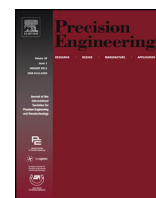




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# Core-shell structured polystyrene coated silica composite abrasives with homogeneous shells: The effects of polishing pressure and particle size on oxide-CMP

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## ABSTRACT

To improve the structural stability of the core-shell organic-inorganic composite abrasives during chemical mechanical polishing (CMP) processes, the polystyrene (PS) coated silica composites with homogeneous shells (amorphous silica networks, 15–20 nm in thickness) were synthesized via the sol-gel process of tetraethoxysilane at acidic aqueous condition in the presence of PS colloids (210–540 nm). Transmission electron microscopy and scanning electron microscopy were applied to characterize the as-synthesized samples. The effects of particle sizes and polishing pressures on oxide CMP performance were explored by atomic force microscopy. The results indicated that the obtained composite abrasives exhibited excellent polishing performance and structural stability during polishing processes. With the increase of the polishing pressures (13.8–41.4 kPa), the layer removal rate (RR) increased correspondingly, while the root-mean-square (RMS) roughness of polished substrates decreased firstly and then increased. Moreover, the RR and RMS for the composite abrasives increased with the increase of PS core sizes. At a given polishing pressure of 27.6 kPa, the highest RR ( $82.5 \pm 7$  nm/min) was obtained for the PS coated silica composites with largest cores (ca. 540 nm), while the lowest RMS roughness ( $0.189 \pm 0.02$  nm) was observed for the composites with smallest cores (ca. 210 nm). Furthermore, the polishing results in our CMP experiments were rationalized according to the indentation-based material removal mechanism (Chen et al. Appl Surf Sci 2012; 258:8469–74).

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## 1. Introduction

Chemical mechanical polishing (CMP) [1,2] is a widely used technique that allows precise abrasion of substrate surfaces with controlled chemical corruptions. In a typical CMP process, a rotating substrate is pressed against a rotating polishing pad while slurry, containing chemical additives and abrasive particles, is fed into the wafer-pad contact area. Many parameters [3–6] are involved in a CMP process, such as the properties of pad, type of abrasive, polishing pressure, relative velocity between the pad and the wafer, chemical components of slurry and slurry flow rate.

In recent years, many efforts have been devoted to the fabrication of the core-shell organic-inorganic composite abrasives (polymethylmethacrylate (PMMA) coated  $\text{SiO}_2$  [7], PMMA coated  $\text{CeO}_2$  [8,9], polystyrene (PS) coated  $\text{SiO}_2$  [10], PS coated  $\text{CeO}_2$  [11]) due to their potential application in achieving defect-free polishing

surfaces. By comparison with conventional solid abrasives, the organic-inorganic composites exhibit special non-rigid mechanical properties (low hardness and low elastic modulus) [12–14]. The polymer cores of the composites can elastically deform and gently transfer the polishing pressure onto the substrate surfaces, which can be in favor of increasing the real contact area between wafer and abrasive and decreasing the contact stress. However, it is worthwhile to note that the inorganic shells for the composites mentioned above are composed of nano-sized inorganic particles, which can be partially exfoliated during the contact process among pad, abrasive and substrate. As a result, some residual nanoparticles can be observed on the polished substrate surfaces and resulted in secondary pollution.

To improve the structural stability of composite abrasives during CMP processes, the PS coated silica composite abrasives with homogeneous shells were fabricated via a modified Stöber procedure [15] that involved the hydrolysis of tetraethoxysilane under acidic condition in the presence of PS colloids with different size. The effects of polishing pressures and composite particle sizes on oxide CMP performance were investigated by atomic force

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microscopy. Furthermore, the CMP results were discussed according to the existing contact area [16,17] and indentation-based material removal mechanism [18,19].

## 2. Experimental

### 2.1. Materials

The monomers of styrene (St, Shanghai Chemical Reagent Company) were purified by treatment with 5 wt.% aqueous NaOH solutions to remove the inhibitor prior to use. 2,2'-azobis(2-methylpropionamidine) dihydrochloride (AIBA) was obtained from Aladdin chemical Company. Poly(vinylpyrrolidone) (PVP,  $M_w = 30,000$ ), ethanol, HCl (37.5 wt.% aqueous solution), aqueous ammonia solution (28 wt.%), sodium dodecyl benzene sulfonate (SDBS), tetraethoxysilane (TEOS) were purchased from Shanghai Chemical Reagent Co. (China) and used as received. Deionized water was employed in the present study.

### 2.2. Synthesis of the core-shell PS coated silica composites

The first synthesis step involved the preparation of monodispersed PS colloids with controlled size via soap-free polymerization [20] in the presence of PVP. The typical synthesis was introduced as follows. 180 g of water, 9 g of St and a certain amount of PVP were added into a three-necked flask at room temperature. This mixture was deoxygenated by bubbling  $N_2$  for 30 min, and then heated to 70 °C under vigorously stirring at 300 rpm. Subsequently, 0.2 g of AIBA (dissolved in 15 g water) was added into the mixture to initiate polymerization. Finally, the reaction was performed with constantly stirring at 70 °C for 24 h under  $N_2$  protection. The samples obtained with PVP amounts of 4.5, 3 and 0 g were denoted as P1–P3, respectively.

The next step involved the synthesis of PS coated silica composites via the sol-gel process [21] using the obtained PS spheres as cores. Briefly, 5 g of the PS colloids was diluted with 10 g of water and 40 g of ethanol. The mixture was initially dispersed by means of an ultrasonic bath. Then, the pH of the dispersion was adjusted to 2 by HCl, and the mixture was slowly heated to 60 °C, followed by slow addition (5 g/h) of the mixed solution containing 3 g of TEOS and 10 g of ethanol. The reaction was performed for 5 h under constant magnetic stirring. The resulting products were collected by centrifugation, washed thrice with water and dried overnight. The samples obtained with different PS cores (P1–P3) were denoted as C1–C3, respectively.

The dimensions and structural details of the samples were characterized by a JSM-6360LA (JEM, Japan) scanning electron microscope (SEM), a SUPRA 55 (Zeiss, Germany) field emission SEM (FESEM) and a JEM-2100 (JEOL, Japan) transmission electron microscope (TEM).

### 2.3. Polishing tests

As a contrast, conventional silica particles with size of ca. 400 nm were obtained from Jiangsu key laboratory for solar cell materials and technology. Polishing slurries were formulated by dispersing the PS coated silica composites or solid silica particles in deionized water. A certain amount of SDBS (0.5 wt.%, based on the total weight of the abrasive particles) was added as dispersant. For each slurry, the pH was adjusted to 8 by 0.1 M NaOH solution. The solid loading of slurry was fixed to 1 wt.%.  $SiO_2$  films (1.1–1.2  $\mu m$  in thickness) were grown on silicon substrates by a thermal oxidation method. Polishing tests were performed on a TegraForce-1/TrgraPol-15 rotary CMP platform (see Fig. 1) for 1 min. Porous polyurethane pads (MD-Chem, Struers) were utilized as polishing pads, and the polishing pressure was 13.8–41.4 kPa. The rotation speeds of the



Fig. 1. Photograph of the TegraForce-1/TrgraPol-15 polisher.

head and platen were set at 120 and 90 rpm, respectively. The slurry flow rate was 100 mL/min.

The thickness of the  $SiO_2$  film before and after polishing was determined by ellipsometry (ELLIP-SR-II, Shanghai Bright Enterprise Development Co., Ltd.) to calculate the layer removal rate (RR, nm/min). The standard deviation on the thickness measurement is  $\pm 1$  nm. An atomic force microscope (AFM, Nanoscope Dimension V, Bruker) was used to evaluate the root-mean-square (RMS) roughness values of the wafers as well as the topographies and profilograms of the surface after CMP. Silicon tips used in tapping mode were obtained from BudgetSensors (Tap300Al-G) with tip radius smaller than 10 nm. The resonance frequency of the tip was 300 kHz, and the scanning rate was 1 Hz. The sample/line was 512. The spring constant of the tip was about 40 N/m. For supporting the validity of the results, the polishing data (removal rate and surface roughness) were the average of three runs.

## 3. Results and discussion

### 3.1. SEM and TEM of samples

Fig. 2 shows the SEM images of the PS microspheres, PS coated silica composites and solid silica particles. The spherical and monodisperse PS particles exhibited the diameter of ca. 210 (P1), 280 (P2) and 540 nm (P3). After the silica coating on the PS cores, the resulting PS coated silica composites were also spherical in shape and rougher than the uncoated cores. And the sizes of the PS coated silica composites increased to ca. 240 (C1), 320 (C2) and 580 nm (C3), respectively, indicating the silica shells were 15–20 nm in thickness. In addition, the uniform size of the solid silica particles for polishing tests was about 400 nm.

The detailed structural characteristics of the bare PS cores (P1) and PS coated silica composites (C3) were further analyzed by TEM (Fig. 3). The evident contrast between the core and the shell was clearly observed, and a well-defined core-shell structure was formed. In addition, the composites were smooth in surface, suggesting that the deposition of silica onto the PS cores occurred in

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