled, which essentially alters various physicochemical properties of the particles, such as size, surface reactivity, surface chemistry, and composition. The various parameters that affect the particle growth of ceria nanoparticles are precursors, the concentration of the precipitating agent, reaction temperature, and pH. Temperature (T) and supersaturation (S) are key parameters controlling the spontaneous precipitation of  $\text{CeO}_2$ . Supersaturation (S) is a driving force for crystallization [4].

CMP performance (Fig. 2c) used 2000 nm thick  $\text{SiO}_2$  films deposited on 200 mm diameter Si wafers via plasma-enhanced deposition using tetraethyl orthosilicate (TEOS) purchased from DK Nanotechnology. The blanket wafers were polished for 1 min on a POLI-500 polisher from G&P technology at 93/90 rpm platen/carrier speed, 3 psi down-pressure, and a slurry flow rate of 150 mL/min. The RRs of TEOS films were calculated by measuring the film thickness using FilmTek™ 2000 Interferometer before and after polishing. Each experiment was repeated twice, and these data were used to compute the average RR.

## RESULTS AND DISCUSSION

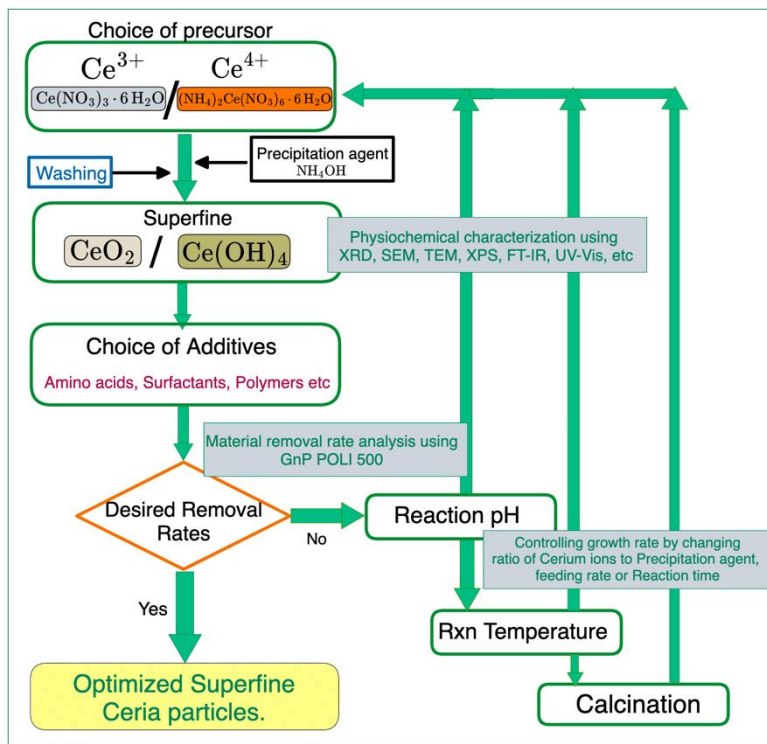
The colloidal nanoparticles are synthesized by the process of chemical reduction, as a bottom-up synthesis method. In this method, metal salt ( $\text{Ce}^{3+}$  or  $\text{Ce}^{4+}$ ) is reacted with a precipitating agent ( $\text{NH}_4\text{OH}$ ) to form colloidal superfine ceria particles. Superfine  $\text{Ce}(\text{OH})_4$  particles were produced from precursor  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  while crystalline  $\text{CeO}_2$  particles were produced from precursor  $\text{Ce}(\text{NO}_3)_3$ :



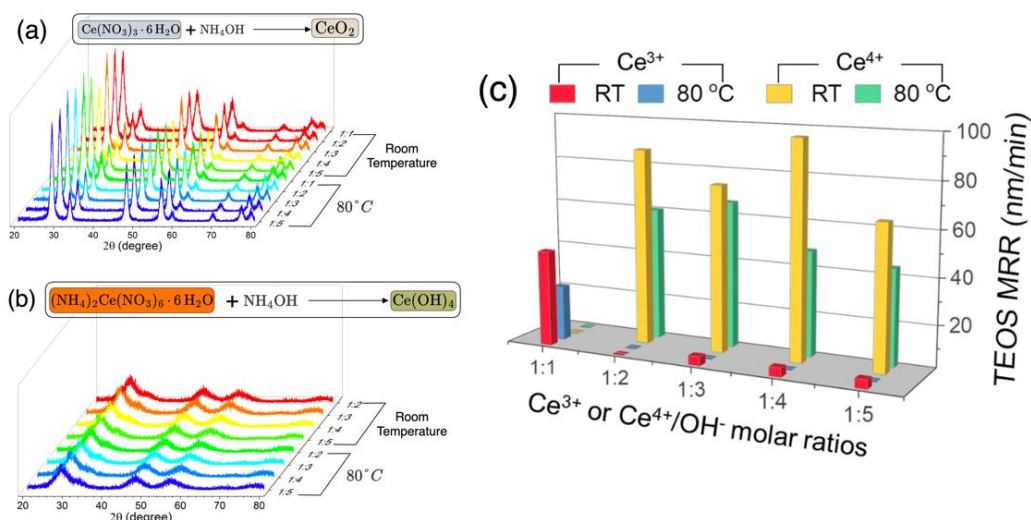
As seen from the synthesized particles XRD Plots (Fig 2a and 2b), we varied **the molar ratios of precursors to precipitating agent** with the increase of molar concentration of precipitating agent while the precursor molar concentration remained unchanged, which resulted in changes in the reaction pH. With reaction pH increasing as we increase the molar concentration of Ammonium Hydroxide, the removal rates decreased under the CMP process with PVA as an additive (Fig 2c). Note that, this trend has been only observed in particles synthesized with  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  which resulted in  $\text{Ce}(\text{OH})_4$  superfine nanoparticles. With the molar ratio 1:1 of  $\text{Ce}^{4+}$  and  $\text{NH}_4\text{OH}$ , no precipitation was observed. From our CMP results (Fig. 2c), the highest RRs were obtained at the molar ratio 1:2 and 1:4 of  $\text{Ce}^{4+}/\text{NH}_4\text{OH}$  while  $\text{CeO}_2$  particles synthesized from  $\text{Ce}^{3+}$  resulted in the lowest RRs (Fig. 2c). The reason for lower RRs from particles we get from precursor  $\text{Ce}^{3+}$  than it is from precursor  $\text{Ce}^{4+}$  was presumably due to their types of nucleation mechanisms. Crystalline  $\text{CeO}_2$  particles collected from precursor  $\text{Ce}(\text{NO}_3)_3$  resulted in no reasonable RR and fail to be dispersed in the solution even for a short amount of time at higher reaction pH values. (Fig 2c)

During our subsequent steps based on our flowchart (Fig. 1), **the reaction temperature** was studied at RT and 80 °C. The RRs have decreased with an increase in reaction temperature for both precursors  $Ce^{3+}$  and  $Ce^{4+}$  (Fig 2c). As the temperature increases, the rate of diffusion also increases, hence resulting in larger ceria nanoparticles and finally, reducing in RR as the size of the particle increases, its physicochemical property, and surface reactivity decrease.

Finally, in the event of no reasonable RRs on changing the above parameters, our strategy was to calcinate the superfine ceria nanoparticles to tune their physical and chemical properties.



**Figure 1.** Flowchart describing the strategies to control the physicochemical properties of the synthesized ceria particles. The synthesis mechanisms may be described as follows. A precipitate is obtained by adding  $NH_4OH$  to  $Ce(NO_3)_3$  or  $(NH_4)_2Ce(NO_3)_6$ . If using  $(NH_4)_2Ce(NO_3)_6$  as cerium precursor, the formation of  $Ce(OH)_4$  was seen. If using  $Ce(NO_3)_3$  as cerium precursor, the formation of  $CeO_2$  was seen. Obtained precipitates have been centrifuged and washed two times to remove all the excess unreacted ions. Extracted abrasives were later dispersed in DI water; Based on our strategy the particles are subjected to various additives; to improve chemical reactivity and support stable dispersion. If there is no reasonable removal rate of  $SiO_2$  was achieved, we synthesized the nanoparticles by changing the precursor, molar ratio of precursor to precipitating agent, reaction pH, and reaction temperature.



**Figure 2.** Depending on the type of precursor and reaction temperature the removal rates have significant changes. (a) shows XRD patterns of particles synthesized using **Cerium Nitrate** with change in molar ratios of Cerium Nitrate to precipitating agent from 1:1 to 1:5 which resulted in formation of crystalline Ceria whereas (b) shows the XRD patterns of particle synthesized using **Ammonium Cerium Nitrate** with change in molar ratios of Cerium Nitrate to precipitating agent from 1:1 to 1:5 which resulted in formation of Cerium Hydroxide compounds, although both were subjected to same synthesis conditions, and molar ratios. On the contrary 1:1 Molar ratio of Ammonium Cerium Nitrate to  $\text{NH}_4\text{OH}$  case, no precipitation was observed. Upon addition of PVA as an additive in the slurry composition for the CMP process we obtained (c) removal rates of synthesized particles using G&P POLI 500 CMP Polisher. It is evident from the removal rate data; room temperature synthesized samples are best performed overall. While coming to precursor, Ammonium Cerium Nitrate yield substantially high removal than particle synthesized from Cerium Nitrate.

## CONCLUSIONS

Superfine  $\text{Ce}(\text{OH})_4$  particles were created from precursor  $\text{Ce}^{4+}$ , while crystalline  $\text{CeO}_2$  particles were synthesized from precursor  $\text{Ce}^{3+}$ . The highest RRs using synthesized ceria particles from precursor  $\text{Ce}^{4+}$  were achieved. However, particle nucleation did not occur for  $\text{Ce}^{4+}$  at the molar ratio 1:1 of  $\text{Ce}^{4+}$  and  $\text{NH}_4\text{OH}$ . With the superfine  $\text{Ce}(\text{OH})_4$  particles, higher reaction temperature resulted in lower RRs. Overall, higher removal using particles synthesized with  $\text{Ce}^{4+}$  precursor was observed when compared with  $\text{Ce}^{3+}$  when synthesized with the same synthesis methods and the reason for this is being investigated. The synthesis of nanoparticles using metal ions can be quite difficult and unpredictable. Another challenge is keeping the colloidal ceria particles suspended evenly throughout the slurry. Additionally, it is important to ensure that the ceria particles are of a uniform size, as larger particles can cause scratches on the wafer surface.

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## Corresponding Author:

Jihoon Seo

Tel: +1 518-545-1345

E-mail: jseo@clarkson.edu

Department of Chemical and Biomolecular Engineering,  
Clarkson University, Potsdam, NY 13676, USA