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Polishing behaviors of ceria abrasives on silicon dioxide and silicon nitride CMP

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ABSTRACT

The effects of ceria (CeO_2) abrasives in chemical mechanical polishing (CMP) slurries were investigated on silicon dioxide (SiO_2) and silicon nitride (Si_3N_4) polishing process. The ceria abrasives were prepared by the flux method, using potassium hydroxide (KOH) as the grain growth accelerator. The primary particle size of the ceria abrasives was controlled in the range of ~84–417 nm by changing the concentration of potassium hydroxide and the calcination temperature without mechanical milling process. The removal rate of silicon dioxide film strongly depended upon abrasive size up to an optimum abrasive size (295 nm) after CMP process. However, the surface uniformity deteriorated as abrasive size increases. The observed polishing results confirmed that there exists an optimum abrasive size (295 nm) for maximum removal selectivity between oxide and nitride films. In this study, polishing behaviors of the ceria abrasives were discussed in terms of morphological characteristics.

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1. Introduction

Ceria is receiving intense attention as a main slurry component for the chemical mechanical polishing (CMP) process in semiconductor manufacturing industry due to the effective removal rate for oxide film and the softness of the particles [1,2]. Ceria-based slurry has been used in CMP of shallow trench isolation (STI) structures consisting of silicon dioxide and silicon nitride deposition due to its high selectivity over nitride. For the STI-CMP process, the use of high selectivity slurries is very important to halt the polishing at the nitride stop layer and reduce the amount of defects such as erosion and dishing [3]. During the past decade, structural properties, chemical aspects and morphological characteristics of the ceria abrasives have been identified as the important parameters that influence the STI-CMP performance [4,5]. Therefore, many approaches to control these properties of ceria abrasives have been extensively investigated.

The commercial method for synthesis of ceria particles involves thermal decomposition of cerium salts such as carbonate and hydroxide [6]. This method leads to very porous ceria particles with high surface area, inducing softness and high chemical reactivity to oxide films. However, the size and the shape of ceria abrasives are very limited since particle growth is difficult to control during calcination process. To achieve the desired particle size and the uniform particle size distribution, mechanical milling and filteration is required [7]. Other methods for preparing ceria abrasives are liquid phase processes [8,9]. These methods can lead to ceria abrasives with desirable morphological characteristics by manipulating reaction parameters. However, the size of ceria abrasives is limited to less than 50 nm. Use of these small size particles results in low removal rates of target layers during CMP.

To overcome these problems, flux method is proposed to synthesize the ceria abrasives with a well-defined morphology. This method consists of adding precursor in the required ratio to a molten salt mixture, which accelerates the kinetics of the formation of ceria particles [10]. The ceria particles obtained by this method have the several advantages over other methods such as narrow size distribution, desirable characteristics including very fine size, high chemical purity and good chemical homogeneity [11]. However, this method has seldom been applied to the synthesis of ceria abrasives for CMP slurry. Furthermore, the polishing performance of ceria abrasives synthesized using flux method has not been reported so far for the silica and silicon nitride films.

In this work, we synthesized the ceria particles of different sizes with uniform particle size distribution using the flux method. For CMP performance evaluation, the effect of ceria abrasives on the removal rate, the oxide-nitride removal selectivity and the within-wafer non uniformity (WIWNU) was investigated.

2. Experiment

2.1. Preparation of ceria abrasive particles by solid state reaction

Cerium (III) nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$) and potassium hydroxide (KOH) were used as the starting materials for synthesis of ceria abrasive particles. 0.5 M of cerium (III) nitrate hexahydrate and 1.0 M of potassium hydroxide were separately dissolved in mixed

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solvent of ethylene glycol ($C_2H_6O_2$) and deionized (DI) water. The volume ratio of ethylene glycol to water was kept at 2:3. The reaction was carried out at a temperature of 50 °C with stirring rate of 100 rpm for 12 h. Air was bubbled into the precipitation reactor with passage through a gas distributor as an oxidizer. The precipitated substance was separated via centrifugation and then redispersed in distilled water under continuous stirring. The weight ratio of distilled water to a precipitated substance was kept 5:1. The suspension solution was put into an autoclave. The hydrothermal reaction was carried out at 230 °C for 6 h. After the hydrothermal reaction, the precipitated particles were washed with distilled water three times via centrifugation and then uniformly wetted in a potassium hydroxide/water mixed solution. The concentration of potassium hydroxide was 0.1–2.0 wt.% depending on the total weight of the precipitated particles. The wetted particles were sintered for 2 h at 800–900 °C temperature. The synthesized particles were washed with distilled water until the ion conductivity of the washed solution was less than 0.5 μS. The schematic diagram of experimental procedure was shown in Fig. 1.

The crystal structure and grain size were identified through X-ray diffraction (XRD) using CuKα radiation. The crystallite size was estimated by the Scherrer equation according to the formula $D = 0.9\lambda/(\beta \cos\theta)$, where D is crystallite size, λ is the wavelength of X-rays, β is the half-width of the diffraction peaks, and θ is the diffraction angle. The broadening of the reflection from the (111) plane was used to calculate the crystallite size. The morphology and sizes of the abrasive particles were also examined by field emission scanning electron microscope (FESEM). The average primary particle size was calculated by measuring ca. 100 particles from FESEM micrographs. The specific surface area (SSA) of ceria abrasives was determined by Brunauer–Emmett–Teller (BET) method using nitrogen adsorption/desorption at 77 K.

2.2. Polishing of wafers

Different ceria-based slurries were formulated by dispersing abrasives each with different primary particle sizes in DI water containing an anionic organic polymer (Poly acrylic acid, PAA; Mw 4000, LG Chem.) as dispersant. The PAA was 2 wt.% based on the total weight of the ceria abrasives. For each slurry, pH was adjusted to 6.5–6.7 by adding ammonium hydroxide (NH_4OH). The solid loading of ceria abrasives was fixed to 2.0 wt.%. Table 1 presents the slurry characteristics used in polishing tests. The abrasive size distribution of slurry was measured using light scattering method (UPA 150, Microtrac Inc.). In order to investigate the adsorption characteristics of ceria abrasives for the additive polymer, slurry A and D were dried at 80 °C for 24 h. The weight loss of the abrasives dried from slurries was measured by thermogravimetric analysis (TGA). TGA was performed in an air flow of 100 ml/min at a heating rate of 10 °C/min from 30 °C to 600 °C.

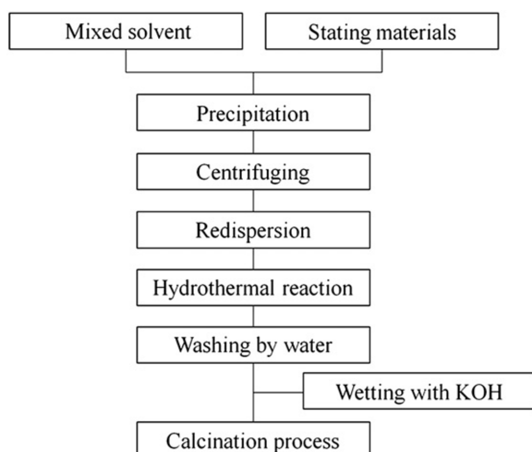

Fig. 1. Schematic diagram of experimental procedure.

Table 1
Comparison of slurries used in this study.

Samples	Calcination conditions		Primary particle Size (SEM, nm)	Grain size (XRD, nm)	Slurry mean size (UPA, nm)	Surface area (m^2/g)
	pH	Temp. (°C)				
Slurry A	0.5	800	84	38	165	20.53
Slurry B	0.2	850	166	43	278	14.06
Slurry C	0.5	850	295	57	483	12.70
Slurry D	0.5	900	417	88	742	5.58

Silicon dioxide film of 2 μm thick was formed on a 5-in. p-type silicon substrates with (001) orientation by plasma enhanced chemical vapor deposition (PECVD). The silicon nitride films were deposited by using low-pressure chemical vapor deposition (LPCVD). Polishing tests were performed on a rotary type CMP machine (GNP POLI 400, G&P technology) for 1 min with each of the ceria-based slurries. IC 1000/SUBA IV stacked pads (supplied by Rodel Inc.) were utilized as CMP pads. The downforce was 280 g/cm^2 and the rotation speed between the pad and the wafer was 90 rpm. The slurry flow rate was 100 mL/min. The film thickness on the wafers before and after CMP was measured using spectroscopic reflectometry (Nanospec 6100, Nanometrics) to calculate the removal rate. In this experiment, the WIWNU was defined as the standard deviation of remaining thickness divided by the average of the remaining thickness after the CMP process. The average polishing data for removal rate was carried by performing the same tests more than three times in order to support the validity of the results from the statistical viewpoint.

3. Results and discussion

3.1. Morphological characteristics of ceria abrasives

Fig. 2 shows the FESEM images of abrasive particles prepared in different calcination conditions as described in Table 1. The primary particle sizes determined using the FESEM micrographs were 84, 166, 295, and 417 nm for slurry A, B, C and D, respectively. As shown in Fig. 2, the ceria particles consisted of crystalline grains with a well-defined morphology. The size of ceria particles increased with the increase in concentration of potassium hydroxide and the calcination temperature. These images indicate that the primary particle size can be controlled by changing the calcination conditions, which influence the crystal growth of ceria particles.

Fig. 3 shows the X-ray diffraction patterns of the prepared particles. As shown in Fig. 3(a), the characteristic peaks corresponding to (111), (200), (220), (311), and (222) planes are located at $2\theta = 28.51$, 33.06, 47.48, 56.20, and 59.05°, respectively. They show very close to the ones with cubic fluorite structure of ceria crystal in JCPDS database. The sharp intensity peaks were observed for ceria abrasives with larger primary particle size as shown in Fig. 3(b). The crystallite size of ceria abrasives was calculated from the Scherrer equation using the line-broadening of the (111) peak in the XRD pattern. The crystallite size gradually increased from 38 nm to 88 nm as the calcination temperature and the concentration of additive were increased. This result coincides with the trend of increasing primary particle size in the FESEM images shown in the Fig. 2.

The synthesis method employed in this study is characterized by a low sintering temperature process, using grain growth accelerator. The eutectic mixed solvents as an accelerator is used to promote the kinetics by enhancing diffusion, due to their low melting temperature. In this study, potassium hydroxide/water mixed solvent was used as the accelerator to reduce sintering temperature. Considering that the

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