Applied Surface Science 290 (2014) 433–439

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Compressive elastic moduli and polishing performance of non-rigid core/shell structured PS/SiO_2 composite abrasives evaluated by AFM

Ailian Chen[a], Weibin Mu[b], Yang Chen[b,*]

[a] College of Mechanical and Energy Engineering, Changzhou University, Changzhou, Jiangsu 213016, PR China
[b] School of Materials Science and Engineering, Changzhou University, Changzhou, Jiangsu 213164, PR China

ARTICLE INFO

Article history:
Received 17 July 2013
Received in revised form
18 November 2013
Accepted 19 November 2013
Available online 28 November 2013

Keywords:
Core/shell composite microspheres
Compressive Young's modulus
Chemical mechanical polishing

ABSTRACT

The core/shell structured polystyrene (PS)/SiO_2 composite microspheres with different silica shell morphology were synthesized by a modified Stöber method. As confirmed by transmission electron microscopy (TEM), the rough discontinuous shell consisted of separate SiO_2 nanoparticles for composite-A, while the smooth continuous one was composed of amorphous silica network for composite-B. Atomic force microscopy (AFM) was employed to probe the compressive Young's moduli (E) and chemical mechanical polishing (CMP) performances of the as-prepared PS/SiO_2 composite microspheres. On the basis of the Hertzian contact mechanics, the calculated E values of the PS microspheres, composite-A and composite-B were 2.9 ± 0.4, 5.1 ± 1.2 and 6.0 ± 1.2 GPa, respectively. Compared to traditional abrasives, thermally grown silicon oxide wafers after polished by the core/shell PS/SiO_2 composite abrasives obtained a lower root mean square roughness and a higher material removal rate value. In addition, there is an obvious effect of shell morphology of the composites on oxide CMP performance and structural stability during polishing process. This approach would provide a basis for understanding the actual role of organic/inorganic core/shell composite abrasives in the material removal process of CMP.

1. Introduction

Core/shell structured organic/inorganic composite microspheres of various compositions have been attracted much attention, because of their enhanced properties including mechanical, chemical, electrical, rheological, magnetic, and optical [1–7]. To date, these kinds of composite microspheres are mainly applied in the area of drug delivery, coatings, catalysis, colloidal crystals, diagnostics and so on.

Chemical mechanical polishing (CMP) has been commonly used to planarize a variety of materials including dielectrics, semiconductors, metals, optical glasses and ceramics. CMP involves removal of materials by a unique combination of chemical and abrasive action to achieve highly planar and ultra-smooth surfaces [8]. Core/shell organic/inorganic composite microspheres as a novel abrasives have an important potential application in efficient and damage-free polishing due to their uniform non-rigid mechanical property. In recent years, the novel organic/inorganic composite abrasives of various core or/and shell compositions, such as polymethylmethacrylate (PMMA)/SiO_2 [9,10], PMMA/CeO_2 [11], ceria/polymer [12], polystyrene (PS)/CeO_2 [13,14] and PS/SiO_2 [15,16], have been introduced in CMP process. Polishing results indicated clearly that the composite abrasives with core–shell structure were beneficial for damage-free polishing in the final stage of CMP process, especially in the context of new challenging materials, such as Cu and low-k dielectrics. The improvement of CMP performance might be attributed to a synergistic effect of the core/shell structure. The spring-like effect resulting from the elastic polymer core could increase the contact area between wafer and abrasives and decrease the contact stress during CMP, in favor of reducing roughness and mechanical damage. The inorganic shell could stiffen the polymer core and enhance the mechanical properties of composite abrasives.

Although there have been a large number of reports on the syntheses, characterization and polishing performance of the organic/inorganic core/shell composite abrasives, the damage-free polishing mechanism of composite abrasives is not clear. Therefore, it is necessary to characterize the mechanical properties (such as Young's modulus, Poisson ratio, and hardness) of the composite abrasives. At micro/nano-scale, direct measurement of force during controlled displacement of a compliant cantilevered probe obtained by an atomic force microscopy (AFM) has been considered as an ideal method for detecting mechanical properties (stiffness and strength). From the contact lines of force–displacement curves obtained by AFM, it is possible to obtain information about the elastic-plastic behavior of samples [17,18]. Usually, the elastic deformation of samples is described by Hertz's and Sneddon's contact model and the compressive Young's modulus (E) are

* Corresponding author. Tel.: +86 519 86330066.
E-mail address: cy.jpu@126.com (Y. Chen).

0169-4332/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2013.11.100

calculated by using different geometries. During the past decades, there has been significant progress in the quantification of the mechanical properties of various materials by AFM including thin films [19–21], fibers [22,23], biological materials [24,25], polymer microspheres [26], core/shell organic/inorganic composite microspheres [27,28] and hollow microspheres [29]. In our previous work [28], the deformation of the core/shell PS/CeO_2 composite microspheres with different core size and/or shell thickness on rigid substrates was evaluated by measuring the force–displacement curves with an AFM cantilever tip. Hertz's model for contact mechanics was employed to analyze the Young's modulus of the composites. The calculated E values of the PS/CeO_2 composite microspheres were 5–15 GPa, which were much lower than that of pure CeO_2 and close to the pure PS.

The aim of the current study is to undertake an in-depth investigation of the effects of shell morphologies on the compressive Young's moduli (E) and CMP performances of the PS/SiO_2 composite microspheres. The positively charged PS microspheres were firstly synthesized by soap-free emulsion polymerization method. The PS/SiO_2 composite microspheres with different silica shell morphology, including raspberry-like discontinuous shell composed of SiO_2 nanoparticles and homogeneous continuous shell, were prepared using a modified Stöber procedure [30] that involved the hydrolysis of TEOS under alkaline and acidic condition, respectively. The effect of the silica shell morphology of the as-synthesized composites on the compressive modulus and oxide-CMP behavior was investigated by AFM. Moreover, this approach would provide a basis for understanding the actual role of organic/inorganic core/shell composite abrasives in the material removal process of CMP.

2. Experimental

2.1. Materials

Styrene (St) was purchased from Shanghai Chemical Reagent Co. (China) and purified by treating with 5 wt% of aqueous NaOH solution to remove the inhibitor. Absolute ethanol, acetone, sodium hydroxide, HCl (supplied as 37.5% aqueous solution), aqueous ammonia solution (28 wt%) and tetraethoxysilane (TEOS) were purchased from Shanghai Chemical Reagent Co. (China) and used as received. Azodiisobutyramidinedihydrochloride (AIBA) was purchased from Aldrich (USA) and used as received. Commercial SiO_2 particles (10–20 and 450–500 nm in diameter) were purchased from Yuda Chemical Co., Ltd China. Deionized water was used throughout the experiment.

2.2. Synthesis of PS/SiO_2 composite microspheres

The positively charged PS microspheres were prepared *via* the soap-free emulsion polymerization method [31,32]. Briefly, St (9 g) and water (180 g) were charged into a 250 mL round-bottom flask equipped with a magnetic stirrer, a thermometer with a temperature controller, and a N_2 inlet. Then the above mixture was deoxygenated by bubbling nitrogen gas at room temperature for 30 min and heated to 60 °C under constant stirring, followed by addition of an aqueous solution (0.18 g AIBA in 15 g water). The reaction was allowed to proceed for 24 h at 70 °C, and then cooled to room temperature. Finally, the positively charged PS microspheres were obtained.

The coating reaction was carried out *via* the hydrolysis and condensation of TEOS, and yielded amorphous silica at alkaline and acidic aqueous media in the presence of PS colloids, respectively. A typical process to prepare silica-coated PS spherical colloids was described as follows: 5 g of the as-obtained PS dispersion was diluted with 10 g of water and 40 g of absolute ethanol. pH of the colloid dispersion was adjusted to 8 by $NH_3{\cdot}H_2O$. Then, the reaction mixture was slowly heated to 60 °C, followed by slow addition (5 g/h) of the mixed solution (3 g TEOS in 10 g ethanol). The reaction was performed for 5 h under constant magnetic stirring. After that, the reacting mixture cooled to room temperature and the resulting composite particles were recovered by repeated centrifugation at 5000 rpm, washed several times and dried overnight. Finally, the core/shell structured PS/SiO_2 composite microspheres obtained under alkaline condition were denoted as composite-A. The composite-B was prepared under acidic condition in a similar approach as above except that HCl was used to adjust pH to 2.

The morphology and particle size of the as-prepared products were observed on a field emission scanning electronic microscope (FE-SEM, S4800, Hitachi) at an accelerating voltage of 15 kV. The core–shell structure of the as-synthesized samples was also characterized by transmission electronic microscopy (TEM, JEM-2100, JEOL) at an accelerating voltage of 200 kV. Thermogravimetric analysis (TGA) was carried out on a thermal analyzer (SDT Q600TA).

2.3. AFM indentation testing

All AFM experiments were performed with a Nanoscope Dimention V scanning probe microscope (Digital Instruments). Topographic images and force–displacement curves were obtained in contact mode for all samples in air and at room temperature. Silicon cantilevers (NSG 10, NT-MDT, Russia) with a tip radius of ~10 nm and spring constant of $K_c = (11 \pm 0.5)$ N/m were used. The cantilever spring constants were determined prior to each experiment by the thermal noise method [33]. In this work, in order to eliminate the effect of the abrasion of the tip, we used a new tip for every AFM experiment. In order to verify whether the abrasion occurred, we have imaged a standard sample before and after AFM indentation to check any possible drift in the measurement. It can be concluded that the tip could still be useful before and after indentation, verifying that there was a slight variation of the tip radius. Furthermore, the value of the tip radius given by the manufacturer is less than 10 nm, and we used the upper limit value for calculation.

The polished thermally grown silicon oxide wafers, which were used as hard non-deformable rigid substrates for photodetectors sensitivity calibration, were ultrasonically cleaned with acetone followed by deionized water. They were then treated with a Piranha solution (7:3, v/v, 98% H_2SO_4/30% H_2O_2) to obtain a hydrophilic surface. After rinsed with deionized water, the wafer substrates were dried in a nitrogen gas flow. A drop of the corresponding solution containing the microspheres was spin-coated onto the treated wafer substrate, and was slowly dried under vacuum.

Mechanical testing was performed using the force-volume mode. And the force-volume images consisting of a two-dimensional array (10 × 10) for force–displacement measurements were recorded. In our measurement, when the speed of the piezo was varied in the range of 0.1–10 μm/s, no difference was observed, which allowed us to interpret the data in terms of pure elastic response (no viscoelasticity effects). The piezo system moved vertically with a constant scan rate of 1 Hz, and the force curves were recorded at rate of 2 μm/s (piezo displacement). The experimental deflection-height curves were transformed into the corresponding load-indentation curves. To calculate the Young's moduli, we analyzed at least 10 force curves measured 3–5 randomly selected microspheres. Mean values were obtained by fitting at least 8 force–indentation curves obtained from different microspheres. In this work, measurements taken not exactly on top of the samples or when the particles moved during indentation resulting in atypical force curves were ignored in our analysis.