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Effects of Grain Size and Abrasive Size of Polycrystalline Nano-particle Ceria Slurry on Shallow Trench Isolation Chemical Mechanical Polishing

Hyun-Goo KANG[1,2,*], Takeo KATOH[1], Sung-Jun KIM[1], Ungyu PAIK[2], Hyung-Soon PARK[3] and Jea-Gun PARK[1,†]

[1]*Nano-SOI Process Laboratory, Hanyang University, 17 Haengdang-Dong, Seoungdong-Gu, Seoul 133-791, Korea*
[2]*Department of Ceramic Engineering, Hanyang University, 17 Haengdang-Dong, Seoungdong-Gu, Seoul 133-791, Korea*
[3]*Hynix Semiconductor Inc., San 136-1, Ami-ri, Bubal-eub, Icheon, Kyungki-do 467-701, Korea*

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In a ceria slurry with an ionic surfactant, the grain size and particle size of the poly-crystalline abrasives were controlled independently by changing the calcination temperature and the mechanical milling time, respectively, during abrasive synthesis. A chemical mechanical polishing (CMP) experiment using the slurry showed that the oxide removal rate increased with both the grain size and the abrasive particle size, while the nitride removal rate was independent of both. On the other hand, examination of the nanotopography impact showed that the planarization efficiency increased with decreasing abrasive size but was independent of the grain size. [DOI: 10.1143/JJAP.43.L365]

KEYWORDS: CMP, shallow trench isolation, ceria, oxide film, grain size, secondary particle size, surfactant, nanotopography

In the shallow trench isolation (STI) process, chemical mechanical polishing (CMP) is applied to planarize the gap-filling oxide film while utilizing a nitride film as a polishing stopping layer. Hence, the removal selectivity between the oxide and nitride films is a major specification for the slurries used in STI-CMP. To improve this selectivity, ceria slurries with ionic surfactants have been used.[1–5] Both the surfactant characteristics and the abrasive characteristics are critical issues for STI-CMP ceria slurries. Since the ceria abrasive is a polycrystalline material, the grain size of the abrasive particles and the size of the particles themselves should be distinguished. Homma *et al.* investigated the dependence of the thermal oxide removal rate on the size of crystallites (=i.e., grains in a poly crystal) by changing the calcination temperature during ceria powder fabrication.[5] In a previous article, we reported on the complex effects of the size of the polycrystalline abrasives and the surfactant concentration, on the basis of experiments using two different ceria powder synthesis methods.[6] For this article, we controlled the grain size and the polycrystalline abrasive size independently by varying the calcination temperature and the mechanical milling time, respectively. With this experimental approach, we investigated the effects of both sizes on the film removal rates. In addition, we examined the nanotopography impact on post-CMP oxide thickness deviations[7–17] in order to investigate the planarization efficiencies of the slurries used.[15,16]

Cerium carbonate was used as a precursor to synthesize ceria powder. The grain size of the polycrystalline ceria abrasives was controlled by employing a calcination process at various temperatures (400, 600, 700, 800, and 900 °C) for 4 h. The abrasive particle size was controlled by a mechanical milling process, through which a longer milling time produced a smaller abrasive. The milling time was varied, with durations of 8, 15, 28, and 40 h. We prepared nine different kinds of abrasives by combining the calcination temperature and milling time as shown in Table I.

The ceria abrasives were dispersed in deionized water and stabilized by adding 100 ppm of a commercially available dispersant (poly-meta-acrylate acid). We also added an anionic organic surfactant (poly-acrylic acid) at a concentration of 0.5 wt%. Each slurry was diluted with deionized water to produce a final ceria abrasive concentration of 1 wt%. Each slurry's pH was adjusted to the range of 7.0–8.0 by adding an alkaline agent. The morphology of the abrasives was observed with a high-resolution transmission electron microscope (HRTEM; JEOL JEM-2010). The secondary particle size in each slurry was measured with an AcoustoSizer II (Colloidal Dynamics). The crystal structure of the abrasives was examined by using the powder X-ray method (Rigaku RINT/DMAX-2500).

Table I. Combinations of calcination temperature and milling time for nine kinds of ceria abrasives.

	Calcination temperature [°C]	Milling time [h]
(a)	400	
(b)	600	
(c)	700	15
(d)	800	
(e)	900	
(f)		8
(g)	900	15
(h)		28
(i)		40

We used conventional 8" silicon wafers prepared by the single-side polishing method. The surface nanotopography height[7–17] was measured with a Nano-Mapper (ADE). We deposited a 7000-Å-thick oxide and a 1500-Å-thick nitride film by chemical vapor deposition (CVD). The films were polished on a Strasbaugh 6EC. We used an IC1000/Suba IV stacked pad (Rodel). The polishing pressure, applied as a down force, was 4 psi = 27.5 kPa. The relative velocity between the pad and the wafer was 0.539 m/s. The polishing time was 30 s. The oxide and nitride film thickness variations of the wafers before and after CMP were measured with a Nano-spec 180 (Nanometrics) and a spectroscopic ellipsometer (MOSS-ES4G, Sopra).

High-resolution TEM images of selected abrasive samples are shown in Fig. 1. In all the images except Fig. 1(a), in which the abrasives were calcined at 400°C, crystal grains

*E-mail address: ceramist@ihanyang.ac.kr
†E-mail address: parkjgL@hanyang.ac.kr

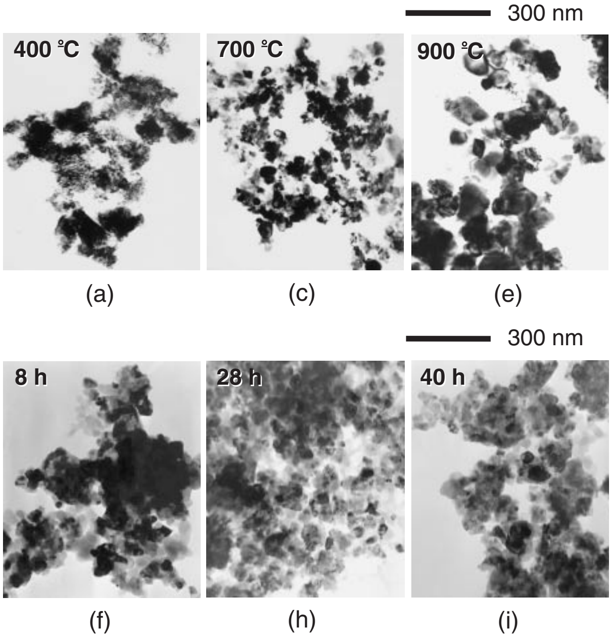

Fig. 1. TEM photographs of the abrasives in selected slurries processed at various calcination temperatures and milling times. The labels (a) through (i) correspond to the process combination listed in Table I.

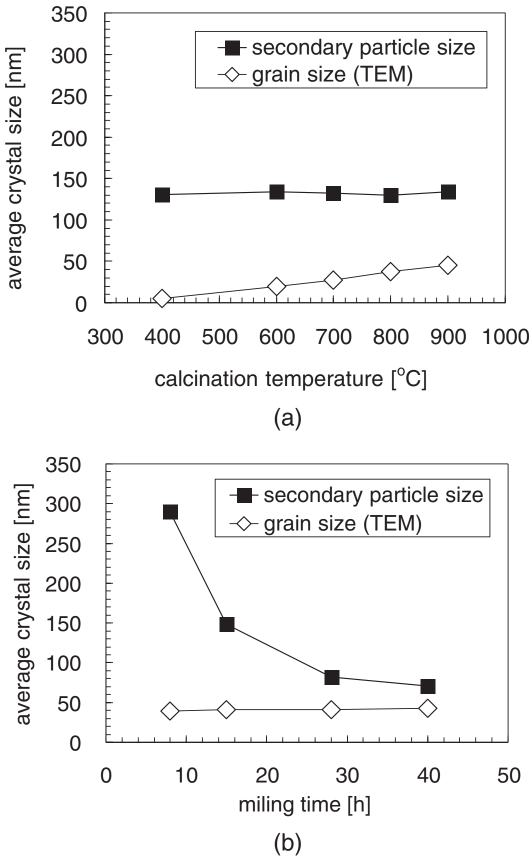

Fig. 2. Average measured secondary particle size of the abrasives and average grain size with respect to (a) calcination temperature and (b) milling time.

with well-defined shapes are observed. The modulating texture observed in Fig. 1(a) is considered to be related to an amorphous phase formed as an intermediate in the decomposition process of cerium carbonate during the low-temperature calcination process.[18] As these images show, the grain size and morphology in the polycrystalline abrasives changed significantly depending on the calcination temperature (Figs. 1(a), 1(c) and 1(e)). On the other hand, increasing the mechanical milling time caused minimal change in the grain size and reduced the abrasive particle size (Figs. 1(f), 1(h) and 1(i)).

The size of the grains was analyzed statistically (30 grains for each condition) and then the averaged value was calculated. However, the abrasive size was difficult to analyze from the TEM photographs due to the small areas of the images, so we used the secondary particle sizes measured with the AcoustoSizer II instead. These results are shown in Fig. 2. With increasing calcination temperature, the grain size increased up to 40–50 nm, while the secondary particle size was maintained at approximately 130–140 nm, as shown in Fig. 2(a). This phenomenon was due to grain growth during the calcination process as atomic diffusion caused wetting of the grain boundaries of adjacent grains. The grain size as a function of calcination temperature was in good agreement with results reported previously.[19] With increasing mechanical milling time, the secondary particle size decreased from 290 to 70 nm, while the grain size was maintained at approximately 40–50 nm, as shown in Fig. 2(b). This occurred because the ceria powder was continuously fractured during the milling process.[20] The variation shown in Fig. 2 demonstrates that both the grain size and the abrasive particle size were well controlled independently.

The removal rates of oxide and nitride films with respect to the calcination temperature and the mechanical milling time are shown in Fig. 3. Figure 3(a) shows that the oxide removal rate markedly increased from 910 to 2870 Å/min as

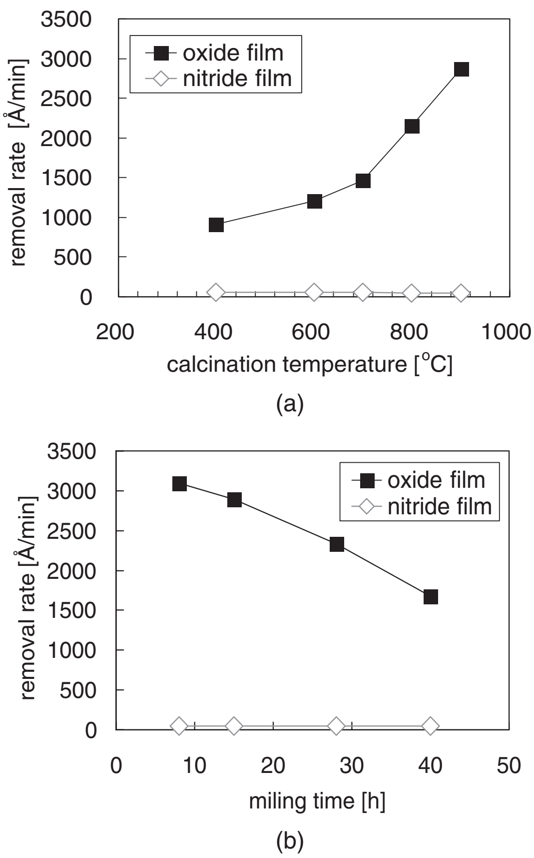

Fig. 3. Oxide and nitride film removal rates with respect to (a) calcination temperature and (b) milling time.

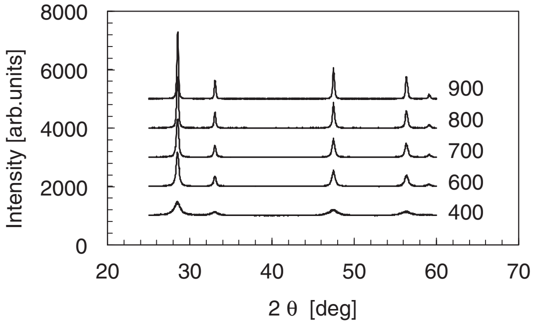

Fig. 4. X-ray diffraction profiles of ceria abrasives calcined at different temperatures.

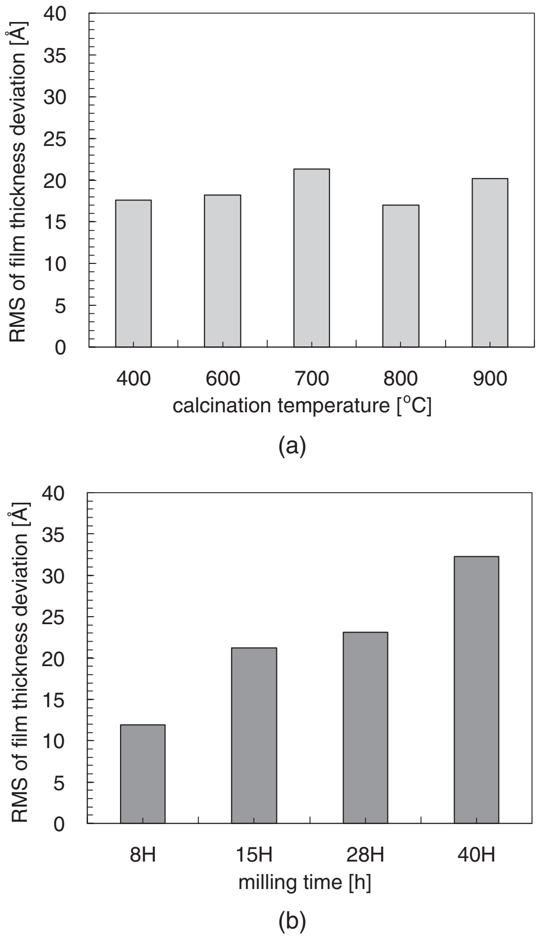

Fig. 5. Standard deviation (Rms) of the post-CMP oxide thickness deviation (OTD) as a function of (a) calcination temperature and (b) milling time.

the calcination temperature increased. On the other hand, the nitride removal rate was maintained at approximately 50 Å/min, which implies that the polishing mechanism of the nitride film is different from that of the oxide film.[21] Figure 3(b) shows that the oxide removal rate decreased from 3090 to 1680 Å/min as the mechanical milling time increased, while the nitride removal rate again was maintained at approximately 50 Å/min. Although we controlled the grain size and the abrasive particle size independently in this study by using completely different methods for each factor, the effects of both sizes on the film removal rates appear similar. Hirai *et al.* proposed a model in which the polycrystalline ceria abrasives are crushed into small particles during polishing.[2] If this model is correct, then the actual size of the abrasives during polishing is considered to depend on both the grain size and the polycrystalline particle size, since the fractures more likely occur along grain boundaries than across grains.

Figure 4 shows X-ray diffraction profiles of ceria abrasives calcined at various temperatures. The peak patterns were identified as the fluorite structure of CeO_2. With increasing calcination temperature, the peak width decreased, indicating that the grain size of the ceria abrasives became larger, which corresponds to the results obtained by TEM, as shown in Fig. 1. We will provide a detailed analysis of the X-ray diffraction profiles and a comparison with BET results in another article.[22]

To analyze the effects of the grain size and abrasive particle size on the planarization efficiency, we examined the nanotopography impact[15,16] on the oxide thickness deviation (OTD) after CMP. The polishing time was controlled to maintain a constant removal depth of 3000 Å.[17] After confirming that the peak and valley positions of the post-CMP OTD coincided well with those of the nanotopography height (pre-CMP), the fluctuations in the post-CMP OTD were attributed to wafer nanotopography. Figure 5 shows the standard deviation (Rms) of the post-CMP OTD as a function of the calcination temperature and the mechanical milling time. Unlike the results for the oxide removal rates, shown in Fig. 3, the calcination temperature did not influence the nanotopography impact, as shown in Fig. 5(a). With increasing milling time, the nanotopography impact increased, as shown in Fig. 5(b). The more the film surface is planarized, the larger is the variation of post-CMP OTD due to nanotopography.[7,15] Thus a higher standard deviation, shown in Fig. 5, denotes a higher planarization efficiency.[15,16] Therefore, it can be said that the polycrystalline abrasive particle size is more important than the grain size as a factor in controlling the planarization efficiency of a ceria slurry.

In summary, we independently controlled the grain size and particle size of the polycrystalline abrasives in a ceria slurry with an ionic surfactant by changing the calcination temperature and the mechanical milling time, respectively, during abrasive synthesis. CMP experiments using slurries with various process combinations showed that the oxide removal rate increased with both the grain size and the abrasive particle size, while the nitride removal rate was independent of both. On the other hand, examination of the nanotopography impact showed that the planarization efficiency increased as the particle size decreased but was independent of the grain size.

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