Synthesis of Homo-compositional Heterostructural $SSiO_2/MSiO_2$ Core/Shell Composite Abrasive Particles: Postprint

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Date: 2023-03-18T00:00:00+00:00

Abstract

Using tetraethyl orthosilicate as the silicon source, ammonia water as the catalyst, and cetyltrimethylammonium bromide as the structure-directing template, mesoporous silica (Mesoporous-SiO_2, $MSiO_2$) shells were coated onto monodisperse solid silica (Solid-SiO_2, $SSiO_2$) cores to synthesize $SSiO_2/MSiO_2$ core/shell composite abrasive particles. The structure of the samples was characterized by small-angle XRD, FESEM, HRTEM, FTIR, TGA, and nitrogen adsorption-desorption measurements. The results demonstrate that $MSiO_2$ with radial mesoporous channels was uniformly and continuously coated on the outer surface of $SSiO_2$ cores (210–230 nm), forming a shell with a thickness of 70–80 nm. The mesoporous channels in the shell (pore size approximately 2–3 nm) were essentially perpendicular to the core surface, and the composite abrasive particles exhibited a large specific surface area (558.2 m^2/g). The polishing characteristics of the prepared composite abrasives on SiO_2 thin films were evaluated using AFM morphology analysis and profilometry. Compared with conventional solid SiO_2 abrasives, the $SSiO_2/MSiO_2$ composite abrasives significantly improved the polished surface quality and increased the material removal rate. This may be attributed to the optimization of the real interfacial contact environment between the abrasive particles and the substrate by the $MSiO_2$ shell through mechanical and/or chemical effects.

Full Text

Preparation of Allotropic Composite Abrasives $SSiO_2/MSiO_2$ with Core/Shell Structure

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Supported by National Natural Science Foundation of China Nos. 51205032 & 51405038 and the Natural Science Foundation of Jiangsu Province of China No. BK2012158.

Manuscript received December 22, 2014; in revised form January 26, 2015.

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Abstract

Core/shell structured composite abrasives with solid-silica ($SSiO_2$) cores and mesoporous-silica ($MSiO_2$) shells were synthesized using tetraethylorthosilicate as silica source, ammonia solution as catalyst, and cetyltrimethylammonium bromide as sacrificial template. The prepared abrasives were characterized by small-angle XRD, FESEM, HRTEM, FTIR, TGA, nitrogen adsorption-desorption isotherm, and the corresponding pore size distribution. The results show that the $MSiO_2$ shells (70–80 nm in thickness) with radial pores are evenly coated on the external surfaces of the $SSiO_2$ cores (210–230 nm). The BET surface area of the prepared abrasives is 558.2 m^2/g. The mesochannels (2–3 nm in pore size) in the $MSiO_2$ shell are perpendicular to the surface of the $SSiO_2$ core. The topography, roughness, and profile curve of silicon wafers with a SiO_2 surface film of approximately 1200 nm were investigated by AFM before and after chemical-mechanical polishing in the presence of abrasives. By comparison with conventional abrasives $SSiO_2$, the composite abrasives favor decreasing the surface roughness and increasing the material removal rate of the polished wafers. The $MSiO_2$ shells of the prepared composite abrasives may contribute to optimizing the real interfacial contact between abrasives and wafer surface through certain mechanical and/or chemical effects.

KEY WORDS inorganic non-metallic materials, mesoporous silica, core-shell structure, composite abrasives, chemical mechanical polishing

Introduction

With the development of semiconductor technology, ultra-large-scale integrated circuits are advancing toward higher integration, larger wafer diameters, smaller feature sizes, and increased numbers of interconnect layers [1,2]. The continuous emergence of new materials and structures presents both novel opportunities and challenges for Chemical Mechanical Polishing (CMP) technology. From the perspective of micro-scale friction and wear, the key to achieving efficient damage-free polishing lies in regulating the interfacial contact state between abrasive particles and the workpiece, thereby improving the contact environment within local real contact regions [3,4].

As essential components of polishing slurries and carriers for mechanical removal, abrasive particles significantly influence polishing-induced defects, mechanical damage, and material removal rates. Developing abrasives with special structures, mechanical properties, and/or chemical characteristics through microstructural design guidance offers a promising approach for realizing efficient, damage-free polishing. Current research on novel polishing media materials primarily focuses on lattice-doped abrasives (Ce_1 Ti O_2 [5], x=0–0.3), core/shell structured composite abrasives (CeO_2/TiO_2 [6], SiO_2/CeO_2 [7], PS/CeO_2 [8,9], PS/SiO_2 [10], $PMMA/SiO_2$ [11], $PMMA/CeO_2$ [12,13]), and porous abrasives (Al_2O_3 [14], Al_2O_3/CeO_2 [15]).

Our research group previously investigated the synergistic effects between organic cores and inorganic shells in PS/SiO_2 and PS/CeO_2 composite abrasives through extensive comparative experiments [16]. Chen et al. [17] employed molecular dynamics simulations to analyze the contact process between porous SiO_2 abrasives and monocrystalline silicon substrates, examining how pore size affects indentation depth and adhesion effects, thereby providing guidance for pore design in this type of abrasive. Numerous polishing experiments have demonstrated that, compared with conventional inorganic abrasives, these novel structured abrasives positively impact polishing surface quality and removal rates for various materials including optical glass, computer hard disks, and copper interconnects in SiO_2 dielectric layers, showing significant potential for important applications.

Combining the design concepts of core/shell composite abrasives and porous abrasives offers a pathway to further improve polishing quality and material removal rates by optimizing both mechanical wear and chemical etching effects. In this work, we prepared homogeneous allotropic silica ($SSiO_2/MSiO_2$) composite abrasives with a regular spherical core/shell structure by coating a uniform, continuous mesoporous silica ($MSiO_2$) shell onto monodisperse solid silica ($SSiO_2$) cores using cetyltrimethylammonium bromide (a cationic surfactant) as a structure-directing template. We then evaluated the CMP performance of these $SSiO_2/MSiO_2$ composite abrasives on SiO_2 films under identical polishing conditions and compared them with conventional $SSiO_2$ abrasives, using AFM to analyze the substrate surface morphology, surface roughness, and micro-scale profiles.

1.1 Experimental Materials

Tetraethyl orthosilicate (TEOS), concentrated ammonia solution (28% aqueous solution), cetyltrimethylammonium bromide (CTAB), and anhydrous ethanol were all analytical grade and used without further purification. Deionized water was used throughout all experiments.

1.2 Sample Preparation and Characterization

Synthesis of Monodisperse $SSiO_2$ Cores: The $SSiO_2$ cores were first synthesized via the Stöber method [18]. In a typical procedure, 40 g of anhydrous ethanol, 5.4 g of deionized water, and 1.6 g of ammonia solution were sequentially added to a conical flask. After stirring uniformly, the mixture was heated in an oil bath to 35°C. Upon reaching temperature stability, a mixture of 2.3 g TEOS and 5 g anhydrous ethanol was slowly added dropwise. The reaction proceeded under continuous magnetic stirring for 3 h. The precipitate was then separated by centrifugation, washed with water and ethanol, dried in a blast oven at 80°C, and ground for subsequent use.

Preparation of $SSiO_2$/$MSiO_2$ Composite Abrasives: CTAB (0.16 g), anhydrous ethanol (9.95 g), and deionized water (30 g) were sequentially added to a beaker. After stirring for 10 min, $SSiO_2$ (0.1 g) was added. The resulting suspension was ultrasonicated for 30 min and then stirred for an additional 30 min to ensure further homogenization. Under magnetic stirring (300 r/min), ammonia solution (0.41 g) and TEOS (0.27 g) were sequentially added dropwise to the reaction mixture, which was then continuously stirred at 25°C for 12 h. The product was centrifuged, washed, dried, and finally calcined in a muffle furnace at 550°C for 4 h with a heating rate of 1°C/min.

Characterization: Sample morphology and structure were observed using a SUPRA 55 field-emission scanning electron microscope (FESEM) and a JEM-2100 high-resolution transmission electron microscope (HRTEM). Small-angle X-ray diffraction analysis was performed on a D/max 2500 PC diffractometer. Fourier-transform infrared (FT-IR) spectra were recorded on an Avatar 370 spectrometer. Thermogravimetric analysis (TGA) was conducted on an SDT Q600 thermogravimetric analyzer. Nitrogen adsorption-desorption isotherms were measured using an ASAP2010C surface area and porosity analyzer, with specific surface area and pore size distribution calculated using the Brunauer-Emmett-Teller (BET) equation and Barrett-Joyner-Halenda (BJH) model, respectively. Particle size distribution was determined using a Nano-ZS laser particle size analyzer.

1.3 Polishing Experiments and Evaluation

Polishing slurries with a mass concentration of 1% were prepared following the method described in references [10,16]. The pH value was adjusted to 8 using ammonia solution, and the slurry was ultrasonicated for 10 min before use. Polishing experiments were performed on a TegraForce-1/TegraPol-15 precision polisher under the following conditions: polishing pressure of 3 psi, upper/lower plate rotation speeds of 120/90 r/min, polishing time of 1 min, slurry flow rate of 100 mL/min, and MD-Chem polishing pad (Struers, porous polyurethane material). The thermal oxide SiO_2 film thickness on the silicon wafer substrates was approximately 1200 nm.

For comparison, conventional $SSiO_2$ abrasives (prepared by the Stöber method, 380–400 nm in diameter) were provided by the Jiangsu Key Laboratory of Solar Energy and Energy Storage Materials and Technology at Changzhou University. The preparation, solid content, and pH of the $SSiO_2$ abrasive slurry, as well as the polishing parameters, were identical to those described above.

Substrates were cleaned using an identical procedure and dried with nitrogen. A NanoScope IIIa MultiMode AFM (equipped with a Dimension V controller) operating in tapping mode was used to analyze the two-dimensional surface morphology before and after polishing, measuring the root-mean-square roughness (RMS) and micro-scale profile curves over a scanning range of 5 m × 5 m. The probe used was a Tap300Al-G (BudgetSensors) with a spring constant of approximately 40 N/m, resonance frequency of 300 kHz, tip radius less than 10 nm, and scanning rate of 1 Hz.

The material removal rate (MRR) during polishing was calculated using the method described in reference [16] (converting mass difference to thickness difference per unit time). All RMS and MRR data reported represent the average of three measurements.

Results and Discussion

2.1 Sample Structure

[Figure 1: see original paper] presents TEM images and particle size distribution curves of the $SSiO_2$ cores used for coating and the $SSiO_2$ abrasives used in comparative polishing experiments. The prepared $SSiO_2$ cores (Fig. 1a) exhibit regular spherical morphology with smooth surfaces and a narrow size distribution of approximately 210–230 nm. The $SSiO_2$ abrasives used for comparison (Fig. 1b) also show good dispersity with diameters of about 380–400 nm, which is essentially identical to the size range of the prepared $SSiO_2/MSiO_2$ composite abrasives (380–420 nm). The inserted size distribution curves indicate narrow particle size distributions, with average diameters of 219.9 nm and 399.6 nm measured by dynamic light scattering.

[Figure 2: see original paper] shows the FT-IR spectra and thermogravimetric curve of the $SSiO_2/MSiO_2$ composite abrasive sample before and after calcination. In the FT-IR spectrum of the sample before calcination (Fig. 2a), characteristic silica absorption peaks appear near 1091, 967, and 468 cm^{-1} [19], while CTAB characteristic peaks are observed near 2921, 2852, and 1486 cm^{-1} [20]. After calcination, the infrared spectrum shows only silica absorption peaks without CTAB peaks, indicating complete removal of the structure-directing template CTAB at 550°C. The TGA curve (Fig. 2b) reveals that weight loss occurs primarily in the 150–250°C range, attributed to decomposition of the CTAB template (decomposition temperature ~230°C [21]) in the composite abrasive shell during calcination.

[Figure 3: see original paper] displays FESEM images of the SSiO$_2$/MSiO$_2$ composite abrasives. The low-magnification image (Fig. 3a) shows that the coated composite abrasives are regularly spherical with uniform size and distribution, without obvious agglomeration. Compared with the original SSiO$_2$ cores, the composite abrasives exhibit significantly increased particle size (approximately 380–420 nm). The size distribution curve indicates a narrow distribution with an average diameter of 421.4 nm. Furthermore, no separate mesoporous SiO$_2$ particles are observed in Fig. 3a, confirming that the MSiO$_2$ shell coating on the SSiO$_2$ core surface is uniform and continuous without phase separation. The high-magnification image (Fig. 3b) reveals a slightly rough surface, though the porous structure cannot be directly observed, likely due to gold coating covering the mesopores or insufficient microscope resolution.

High-resolution TEM analysis of the SSiO$_2$/MSiO$_2$ composite abrasives is shown in [Figure 4: see original paper]. The low-magnification TEM image (Fig. 4a) shows clear contrast between the edge and core regions, confirming the core/shell structure. The MSiO$_2$ shell thickness is estimated to be approximately 70–80 nm. The high-magnification TEM image (Fig. 4b) reveals radial (worm-like) mesoporous channels in the shell layer with pore diameters of 2–3 nm. These radial channels differ from the parallel channels in conventional mesoporous silica materials such as MCM-41 [22]. The TEM results demonstrate that, under the direction of the CTAB template, the calcined composite abrasives possess a homogeneous allotropic core/shell structure with solid SiO$_2$ cores and mesoporous SiO$_2$ shells. The proposed formation mechanism is as follows: the SSiO$_2$ surface prepared by the Stöber method carries negative charges [18], and positively charged cationic surfactant CTAB adsorbs onto the SSiO$_2$ core surface via electrostatic interaction, forming radial micelles. TEOS undergoes sol-gel reaction under alkaline conditions, generating silica that coats the SSiO$_2$ core surface. The hydrolyzed silica and CTAB self-assemble through electrostatic interactions to form a networked, templated silica-gel micelle structure, which upon calcination removes the CTAB template and ultimately forms the MSiO$_2$ shell on the SSiO$_2$ surface.

[Figure 5: see original paper] presents the small-angle XRD pattern, nitrogen adsorption-desorption isotherm, and pore size distribution curve of the SSiO$_2$/MSiO$_2$ composite abrasive sample. As shown in Fig. 5a, the diffraction pattern exhibits a distinct (100) diffraction peak in the 2 = 2°–3° range. Compared with mesoporous SiO$_2$ (MCM-41), this diffraction peak is relatively broad, and no (200) or (110) peaks are observed. The presence of the (100) peak indicates the existence of mesopores but does not demonstrate long-range ordering of the mesoporous channels [23]. Both XRD and TEM (Fig. 4) results confirm the presence of SiO$_2$ mesoporous channels in the composite abrasive shell, albeit without long-range order. Fig. 5b clearly shows that the nitrogen adsorption-desorption isotherm is type IV with a pronounced H4-type hysteresis loop, characteristic of mesoporous materials [24]. The obvious desorption hysteresis in the medium relative pressure region may be related to capillary condensation of nitrogen in mesoporous channels at 77 K. The BET surface area of the sample is 558.2 m^2/g, significantly higher than that of solid SiO_2 particles of comparable size (380-400 nm, 13.1 m^2/g). The inserted BJH pore size distribution curve indicates uniform mesopore sizes of approximately 2.2 nm in the $MSiO_2$ shell, consistent with TEM observations. These mesopores in the composite abrasive shell are residual pores after removal of the CTAB template at 550°C.

2.2 CMP Performance Results and Analysis

[Figure 6: see original paper] shows two-dimensional AFM images of substrate surfaces over a 5 m × 5 m area before and after polishing (vertical scale: 5 nm). The initial substrate surface (Fig. 6a) is quite rough with noticeable linear scratches, exhibiting an RMS roughness of 0.902 nm. After polishing with $SSiO_2$ abrasives (Fig. 6b), the surface quality improves significantly, with an RMS value of 0.357 nm and a calculated MRR of 145 nm/min. Under our experimental conditions, the $SSiO_2$/$MSiO_2$ composite abrasives demonstrate superior polishing performance (Fig. 6c), achieving an RMS value of 0.189 nm and an MRR of 312 nm/min.

Further micro-scale profile analysis of the substrate surfaces before and after polishing was conducted using AFM ([Figure 7: see original paper]). For comparison, a diagonal line from each 2D AFM image was selected as the measurement position for profile curves. The results intuitively show that the initial substrate surface exhibits micro-scale fluctuations within $±$2 nm, which decrease to $±$1 nm and $±0.5nmafterpolishingwithSSiO_{2}$ abrasives and composite abrasives, respectively. These analyses demonstrate that, under equivalent particle size and identical polishing conditions, the prepared $SSiO_2$/$MSiO_2$ composite abrasives effectively reduce surface roughness, increase polishing rate, and minimize micro-scale profile fluctuations compared with conventional $SSiO_2$ abrasives.

The mechanical properties of porous materials differ significantly from those of bulk materials, showing reduced elastic modulus and hardness [25-27]. Moreover, the mechanical characteristics of porous materials can be tuned by controlling their internal pore structure, pore size, and porosity. For instance, Swain et al. [25] from the University of Sydney and Clément et al. [26] from the University of Lyon found that the elastic modulus and hardness of porous hydroxyapatite and porous calcium sulfate films decrease with decreasing pore size. Jauffrès et al. [27] from CNRS-INPG further noted that the pore structure of SiO_2 films significantly influences their fracture behavior: under external force, macroporous and hierarchically porous films undergo minimal elastic deformation followed by macropore collapse, whereas mesoporous films exhibit pronounced elastic recovery and elastoplastic transition.

Based on experimental results and the above analysis, $SSiO_2$/$MSiO_2$ composite abrasives exhibit high specific surface area and low hardness/elastic modulus compared with conventional $SSiO_2$ abrasives. From a mechanical perspective, the $MSiO_2$ shell may undergo micro-scale elastic deformation during abrasive-wafer contact, providing necessary cushioning and more gently transmitting polishing pressure to the workpiece surface. This facilitates increased contact area between abrasives and the wafer surface, reduced indentation depth, and consequently less mechanical damage. From a chemical perspective, the $MSiO_2$ shell can absorb and retain more polishing slurry through its abundant pore volume while utilizing its high specific surface area to enhance adsorption/release of active chemical components in the slurry. This promotes chemical reaction activity in the confined contact region between abrasives and the wafer surface, thereby increasing material removal rate. In summary, $SSiO_2/MSiO_2$ composite abrasives can improve the contact state and environment in local real contact regions between abrasives and the workpiece surface through their structural features, influencing material removal mechanisms and processes via synergistic mechanical and chemical effects. Consequently, compared with conventional $SSiO_2$ abrasives, $SSiO_2/MSiO_2$ composite abrasives achieve lower RMS roughness and higher MRR, demonstrating significant potential for efficient, damage-free polishing applications.

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3 Conclusion

Using cetyltrimethylammonium bromide as a structure-directing template enables in-situ coating of mesoporous silica ($MSiO_2$) onto solid silica ($SSiO_2$) cores, successfully synthesizing homogeneous allotropic $SSiO_2/MSiO_2$ core/shell composite abrasives. The composite abrasives consist of $SSiO_2$ cores (210–230 nm) and $MSiO_2$ shells (70–80 nm thickness) containing radial mesoporous channels (approximately 2-3 nm in diameter) oriented essentially perpendicular to the core surface. The specific surface area of these composite abrasives (558.2 m^2/g) is substantially higher than that of $SSiO_2$ particles (380–400 nm, 13.1 m^2/g). Polishing of SiO_2 film substrates with $SSiO_2/MSiO_2$ composite abrasives achieves an RMS roughness of 0.189 nm and MRR of 312 nm/min, which are significantly superior to those obtained with conventional solid $SSiO_2$ abrasives (0.357 nm, 145 nm/min). These results indicate that this type of homogeneous allotropic silica ($SSiO_2/MSiO_2$) core/shell composite abrasive is promising for achieving efficient, damage-free surface planarization.

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