

Effect of calcination time on the physical properties of synthesized ceria particles for the shallow trench isolation chemical mechanical planarization process

Sang-Kyun Kim, Ungyu Paik* and Jea-Gun Park^a

Department of Ceramic Engineering, Hanyang University, Seoul 133-791, Korea

^aNano-SOI Process Laboratory, Hanyang University, Seoul 133-791, Korea

The influence of the calcination time on the physical properties of synthesized ceria particles and their subsequent influence on shallow trench isolation (STI) chemical mechanical planarization (CMP) process performance were investigated. Two different kinds of ceria particles were synthesized by a solid-state displacement method which utilized calcination times of 4 and 6 hours. After the mechanical milling process, both the crystallinity and particle size distribution of the synthesized ceria particles were found to be markedly different between particles formed with different calcination times. Due to incomplete calcination, the ceria particles synthesized with a 4-hour calcination time had a smaller crystallite size than the particles synthesized for 6 hours. This smaller crystallite size ultimately resulted in large agglomerated particles. The differences in the characteristics of the ceria particles further translated into great discrepancies between the STI CMP performances of the ceria slurries made from the two types of particles.

Key words: ceria, crystallinity, agglomeration, calcination, STI CMP.

Introduction

Chemical mechanical polishing (CMP) is a key process in contemporary ultra large scale integration (ULSI) fabrication [1]. The shallow trench isolation (STI) process is still one of the most crucial applications of CMP technology. STI has replaced the local oxidation of silicon (LOCOS) method by significantly reducing the area required to isolate transistors, enhancing the packing density, and offering the necessary degree of planarity required to meet stringent photolithography requirements [2-4]. A ceria slurry is typically used in the STI CMP process because this slurry offers improved selectivity for the planarization of the trench-fill material while maintaining the polish stop layer at a uniform thickness when compared to other abrasive slurries [5-7]. Unfortunately, the ceria slurry induces defects on the wafer surface because of the large, agglomerated particle abrasives that result from poor dispersion stability [8-10]. Therefore, in order to avoid surface defects, agglomeration of the ceria particles must be minimized.

The ceria slurry is typically stabilized to prevent particle agglomeration and reduce surface defects [11]. Slurry stabilization is normally achieved through the addition of a polymeric dispersant; however, the successful elimination of the scratch-inducing agglomerated particles in the slurry is limited. The natural properties

of the abrasive particle predominantly affect the stability of the slurry [11,12]. Since the incompletely-calcined ceria particles have highly activated surfaces due to oxygen vacancies, particle agglomeration occurs readily [13-15]. Thus, the calcination process should be strictly controlled to ensure the complete crystallization of the particles. The solid-state displacement reaction method is widely used for the synthesis of ceria particles due to the high crystallinity that results. In this process, the properties of the ceria powders are strongly dependant on their chemical, physical, and structural characteristics which are in turn determined by calcination conditions, such as temperature and time [13,16]. High crystallinity of the ceria particles can be obtained through high temperature calcination. However, the resulting larger crystallite size due to high calcination temperatures easily induces many scratches on the wafer surface [8-10]. Thus, a complete calcination method carried out at low temperatures should be developed to avoid improper crystal growth.

The calcination process that transforms the cerium precursor to cerium oxide consists of a five-step mechanism. This mechanism includes the mass-transfer of the reacting agent (oxygen) from the bulk atmosphere to the periphery of the carbonate, its diffusion through the carbonate pores, its adsorption onto the carbonate, the reaction with the cerium carbonate, and finally, the desorption of the reaction by-product (carbon dioxide) [17,18]. In this process, the de-carbonation reaction is dependant on the calcination time, since the effectiveness of the diffusion process is proportional to the reaction time. Without allowing sufficient time, the

*Corresponding author:
Tel : +82-2-2220-0502
Fax: +82-2-2281-0502
E-mail: upaik@hanyang.ac.kr

calcination in the inner part of the ceria particles will be incomplete. Consequently, the calcination process as a function of both time and the physical properties of the synthesized ceria particles should be investigated to determine which parameters yield good performance in STI CMP.

In this study, two different kinds of ceria particles were synthesized using calcination times of 4 and 6 hours. The effect of the calcination time on the physicochemical properties of the synthesized ceria particles and its influence on the subsequent STI CMP performance were investigated with the goal of improving removal selectivity and uniformity while reducing scratches on wafers.

Experimental Procedures

Ceria powders were synthesized by the solid-state decomposition method. Calcination times of 4 and 6 hours were used. The calcination temperature was fixed at 650 °C. The morphology and the particle size of two the different kinds of ceria were compared through scanning electron microscopy (SEM) (S-900, Hitachi, Japan). After the calcination process, the ceria powders underwent mechanical milling for several hours to reduce their size to a target value (250 nm). After mixing the particles with de-ionized water, commercially-available anionic acrylic polymers were used as a dispersant. The solid content of the slurry was controlled at a weight fraction of 5%.

The crystallite size of the ceria particles was measured by X-ray diffraction (RINT/DMAX-2500, Rigaku, Japan) and calculated from the Debye-Scherrer equation. In addition, the specific surface area of powders was estimated through the Brunauer, Emmett & Teller (BET) method (ASAP 2010, Micromeritics, USA), and powder density was measured using a pycnometer (Accupyc 1330, Micromeritics, USA). The grain size was observed using transmission electron microscopy (TEM) (JEM-2010, JEOL, Japan).

To investigate particle agglomeration in the slurries, the number of large particles (over 1 μm) per unit volume was measured using a slurry particle counter (Accusizer 780/FX, PSS/Nicomp, USA), which detects single particles optically and counts the number of particles in the tail of a submicrometre distribution. The accuracy of this particle counter was verified with standard 1.59- μm latex particles.

A field evaluation of CMP was performed using two kinds of slurries produced in this study. In the CMP evaluation, an 8" (200 mm) wafer CMP tool (6EC, Strasbaugh, USA) was used. The polishing pad was a grooved IC1000/SubaIV (Rodel, USA). The film thickness was measured using a Nanospec 180 (Nano-metrics, CA, USA.) to calculate removal rates. For this experiment, the "within wafer non-uniformity" (WIWNU) was defined as the ratio of the standard deviation of the

Table 1. Field evaluation conditions of the STI CMP process

Machine model	Strasbaugh 6EC
Pad	IC1000/Suba IV k-groove
Table speed	70 rpm
Spindle speed	70 rpm
Down pressure	0.028 MPa
Back pressure	0 Pa
Time	30 s
Flow rate	100 ml minute ⁻¹

remaining thickness to the average of the remaining thickness after CMP. The scratches on the oxide film (high density plasma SiO₂) film were measured using a Surfscan SP1 (KLA-Tencor, USA). After CMP, the wafers were cleaned using an APM solution (NH₄OH : H₂O₂ : H₂O = 1 : 1 : 10) at 80 °C to eliminate residual particles. The polishing test conditions are shown in Table 1.

Results and Discussion

Figure 1 shows SEM images of unmilled ceria particles and TEM images of milled ceria particles that were either calcined for 4 hours, A, or 6 hours, B. As seen in the SEM images, particle morphology was similar for both calcination times. However, the TEM images of the ceria particles taken after mechanical milling confirm that there was less crystal growth in the ceria particles calcined for four hours, even though the particle size before mechanical milling was the same as the samples calcined for six hours. This may have resulted from the low crystallinity of the unreacted carbonate due to a shorter calcination time. Although the oxidation of Ce³⁺ to Ce⁴⁺ at 650 °C was achieved [16], the inner part of the particle was not fully calcined. The crystalline defects and amorphous phases that these particles possess could translate into particles that are more brittle and are easily broken down to smaller particles during the mechanical milling process [19].

The crystallite size of the ceria particles before and after mechanical milling was measured by XRD and these data are listed in Table 2. In the XRD method, the X-ray penetrates just under ten micrometres into the powder surface, diffracting near the surface ash layer in reference to the diameter of the synthesized particle [20]. Therefore, the inner part of the ceria particles cannot be measured with XRD alone after the calcination. Subjecting the particle to mechanical milling, however, allowed the inner part of the particle to be exposed. Thus, even though the crystallite sizes of the initial powders were near 29 nm, the particles sizes after mechanical milling were 22.5 nm and 27.9 nm for A and B particles, respectively. This crystallite size data was evidence of the different crystalline structures of the particles formed under different calcination times.

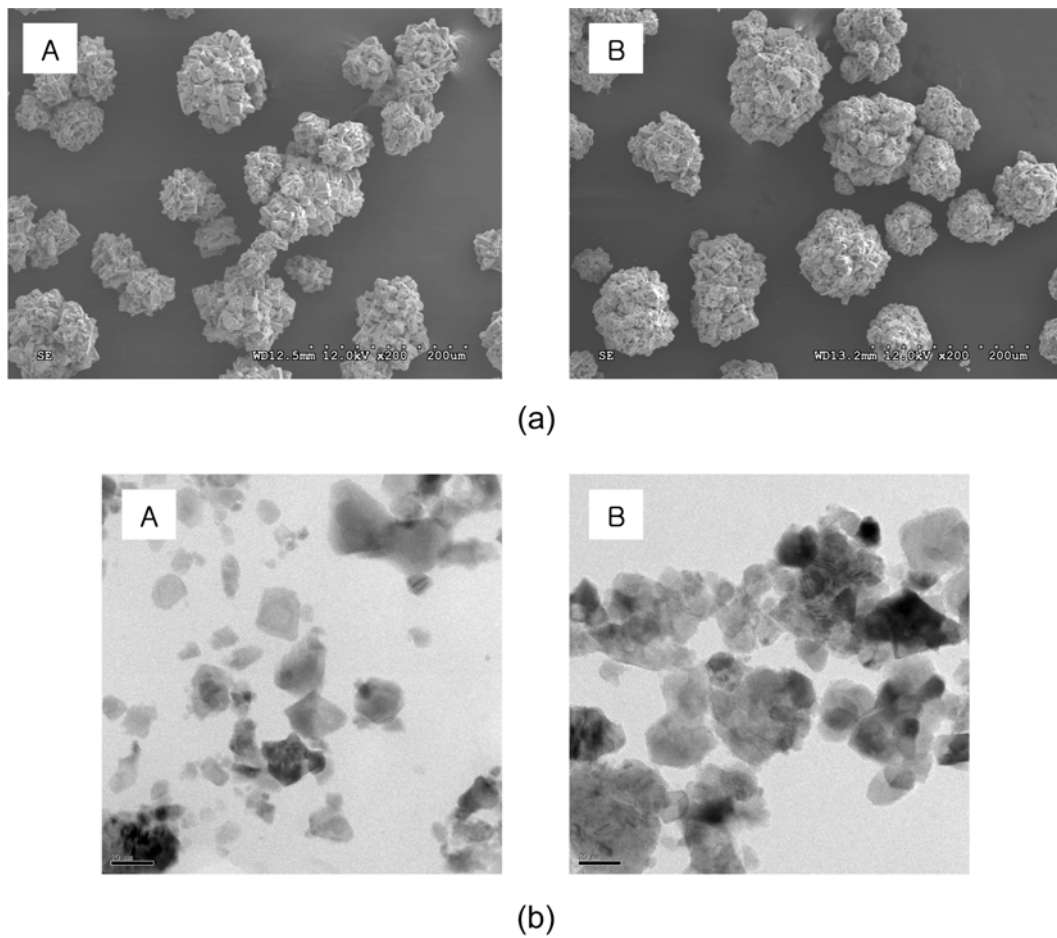


Fig. 1. (a) SEM images of unmilled ceria particles and (b) TEM images of milled ceria particles calcined for A, X hours and B, Y hours.

Table 2. The crystallite size of ceria particles before and after mechanical milling

sample (calcination time)	average grain size		decrement
	Before milling	after milling	
4hr	28.9 nm	22.5 nm	6.4 nm
6hr	29.1 nm	27.9 nm	1.2 nm

Figure 2 shows the BET surface area and density of the ceria powders after mechanical milling. The A particles have a larger surface area and lower density than the B particles. As mentioned above, the incompletely-calcined ceria particles are easily broken-down to smaller particles during the mechanical milling process because the inner part of the particle has a low density. Thus, the specific surface areas of these particles increased after mechanical milling. The actual synthesis of the ceria particle is predominantly controlled by the calcination temperature during the calcination process [16]. However, without sufficient time for calcination, the crystallization of the internal portion particle is incomplete. Thus, although the initial crystallite size of both particles was similar due to the same calcination temperature, the physical characteristics of particles

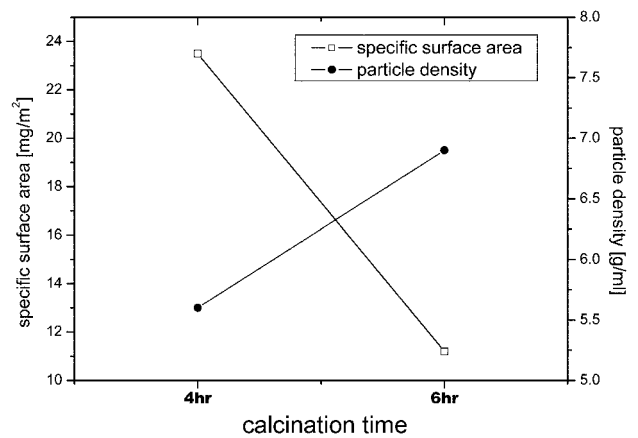


Fig. 2. Specific surface area and density of the ceria powders after mechanical milling.

were very different between the particles formed at different calcination times.

Figure 3 compares the particle size distribution (a) and the large particle counts (b) for each sample. The mean particle size (Fig. 3a) of the samples was measured to be 154 nm for A particles and 180 nm B particles. In spite of a lower mean particle size, the sample calcined for 4 hours, sample A, had more large

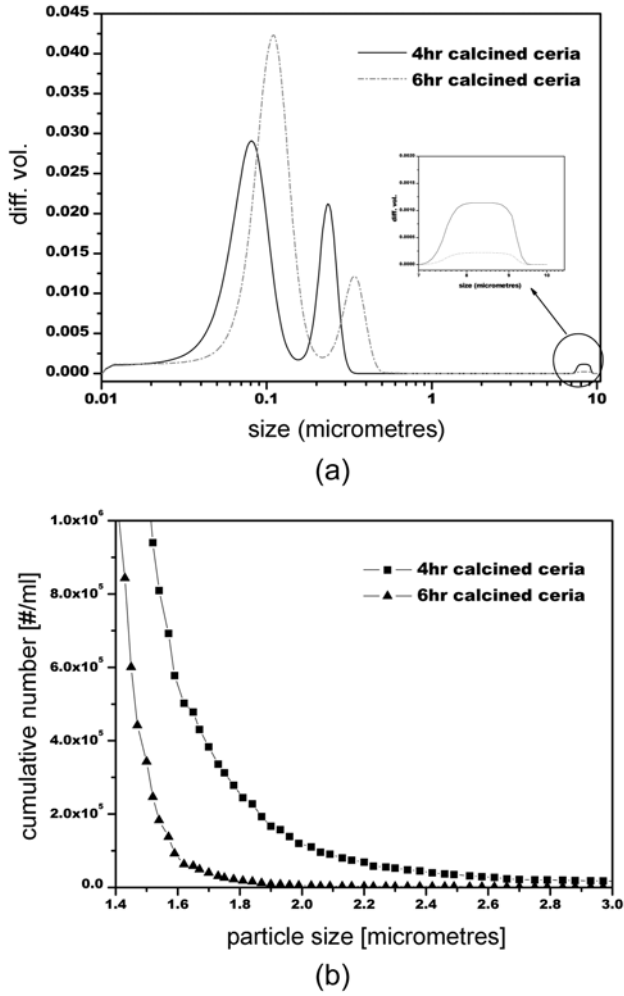


Fig. 3. (a) Particle size distribution and (b) the large particle counts for samples A and B.

agglomerated particles than the sample calcined for 6 hours, sample B. As shown in Figure 2, the small particles in sample A had a large surface area which, in turn, enhanced the ability of the particles to form agglomerates and increased the frequency of large particles. Figure 3(b) clearly shows the agglomeration of the smaller particles in the ceria slurry. Thus, it could be concluded that the smaller particles from the incompletely-calcined ceria were easily agglomerated, even though slurry stabilization was achieved by addition of a polymeric dispersant.

The removal rate along the radius and the scratch counts on the oxide film are shown in Figure 4. In Figure 4(a), the ceria slurry of B particles showed a higher removal rate and better planarization than the slurry composed of A particles. The oxide removal rate can be influenced by two CMP processing parameters: mechanical grinding and chemical interaction [21]. These mechanisms play simultaneous roles in polishing. Concerning the chemical interaction between the oxide film and ceria slurry, it was reported that Si-O-Ce bonding on a surface is a dominant mechanism [22]. During the

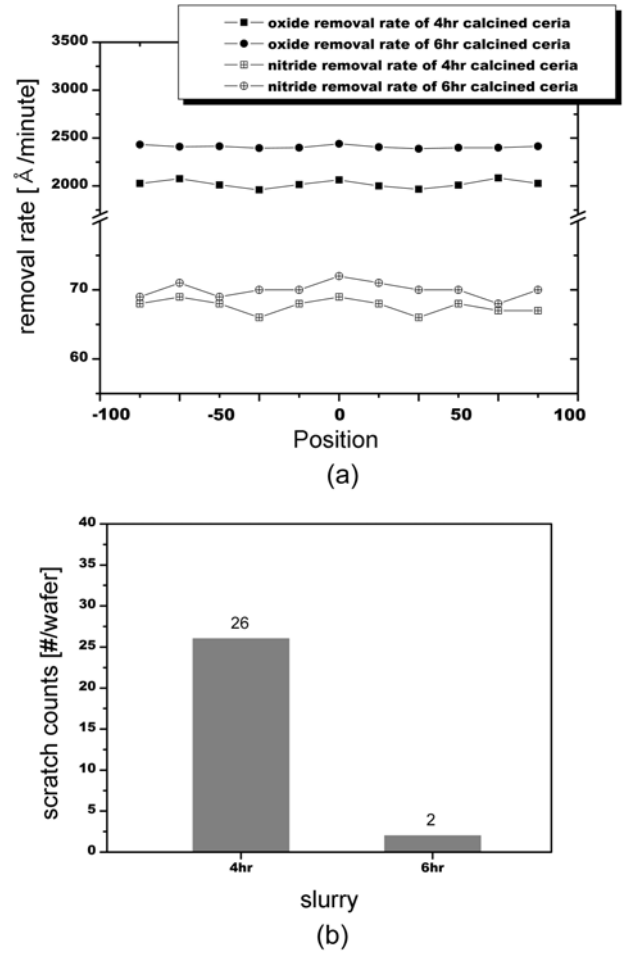


Fig. 4. (a) The removal rate at the radius and (b) the scratch counts on the oxide film.

polishing of the oxide film, the SiO₂ surface first reacts with the ceria particles and numerous chemical bonds of Si-O-Ce are formed on the surface. Then the mechanical tearing of the Si-O-Si bonds leads to the removal of the SiO₂ or Si(OH)₄ monomer as a lump, which is then released from the ceria particles downstream [23]. Highly-crystallized ceria particles exhibit a strong tendency to form bonds between Ce and Si. This might increase the chemical reaction rate, that is, the oxide removal rate. As mentioned above, ceria B particles had a higher crystallinity than A particles, which was confirmed by the XRD results shown in Table 2. Additionally, during CMP the agglomerated particles stuck easily to the wafer surface because of the small interactive forces between the abrasive and oxide film. It was these agglomerated particles, in particular, that induced the surface scratches on the wafer due to the compressive and shear forces between the wafer and pad. Therefore, as shown in Figure 4(b), the agglomerated particles in sample A easily induced the surface scratches during the CMP process. The scratch counts of sample A were greatly larger than those of sample B. Consequently, the ceria particle must be calcined for

a sufficient time in order to avoid the large particles agglomerations that form from incompletely-calcined particles.

Conclusions

In this study, the effect of the calcination time on the physical properties of synthesized ceria particles and their influence on the STI CMP process performance were investigated. Without a sufficient calcination time, the calcination of the particles was incomplete within the inner portion of the particle. Since the incompletely-calcined particles have low crystallinity, these particles were easily broken down into smaller particles. These smaller particles induced particle agglomeration due to their high surface area. This agglomeration resulted in a low removal rate and surface scratches in the STI CMP process. Thus, the complete calcination of ceria particles by allowing for sufficient calcination time is a key factor for a successful STI CMP process.

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