



Synergetic effect of organic cores and inorganic shells for core/shell structured composite abrasives for chemical mechanical planarization



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ABSTRACT

Core/shell structured organic/inorganic composite microspheres has an important potential application in efficient and damage-free chemical mechanical planarization/polishing (CMP) as a kind of novel abrasive due to its uniform non-rigid mechanical property. However, the synergistic effect of material removal between organic cores and inorganic shells of composite abrasives is ambiguous. In this work, oxide-CMP performances of various slurries, containing polystyrene (PS) spheres, solid abrasives (SiO_2 or CeO_2), mixed abrasives ((PS + SiO_2) or (PS + CeO_2)), core/shell composites (PS/ SiO_2 or PS/ CeO_2), were investigated by atomic force microscopy. Experiment results indicated that the surfaces polished by composite abrasives exhibited lower surface roughness, fewer scratches as well as lower topographical variations than those by other type of abrasives. The core/shell structure of composite abrasives plays an important role in improving CMP behavior. Moreover, the organic cores are mainly beneficial to decrease surface roughness and mechanical damages, and the inorganic shells are in favor of improving material removal rate.

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1. Introduction

Core/shell structured organic/inorganic composite abrasives [1–3] are a type of novel polishing medium materials for chemical mechanical planarization/polishing (CMP). Compared to traditional abrasives (silica [4,5], alumina [6,7], ceria [8,9] and titania [10] etc.), composite abrasives exhibit especial non-rigid mechanical properties, which are attributed to their specific core–shell structure. CMP test results confirm that the core–shell structured composite abrasives contribute to eliminate scratches and damages of the polished wafer surfaces, and demonstrate both high planarization efficiency and good planarization quality.

Recently, the factors including the shell thickness, the shell morphology, the core size, the shape and size of particles in inorganic shell on CMP performance have been investigated. Armini et al. [11] investigated the effect of the shape of the silica particles at the shell of the polymethylmethacrylate (PMMA)/ SiO_2 composite abrasives on the oxide CMP process. The results indicated that fewer and shallower scratches were detected for the composites with a colloidal silica shell as compared with the composites with a fumed silica shell. Moreover, Armini et al. [12] examined the

dependence of oxide CMP performance on both PMMA core and colloidal SiO_2 shell particle sizes. The highest material removal rate (MRR) was achieved for the largest diameter cores combined with the smallest silica particles. Further analysis showed that the larger cores might elastically deform and gently transfer the applied pressure to a higher number of SiO_2 particles with respect to smaller cores. In our previous work [13], we investigated the CeO_2 shell thickness of polystyrene (PS)/ CeO_2 composites on polishing behavior. SiO_2 -CMP results revealed that there was an obvious effect of the shell thickness on the surface roughness and topographical variation. Recently, Chen et al. [14] explored the silica shell morphology of PS/ SiO_2 composites on the compressive modulus and oxide-CMP behavior by atomic force microscopy (AFM). It was found that the composites with a continuous shell exhibited a better structural stability than the discontinuous one during contact processes among wafers, abrasives and pads. Current researches about composite abrasives are generally focused on the synthesis of composites and the characterization of polishing performance. However, the material removal mechanism of the core–shell structured organic–inorganic composite abrasives is not clear.

In this paper, well-defined PS/ SiO_2 and PS/ CeO_2 composites with core–shell structure were prepared by chemical precipitation technique. The difference of oxide-CMP performance among traditional solid abrasives, organic–inorganic mixed abrasives and composite abrasives were investigated by atomic force microscopy (AFM).

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Importantly, we shed light on the synergistic effect of material removal between organic cores and inorganic shells of composite abrasives.

2. Experimental

2.1. Materials

Styrene (St) was treated with 5 wt% of aqueous NaOH solution to remove the inhibitor. Absolute ethanol, sodium hydroxide, ammonia (28 wt%), potassium persulfate (KPS), methacrylic acid (AA), tetraethoxysilane (TEOS), cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3$), Poly(vinylpyrrolidone) (PVP, $M_w = 30,000$), urea, and hexamethylenetetramine (HMT) were purchased from Shanghai Chemical Reagent Co. (China) and used without any treatment. Azodiisobutyramidinedihydrochloride (AIBA) was purchased from Aldrich (USA) and used as received. Deionized water was used throughout the experiment.

2.2. Synthesis of samples

2.2.1. Composites

For the preparation of core-shell structured PS/SiO₂ composites, PS (+) core charged positively was prepared by soap-free emulsion polymerization using AIBA as an initiator [14]. Briefly, St (10 g) and PVP (3 g) were mixed in water (150 g). This mixture was deoxygenated by bubbling N₂ under magnetic stirring at room temperature for 1 h and then placed into an oil bath at 70 °C, followed by addition of initiator (0.2 g AIBA in 30 g water). The polymerization reaction was performed in N₂ protection and constant stirring for 24 h. To synthesize PS/SiO₂ composites, the obtained positively charged PS colloid (5 g), water (10 g) and ethanol (40 g) were mixed and magnetically stirred for 0.5 h. The pH value of the suspension was controlled to 8 by ammonia. The reaction mixture was slowly heated up to 60 °C. Then, a mixed solution containing TEOS (3 g) and ethanol (10 g) was added drop by drop into the mixture, and the reaction was carried out at 60 °C for 5 h under constant magnetic stirring. The precipitates were centrifuged and washed with ethanol for three times. The obtained products were dried at 70 °C for 24 h.

For the preparation of PS/CeO₂ composites, the negative-charged PS (−) microspheres were prepared by emulsifier-free emulsion polymerization using KPS as an initiator [15]. St (10 g), AA (0.32 g) and water (150 g) were mixed under magnetic stirring. The mixture was continuously deoxygenated by bubbling N₂ and stirred for 0.5 h, and was heated to 70 °C gradually in an oil bath. Then, 0.41 g KPS (dissolved in 30 g water) was added to initiate polymerization. Finally, the polymerization was maintained for 7 h, and then the emulsion was cooled to room temperature for stopping the polymerization. To synthesize PS/CeO₂ composites, PS colloids (4 g) were dispersed into water (200 g) with ultrasonic vibration for 10 min, and then $\text{Ce}(\text{NO}_3)_3$ (1.5 g, dissolved in 50 g water) and HMT (2.5 g, dissolved in 50 g water) were added. The obtained aqueous suspension was reacted at 75 °C for 2 h under magnetic stirring. The resulting precipitates were separated by centrifugation and washed with ethanol, then dried at 80 °C in air for 2 h.

2.2.2. Conventional SiO₂ and CeO₂ abrasives

Submicrometer SiO₂ particles were prepared by a modified Stöber procedure [16]. First, solution containing ethanol (40 g), ammonia (1.9 g) and water (5.4 g) were stirred for 10 min to ensure complete mixing. Then, a mixture of 2.3 g TEOS and 5 g ethanol was slowly added to the above solution and the reaction proceeded at ambient temperature under continuous stirring for 5 h. Thereafter, the product was separated by high-speed centrifuge and washed

by ethanol for three times, then dried at 80 °C in air for 2 h. Finally, the obtained samples were calcined at 600 °C in air for 2 h.

Submicrometer CeO₂ particles were prepared based on the literature method [17]. The procedure was as following: $\text{Ce}(\text{NO}_3)_3$ (1.39 g) and urea (7.69 g) were dissolved completely in water (160 g). The resulting mixture was constantly stirred for 30 min to form homogeneous solution, and then heated to 80 °C for 2 h. The precipitates were centrifugated, redispersed in ethanol three times, and then dried at 80 °C. The samples were obtained after calcination at 600 °C in air for 2 h.

Nano-sized CeO₂ particles were obtained by the procedure proposed by Chen et al. [18], and described as follows: a certain amount of $\text{Ce}(\text{NO}_3)_3$ and HMT with a molar ratio of 1:10 were dissolved in water (100 g) with magnetic stirring to form a transparent solution. Then, the mixture was heated to 75 °C for 1 h. Finally, the precipitates were centrifuged, washed, dried at 80 °C, and calcined at 600 °C for 2 h.

2.2.3. Characterization

Scanning electron microscopy (SEM) images of samples were obtained on a JSM-6360LA and a ZEISS SUPRA 55 microscope. Transmission electron microscopy (TEM) investigation was performed on a Tecnai-12 and a JEOL-2100 microscope. Thermogravimetric analysis (TGA) was performed in air from room temperature to 800 °C at the rate of 10 °C/min on a SDT Q600TA thermal analyzer.

2.3. Oxide-CMP tests

For the CMP tests, 1200 nm thermal oxide wafers on silicon were used as substrates. Wafers were polished on a rotary polisher (TegraForce-1/TrgraPol-15, Struers, Denmark). Porous polyurethane pads (MD-Chem, Struers) have been employed for CMP. The pad was conditioned for 5 min prior to each CMP test using a diamond pad conditioner. The rotation speeds of the head and platen were set at 120 and 90 rpm, respectively. The pressure of the carrier was 3.8 psi, and the polishing time was set at 1 min. The pH of slurry was adjusted to 10 by addition of NaOH, and the flow rate was 100 mL/min. The solid content of slurry was 1 wt%. A shaker was applied to the slurries for 10 min before the CMP tests.

In this work, we prepared four types of slurries based on PS/SiO₂ and PS/CeO₂ composite abrasives, pure PS microspheres, and pure conventional SiO₂ and CeO₂ abrasives (PS+SiO₂) and (PS+CeO₂) mixed abrasives, respectively. For the mixed abrasive slurries (MAS), the PS colloids were simply mixed with SiO₂ or CeO₂ nanoparticles (10–20 nm). Commercial SiO₂ nanoparticles (LM-150, 20–30 nm) were obtained from Cabot Corporation. The amounts of inorganic components in MAS were determined by the TGA curves of composite abrasives. The abrasives tested in the experiment are summarized in Table 1.

The experiments were repeated three times and the reported trend in MRR, which was calculated according to the formula: $MRR = (m_0 - m) / \rho t s$, where ρ is the density of the SiO₂ layer, s is the area of the wafer, t is the polishing time, m_0 and m is the mass of wafer before and after CMP, respectively. The surface topographies and profilograms of the wafers were determined by an a Nanoscope Dimension V atomic force microscope (Bruker) in tapping mode, and the root mean square (RMS) roughness was calculated within $5 \mu\text{m} \times 5 \mu\text{m}$.

3. Results and discussion

3.1. Characterization of abrasive samples

Fig. 1 shows the SEM and TEM images of the as-prepared SiO₂ and CeO₂ particles. The uniform SiO₂ microspheres were highly

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