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Original Research Paper

Core/shell structured $sSiO_2/mSiO_2$ composite particles: The effect of the core size on oxide chemical mechanical polishing

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ABSTRACT

In a typical chemical mechanical polishing (CMP) process, the type, morphology, structure, mechanical, and surface characteristics of abrasive particles play an important role in influencing the material removal process. The novel abrasive particles with special mechanical and/or tribochemical properties have been introduced into CMP processes for the improvement of surface quality and finishing efficiency. In this work, the composite particles containing solid silica ($sSiO_2$) cores and mesoporous silica ($mSiO_2$) shells were prepared *via* a developed Stöber method using cetyltrimethylammonium bromide as a structure-templating surfactant. The as-synthesized core/shell structured $sSiO_2/mSiO_2$ composite particles were characterized by powder X-ray diffraction, field emission scanning electron microscopy, transmission electron microscopy, and nitrogen sorption–desorption measurements. The effect of the $sSiO_2$ core size of the composite particles on oxide CMP performance was evaluated in terms of surface roughness and material removal rate (*MRR*). The root-mean-square surface roughness (0.15–0.31 nm) of the polished substrates slightly increased with increasing of the $sSiO_2$ core size (168–353 nm) of the composites with a comparable $mSiO_2$ shell thickness (16–18 nm). The $sSiO_2/mSiO_2$ composite particles with a relatively smaller or larger core presented a relatively high *MRR* for silicon oxide films. These oxide CMP results could be rationalized according to the contact area mechanism and indentation-based mechanism, incorporating the total contact area and chemical reactivity between particles and wafers, and the indentation depth of an abrasive particle onto the substrate surface.

1. Introduction

Chemical mechanical polishing (CMP) is a widely used technique for achieving ultra-smooth surfaces of ceramic [1,2] and metallic materials [3]. CMP is a synergistic material removal process of chemical reaction with slurry chemicals and mechanical abrasion with abrasives. The type, shape, size and size distribution, and physical and chemical properties of abrasive particles present significant effects on the material removal rate (*MRR*), type and number of defects, and surface roughness, which are benchmarks for CMP performance.

SiO_2, CeO_2, and Al_2O_3 particles are the most commonly used as abrasives in CMP applications. The conventional inorganic particles, with large hardness, high modulus, and irregular shape, are likely to scratch the polished substrates and limit the improvement of the finished surface qualities. For improving CMP performance, the core/shell structured composite abrasives [4–8], porous abrasives [9,10], and doped abrasives [11,12] have been developed and applied in CMP processes. Among these novel abrasive particles, the core/shell structured composites have attracted increasing attention in recent years. For example, the non-rigid polymethylmethacrylate (PMMA)/SiO_2 [4], PMMA/CeO_2 [5], Polystyrene (PS)/SiO_2 [6], and PS/CeO_2 [7] composite abrasives exhibited an improved copper and oxide CMP performance by comparison with traditional inorganic abrasives. It was also confirmed that the CeO_2 coated SiO_2 nanoparticles [8] were also contributed to the improvement in selective removal between SiO_2 and SiN wafers. Recently, the core/shell polymer/CeO_2-Fe_3O_4 multicomponent particles [13] and polyurethane/CeO_2 particles [14] were further applied in magnetic-field-assisted polishing for soda-lime glass or electrochemical mechanical polishing for single-crystalline SiC.

In our pervious work [15,16], the composite abrasives, containing PS or solid silica ($sSiO_2$) cores and mesopours silica ($mSiO_2$) shells, were fabricated *via* a modified Stöber process using cetyltrimethylammonium bromide as a structure directing agent.

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These novel composite abrasives combine the advantages of the core/shell composite abrasives and porous abrasives. After polishing with the *s*SiO_2/*m*SiO_2 composites, the surface roughness and *MRR* for oxidized silicon wafers were evidently improved by comparison with conventional *s*SiO_2 particle abrasives. The improved oxide-CMP behavior might result from their special mechanical and surface properties.

Theoretical analyses indicate that the CMP behaviors of *s*SiO_2/*m*SiO_2 composites are affected by their core size, shell thickness, and diameter and organization of the mesopore in the shells. However, the relationship between the structure of the *s*SiO_2/*m*SiO_2 abrasives and the polishing performance is still ambiguous. In this paper, we investigate the effect of the *s*SiO_2 core size of the *s*SiO_2/*m*SiO_2 composite abrasives on oxide CMP processes. And we attempt to rationalize the *MRR* and surface roughness with the help of already existing models based on the indentation and contact area mechanisms.

2. Experimental section

2.1. Preparation and characterization of sSiO₂/mSiO₂ composite particles

Tetraethyl orthosilicate (TEOS, 98%), ammonia solution (28–30%), ethanol, acetone and sodium hydroxide (NaOH) were obtained from Shanghai Chemical Reagent Co. (China). Cetyltrimethylammonium bromide (CTAB, 99%) was purchased from Shanghai Lingfeng Chemical Reagents Company. All chemicals were obtained from commercial suppliers and used without further purification.

The monodispersed *s*SiO_2 (no mesoporous channels) spheres were prepared *via* a Stöber method [17]. In a typical process, absolute ethanol (20.5 mL), ammonia (9.0 mL) and deionized (DI) water (25.0 mL) were mixed and stirred at room temperature. Subsequently, a mixture containing a certain amount of TEOS and ethanol (46.1 mL) was added dropwise, and the resulting mixture was stirred at room temperature for 2 h. Finally, the solid products were isolated by centrifugation and washed with ethanol and DI water and dried at 80 °C. The *s*SiO_2 particles obtained with the TEOS amounts of 1.0, 3.0, or 6.0 mL were denoted as *s*SiO_2-1, -2, and -3, respectively.

The core/shell structured *s*SiO_2/*m*SiO_2 composite particles were synthesized following our previous procedure [16]. Briefly, *s*SiO_2 particles (0.4 g) were dispersed in a mixed solution containing ethanol (12.7 mL) and DI water (30 mL) under ultrasonic treatment for 10 min, and followed by addition of CTAB (0.16 g). After stirring at 25 °C for 30 min, a mixture containing a certain amount of TEOS and ammonia (0.4 mL) was added drop by drop into the above solution. The reaction was maintained at room temperature for another 10 h under magnetic stirring. Subsequently, the resultant products were collected through centrifugation, washed twice with DI water and ethanol, and dried at 80 °C. Finally, the composite particles were obtained after calcination at 550 °C for 2 h in air. The *s*SiO_2/*m*SiO_2 composites with different cores (*s*SiO_2-1, -2, or -3) prepared with the TEOS amounts of 0.35, 0.28, or 0.14 mL were denoted as *s*SiO_2/*m*SiO_2-1, -2, and -3, respectively.

Transmission electron microscopy (TEM) images were taken using a JEM 2100 microscope (JEOL). For TEM measurements, the particle samples were dispersed in ethanol and then dried on a holey carbon film Cu grid. Field emission scanning electron microscopy (FESEM) images were obtained on a SUPRA-55 microscope (ZEISS). Powder X-ray diffraction patterns were acquired on a D/-max diffractometer (Rigaku) using Cu Kα radiation. Nitrogen adsorption-desorption measurements were conducted at 77 K using an ASAP 2020 apparatus (Micromeritics). The pore volumes and pore size distributions were derived from desorption branch of the isotherms based on the Barrett-Joyner-Halenda (BJH) model. The surface areas were calculated *via* the Brunauer-Emmett-Teller (BET) method.

2.2. Polishing tests of sSiO₂/mSiO₂ composite particles

Thermally grown silicon oxide films (ca. 1.2 μm in thickness) were obtained from Changzhou Huacheng Changban Microelectronics Limited Company and used as substrates. Each of these wafers was cut into several pieces (2.0 cm × 2.0 cm) for polishing experiments.

Polishing tests were performed on a TegraForce-1/TrgraPol-15 (Struers) polisher equipped with a porous polyurethane pad (MD-Chem, Struers). The detailed polishing conditions were described as follows: the platen rotation speed was 90 r/min, the carrier rotation speed was 120 r/min, the applied pressure was 3.3 psi, the polishing time was 1 min, the slurry supplying rate was 100 mL/min, and the solid content of abrasive particles in slurries was 1%. For the preparations of polishing slurries, the *s*SiO_2/*m*SiO_2 composite particles dispersed in DI water, and the pH of the suspensions was adjusted to 8.6 by 0.1 mol/L NaOH. The polishing slurries were simultaneously sonicated for 10 min prior to use.

The surface topography, roughness and profile curve of the substates, before and after polishing, were investigated using a atomic force microscope (AFM, Multimode Nanoscope, Veeco) in tapping mode. Silicon probes (Tap300Al-G, BudgetSensors) were used in all AFM measurements, and the scan speed and pixels per line was 1 Hz and 256, respectively. Before measurements, the wafers were cleaned by acetone and DI water under sonication, and then dried in an ultra-clean room.

Material removal rate (*MRR*, nm/min) was calculated as follows: $MRR = \Delta m/\rho st$. Here, Δm is the mass loss of the substrate before and after polishing, determined by a professional electronic balance (XS105, Mettler Toledo, exact to 0.01 mg). ρ is the density of silicon oxide layer (2.2 g/cm^3), s is the substrate area, and t is the polishing time. The presented surface roughness and *MRR* data were the average of 3 runs.

3. Results and discussion

3.1. Characterization of sSiO₂/mSiO₂ composite particles

In our pervious work [15], the compositions of *s*SiO_2/*m*SiO_2 composite particles before and after calcination were characterized with Fourier transformed infrared (FT-IR) spectroscopy. And the results confirmed that the structure-templating CTAB surfactants were completely removed after calcination at 550 °C.

The morphology and size of the obtained *s*SiO_2 particles and *s*SiO_2/*m*SiO_2-3 composites were tracked by FESEM (Fig. 1). The *s*SiO_2 particles (Fig. 1a–c) are well dispersed and are spherical in shape with smooth appearances. Moreover, the *s*SiO_2 particle sizes increase with increasing TEOS concentration, and the particle size of *s*SiO_2-1, -2 and -3 is 168 ± 9, 263 ± 12 and 353 ± 7 nm, respectively. The average particle sizes were calculated from the diameters of more than 50 particles in FESEM images. After silica coating, the uniform spherical morphology remains for the *s*SiO_2/*m*SiO_2 composite particles (Fig. 1d) with relatively rough surfaces. From individual broken samples (indicated by white arrows), it can be clearly observed that the shells peel off and internal cores are exposed, indicating the formation of the core/shell structure of the *s*SiO_2/*m*SiO_2 composites.

The core/shell structure of *s*SiO_2/*m*SiO_2 composite particles was further characterized by TEM observations (Fig. 2). The bright- and

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