Microelectronic Engineering 96 (2012) 51–55

Contents lists available at SciVerse ScienceDirect

Microelectronic Engineering

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

Synthesis of non-rigid core–shell structured PS/SiO_2 composite abrasives and their oxide CMP performance

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ARTICLE INFO

Article history:
Received 21 August 2011
Received in revised form 11 January 2012
Accepted 23 February 2012
Available online 24 March 2012

Keywords:
PS/SiO_2 composite abrasives
Core–shell structure
Chemical mechanical polishing (CMP)

ABSTRACT

The positively charged PS microspheres were prepared via soap-free emulsion polymerization method by using azobisisobutyronitrile (AIBN) as initiator. Tetraethylorthosilicate (TEOS) hydrolysis catalyzed and the negatively charged SiO_2 could be absorbed onto the surfaces of the positively charged PS microspheres. The microstructures of the composites were characterized by scanning electron microscope (SEM), transmission electron microscope (TEM), fourier transform infrared spectrum (FT-IR), and X-ray diffraction (XRD). The composites were collocated into polishing slurries for the chemical mechanical polishing (CMP) of silicon dioxide dielectric layer. The dielectric layers were investigated by atomic force microscope (AFM). The results indicated that the particle size of composites is about 550 nm, and the PS microsphere is uniformly coated by SiO_2 shell (about 20 nm in thickness). After CMP, the composite abrasives led to lower topographical variations and surface roughness, compared with pure SiO_2 abrasives and PS microspheres. The root mean square (RMS) value within 5×5 μm area of dielectric layer polished by PS/SiO_2 composite abrasives is 0.209 nm, and the material removal rate (MRR) can reach 367.1 ± 48.0 nm/min.

1. Introduction

Recently, the synthesis of polymer/inorganic composite microspheres has received much attention because such these hybrid particles can possess combined properties of both incorporated inorganic materials and base polymers [1]. The polymer/inorganic composite particles have found diverse applications as drug-delivery system, diagnostic, coating and catalyst because of their novel and excellent properties such as mechanical, chemical, electrical, magnetic and catalytic, by varying their composition, dimension, and structure of the materials [2–7].

For example, Fang et al. [8] prepared novel core–shell structured polystyrene (PS)/Fe_3O_4 microbeads via a facile method to improve magnetorheological (MR) performances. The results indicated that the PS/Fe_3O_4 microbeads can improve MR performances due to its smaller density compared with most magnetic materials. Li et al. [9] prepared high-quality and stable PS/TiO_2 core–shell microsphere colloidal crystals by electrostatic colloid stabilization combined with two-substrate vertical deposition method. The results showed these colloidal crystals were gifted with higher mechanical stability than TiO_2 microspheres. Zhu et al. [10] prepared magnetic drug capsules via layer-by-layer (LBL) self-assembly by dissolving the MF microspheres core. The results indicated that the capsules containing drugs had fine magnetic response and drug-delivery. Liang et al. [11] synthesized TiO_2-coated coarse nylon and polyethylene particles composite abrasives. The results indicated that the composite particles helped to improve the attenuation of the UV spectrum as compared with pure TiO_2.

Chemical mechanical polishing (CMP) is the only finish machining technique up to date for surface global planarization [12]. With a demand of decreasing surface roughness and defects and increasing material removal rate (MRR), it is found that just one kind of abrasive was hardly up to the requests. Recently, some researchers have attempted to apply the modified and/or core–shell structured composites to CMP due to the unique properties. Zhang et al. [13] prepared monodisperse polystyrene/silica core–shell nano-composite abrasive, and the Cu-CMP performance was also investigated. Zhang and Lei [14] and Lei et al. [15] modified α-alumina abrasives by polymethacrylic and polyacrylamide, respectively. The polishing tests results showed that the modified abrasives exhibited a better CMP performance on glass substrate than pure α-alumina abrasives. The improvement of CMP behavior might be attributed to better dispersion stability. Cecil et al. [16] prepared the composite particles which contained nanoparticles of CeO_2 dispersed within cross-linked polymeric microspheres, and studied their oxide CMP performance. Chen et al. [17,18] reported a simple and efficient route to fabricate well-defined PS/CeO_2 core–shell microspheres and studied the effect of shell thickness on silicon dioxide CMP. Armini et al. [19–22] prepared composite PMMA core-silica shell

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0167-9317/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.mee.2012.02.047

abrasives by either using silane-coupling agents or tuning pH in order to form electrostatic attractive interactions between the core and the shell, and investigated their CMP behavior for copper and SiO_2 dielectric layers. The experimental result indicated that the composite particles resulted in reduced defectively after CMP. But, the method was complicated and the shell composed of large SiO_2 particles was incomplete, which might easily result in scratches.

In this work, we design a simple and novel method to synthesis core–shell structured PS/SiO_2 composite microspheres. The positively charged PS microspheres were prepared via soap-free emulsion polymerization method by using azobisisobutyronitrile (AIBN) as initiator. Tetraethylorthosilicate (TEOS) hydrolysis catalyzed and the negatively charged SiO_2 could be absorbed onto the surfaces of the positively charged PS microspheres. The SiO_2 shell completely appeared as an amorphous structure around the PS core. We firstly applied the novel core–shell structured PS/SiO_2 composite abrasives to improve oxide CMP performance.

2. Experimental

2.1. Materials

The monomers of styrene (St) supplied from Shanghai Chemical Reagent Co. (China) was purified by treatment with a 5 wt.% aqueous NaOH solution to remove the inhibitor.

Polyvinylpyrrolidone (PVP), azobisisobutyronitrile (AIBN), tetraethylorthosilicate (TEOS), ammonia solution ($NH_3 \cdot H_2O$), deionized water and ethanol were used in the synthesis. Above chemicals were purchased from Shanghai Chemical Reagent Co., (China) and used as received.

2.2. Synthesis of PS microspheres

The PS microspheres were prepared by soap-free emulsion polymerization. Deionized water (100 mL), St (5 g), and PVP (0.5 g) were charged into a 250 mL three-neck flask equipped with a magnetic stirrer, a thermometer with a temperature controller and a N_2 inlet. In a typical process, the nitrogen was used to eliminate the inhibition effect of oxygen. The solution was heated to 75 °C and stirred for 15 min. Then, AIBN (0.125 g, dissolved in 5 mL ethanol) was added to the reaction system. After 7 h with magnetic stirring at 300 rpm at 75 °C, the reaction was cooled to room temperature to stop the polymerization. The PS emulsion was obtained.

2.3. Synthesis of PS/SiO_2 core–shell composite microspheres

To a 250 mL flask equipped with a magnetic stirrer, PS emulsion (11 g), ammonia solution (0.85 g) and 50 mL ethanol were added at room temperature. Then, TEOS (2.5 g) was dissolved into 40 mL ethanol. The mixture was added into the flask with stirring in the rate of 3 mL/min. Finally, the reaction was performed with vigorously stirring at 35 °C for 5 h. The obtained precipitates were separated by centrifugation at 5000 rpm, washed several times and dried at 80 °C for 2 h.

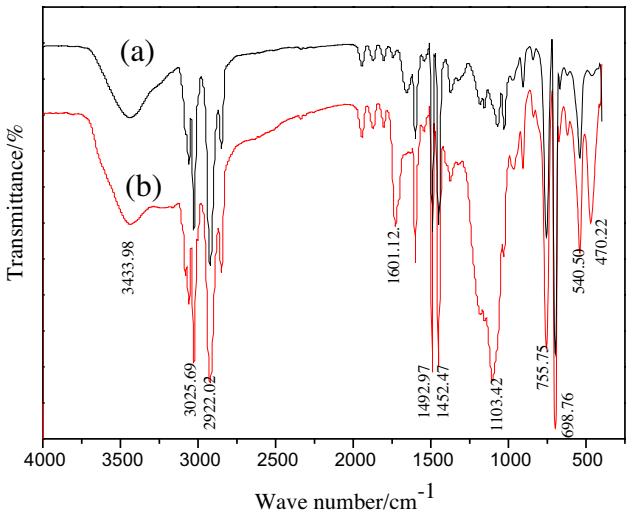

Fig. 1. FT-IR spectrum of (a) PS microspheres and (b) PS/SiO_2 composite microspheres.

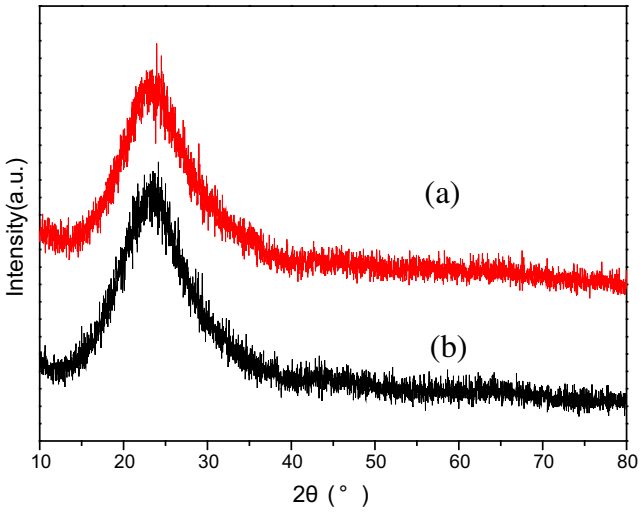

Fig. 2. XRD patterns of (a) PS microspheres and (b) PS/SiO_2 composite microspheres.

2.4. Characterization

The sizes and morphologies of PS and PS/SiO_2 composite microspheres were investigated by SEM (JSM-6360LA, Electronics Co., Ltd, Japan). The core–shell structure and shell thickness were estimated from TEM (JEM-2100, Electronics Co., Ltd, Japan) observation. The FT-IR spectra analysis of samples was carried out by employing IR measurement system (Avatar370, Nicolet, USA). Crystallinity of the samples was examined by XRD (D/max 2500 PC, Rigaku, Japan).

Table 1
Parameters of polishing process.

Carrier pressure (psi)	4	Polishing time (min)	1
Solid content (wt.%)	1	pH value	10
Slurry flow rate (mL/min)	100	Head speed (rpm)	120
Polishing pad	IC 1000/Suba IV (Rohm and Haas Electronic Materials, USA)	Platen speed (rpm)	90