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Atomic force microscopy indentation to determine mechanical property for polystyrene–silica core–shell hybrid particles with controlled shell thickness

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ABSTRACT

The positively charged polystyrene (PS) particles with a size of ca. 200 nm were synthesized by soap-free polymerization. The PS cores were coated with silica shells of tunable thickness employing the modified Stöber method. The PS cores were removed by thermal decomposition at 500 °C, resulting in well-defined silica hollow spheres (10–30 nm in shell thickness). The elastic response of the as-synthesized samples was probed by an atomic force microscope (AFM). A point load was applied to the particle surface through a sharp AFM tip, and the force–displacement curves were recorded. Elastic moduli (E) for the PS particles (2.01 ± 0.70 GPa) and the core–shell structured hybrid particles were determined on the basis of Hertzian contact model. The calculated E values of composites exhibited a linear dependence on the silica shell thickness. While the shell thickness increased from ca. 10 to 15 and 20 nm, the E values of composites increased from 4.42 ± 0.27 to 5.88 ± 0.48 and 9.07 ± 0.94 GPa. For core–shell structured organic/inorganic composites, the E values of the hybrid particles were much lower than those of inorganic shells, while these values were much close to those of organic cores. Moreover, the moduli of elasticity of the composites appeared to be determined by the properties of the polymer cores, the species of inorganic shells and the thickness of shells. Besides, the inorganic shells enhanced the mechanical properties of the polymer cores. This work will provide essential experimental and theoretical basis for the design and application of core–shell structured organic/inorganic composite abrasives in chemical mechanical polishing/planarization.

1. Introduction

Chemical mechanical polishing/planarization (CMP) [1] is a critical technique in the fabrication of ultra-large scale integrated circuits (ICs). With the decrease of the feature size of ICs, a large number of materials and structures have been applied in the manufacturing process. For example, next generation ICs will require the use of lower dielectric constant porous materials other than silica. However, porous dielectric materials often suffer mechanical damages during CMP [2,3]. Accordingly, CMP technology confronts the important opportunities and great challenges.

Typical polishing slurries contain abrasive particles and chemical reagents. It is commonly believed that a chemical reaction softens the material during mechanical abrasion in CMP process [1]. For improving the surface quality, it is critical to control the mechanical properties of abrasives and their interactions with the polished surfaces [4,5]. Moreover, the behavior of abrasives is mainly determined by the structures and morphologies of the particles.

Up to date, composite particles and porous particles have been introduced to CMP process as abrasives. In order to increase the material removal rate (*MRR*) for ZF7 glass, Fu et al. [6] synthesized the titanium-doped ceria $Ce_{1-x}Ti_xO_2$ (x = 0–0.3) powders via wet-solid phase mechanochemical processing. The improvement of *MRR* might be attributed to the enhancement of the interfacial interaction between abrasives and wafers. Kang et al. [7] proposed an approach of precipitating Fe nanoparticles on the surfaces of colloidal silica to improve the dispersion stability. W-CMP results indicated that the W removal rate was a strong function of both Fe ions and peroxide concentration. In recent years, core–shell structured composite abrasives, such as SiO_2/CeO_2 [8], polymethylmethacrylate (PMMA)/SiO_2 [9], PMMA/CeO_2 [10], polystyrene (PS)/CeO_2 [11,12] and PS/SiO_2 [13,14], have become a hot research topic in CMP technology. SiO_2- and Cu-CMP tests showed that the core–shell composite abrasives were in favor of increasing *MRR* and decreasing mechanical damage due to the synergistic effect of a core and a shell. Furthermore, Lei et al. developed a series of porous abrasives (Al_2O_3 [15], Cu-incorporated Al_2O_3 [16], Fe_2O_3/SiO_2 [17] and Al_2O_3/CeO_2 [18]) by sol–gel method and hydrothermal method. For hard disk substrate CMP, it was found that the surfaces polished with porous abrasives exhibited a larger *MRR*, lower topographical variation

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and surface roughness than those of polished with traditional solid abrasives.

Although the non-traditional abrasives mentioned above have exhibited an important potential application in efficient and damage-free polishing, the actual material removal mechanism of the composite and/or porous abrasives is still unclear. The applications of non-traditional abrasives in CMP technology require direct insight into the particles' mechanical properties, such as elastic modulus (E), Poisson ratio (ν), hardness (H), interfacial adhesion and friction, as well as their size-dependent effects [4]. In order to acquire quantitatively this information, different measurement methods have been developed, mainly including nano-indentation with an atomic force microscope (AFM) [19,20], in-situ compression, bend and tension [21,22] by a transmission electron microscope–scanning probe microscope (TEM–SPM) platform. So far, in-situ high resolution TEM is considered as the most advanced instrument to accurately measure the mechanical properties of micro/nano-scaled samples. For example, Huang et al. [21] investigated the compressive deformation, fracture mechanisms and the fracture strength of individual GaN nanowires in real time using a TEM–SPM platform. The dislocation nucleation from a free surface and plastic deformation between the SPM probe and the sample contact surface were observed in-situ. Moreover, Tang et al. [22] analyzed the tensile properties of multiwalled WS_2 nanotubes under uniaxial tension using in-situ TEM tests. It was found that the thick WS_2 nano-tubes could sustain a much higher tensile force than "defect-free" thin nano-tubes. Unfortunately, the measurement processes of mechanical property with a TEM–SPM platform are commonly very complicated.

AFM nano-indentation technique is considered as a convenient method for detecting the elastic behavior of the samples by force–displacement curves and nano-indentation data. In the past, there has been a significant progress in the quantification of the mechanical properties of various materials by AFM. For thin films, Passeria et al. [23] reported the measurement of elastic modulus and hardness of polyaniline films on glass substrates using an AFM tip as an indenter. Nowatzki et al. [24] calculated the E values of the obtained films by a thin-film Hertz model. Besides, Song et al. [25] investigated the elasticity of cross-linked poly(dimethylsiloxane) with Sneddon's contact mechanics theory using AFM data by employing the hyperboloid tip shape model. Furthermore, AFM can also be applied to measure the mechanical properties of one-dimensional nano materials by performing a nano-scale three-point bending test, in which an AFM cantilever was used to apply a known force on the center of the fiber. For example, Guhados et al. [26] measured the elasticity of bacterial cellulose fibers (35–90 nm in diameter), and determined an E of 78 ± 17 GPa. Iwamoto et al. [27] determined the E values for single microfibrils from tunicate (*Halocynthia papillosa*) cellulose. For biological materials, Hansen et al. [28] used AFM and Hertz model to examine the hypothesis that nano-scale topography affects osteoblastic cell modulus. In addition, Touhami et al. [29] measured quantitatively the local mechanical properties of hydrated yeast cells, and the obtained force–indentation curves were fitted with the Hertz model. For particle samples, Tan [30] and Armini et al. [31] evaluated the E values of PS, PMMA spheres and PMMA/SiO_2 composites by AFM force volume technique and Hertz's theory of contact mechanics. Besides, Zhang et al. [32] investigated the mechanical properties of hollow silica spheres (15–70 nm in shell thickness), and the calculated Young's modulus (18 ± 6 GPa) was about 4 times smaller than that of fused silica (72 GPa [33]). In our previous work [34], the elastic deformation of the PS/CeO_2 composites deposited on a rigid substrate was evaluated by measuring the AFM force curve technique.

Herein, we report the results of our experiments on the core–shell structured PS/SiO_2 hybrid particles with different shell thicknesses, which were controlled by changing the concentration of tetraethoxysilane. The elastic response of the PS particles and PS/SiO_2 hybrid particles was investigated by AFM force curve technique, and the E values of samples were calculated based on the Hertzian contact model. In particular, we focus on the effect of the shell thickness of the as-synthesized composites on the compressive elastic moduli. Moreover, this work aimed at detecting relative changes in elastic properties rather than focusing on absolute values.

2. Experimental details

2.1. Materials

Styrene (St) was 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 Co., Ltd. Poly(vinylpyrrolidone) (PVP, M_w = 30,000), tetraethoxysilane (TEOS), ethanol, and ammonia ($NH_3 \cdot H_2O$, 28–30% aqueous solution) were purchased from Shanghai Chemical Reagent Co. (China). Deionized water was applied for all polymerization and treatment processes.

2.2. Synthesis of PS latex and PS/SiO_2 hybrid particles

The monodisperse PS particles with size around 200 nm were synthesized by soap-free polymerization [11]. Typically, 9 g St, 180 g H_2O and 4.5 g PVP were added to a 250 mL four-necked flask equipped with a magnetic stirrer, a thermometer with a temperature controller, a N_2 inlet and a water-cooled reflux condenser. The mixture was deoxygenated by bubbling nitrogen gas for 30 min, then heated at 70 °C, followed by addition of an aqueous solution containing AIBA (0.18 g, dissolved in 15 g water). After 24 h, the positively charged PS emulsions were obtained with a solid content of ca. 5 wt.%.

The SiO_2 was coated on the surfaces of PS cores following a modified Stöber process [35] that involved the hydrolysis of TEOS in aqueous solution. A typical process was carried out as follows: 5 g PS emulsion, 40 g ethanol and 10 g H_2O were charged in a 250 mL flask equipped with a magnetic stirrer. After that, the pH of the dispersion was adjusted to 8 by $NH_3 \cdot H_2O$. Subsequently, the reaction mixture was slowly heated to 60 °C, followed by slow addition (5 g/h) of the mixed solution (a certain amount of TEOS dissolved in 10 g ethanol). The reaction was performed with vigorous magnetic stirring for 5 h. The resulting precipitates were separated by centrifugation at 5000 rpm, washed with ethanol and dried at 80 °C for 24 h to yield dried powders. The samples obtained with TEOS amounts of 1.5, 3 and 4.5 g were denoted as A1–A3 respectively.

The SiO_2 hollow microspheres were obtained after removing the PS cores. The hybrid particles were heated to 500 °C at a rate of 2 °C/min, kept at 500 °C for 2 h in air, and then cooled to room temperature.

The structures of the samples were studied by a JEOL-2100 transmission electron microscope (TEM) operated at an acceleration voltage of 200 kV. Scanning electron microscopy (SEM) was carried out with a JSM-6360LA (JEM, Japan) and a SUPRA 55 (Zriss, Germany) field emission SEM (FESEM). Fourier transform infrared (FT-IR) spectra were measured with a Nicolet Avatar 370 spectrophotometer using the KBr method.

2.3. AFM imaging and force curves

AFM imaging and force–displacement curves of the obtained samples were recorded with an atomic force microscope (ICON, Bruker, Germany) under ambient conditions of 25 °C and 50% relative humidity. All measurements were performed using commercial silicon rectangular cantilevers (NSG-10, NT-MDT, Russia) with an approximate tip radius of 10 nm determined by SEM. The spring constants (K_c, 3.1–37.6 N/m, typical K_c is 11.8 N/m) of the cantilevers were checked prior to each experiment by the thermal noise method.

Hydrophobic treated silicon oxide wafers were used as hard nondeformable substrates, and the samples were dispersed on the