Superior chemical–mechanical polishing performance of silica slurries made of surface-active siloxane/acrylic polymers

Abstract Two new anionic polymers have been synthesized by opening the epoxide ring attached with polysiloxane (SHE) and polyacrylic (CHS) backbones with a comparable weight-average molecular weight range. The colloidal stability of the experimental silica slurries made of these polymers has been investigated and their performance in the chemical–mechanical polishing (CMP) has been studied. A nonionic polysiloxane copolymer (SHE) was also used as a cosurfactant. It was observed from surface tension and fluorescence studies that all these polymers transfer to the air–water interface before forming any aggregates and the ease of forming the aggregates is in the order CHS–SHE (1:1 blend) = SHE–SHE (1:1 blend) > SHE > SHS > CHS. The apparent viscosity data and the scanning electron microscopy micrographs of the silica slurries indicate that all the polymers provide good colloidal stability over a wide range of concentrations. The superior CMP performance over commercial slurry is reported and the order of performance due to the presence of these polymers was also determined and is correlated with the dynamic contact-angle values. The results were interpreted in view of the hydrophilicity of the copolymers and their surface wetting ability.

Key words Copolymer · Anionic · Nonionic · Colloid · Silica

Introduction

With the increased scale of integration and reduced feature size, integrated circuit interconnect structures need global planarization to minimize the depth of focus constraints in the photolithographic process. Chemical–mechanical polishing (CMP) is the preferred method by which the global planarization can be achieved simply and economically, and has now become the standard ultra-large-scale integrated circuit manufacturing process for sub-0.25-μm Si devices [1, 2].

The CMP process is a complex phenomenon that involves chemical as well as mechanical interactions between the wafer materials, the slurry and the polishing pad. The polishing slurry provides the means by which both chemical and mechanical actions are used to planarize the wafer surface. The effect of the physical properties of the slurry on the polishing rate is not very well understood; however, the rheological properties of the slurries affect the material removal rate and the surface quality of the semiconductor wafers a lot [3]. The compositions of the polishing slurry play a major role in CMP as it modifies the film surface in such a way so that the materials can be removed in a smooth and uniform manner [2–5]. A typical CMP slurry always consists of an abrasive (silica or alumina) as a major component for mechanical working and remains in dispersion form generally in aqueous media. Thus, the dispersion technology of abrasives in CMP is of considerable interest to researchers in industry as well as in academia [6, 7]. The dispersants are commonly used as surface-active
agents, which provide either an electrostatic barrier between the particles [8] or steric stabilization [9] against coagulation of the particles. Different commercial surfactants have been tried to manufacture CMP slurries by different manufacturers [10]; however, the dispersion agents are generally considered proprietary and are not disclosed to the users.

In our present investigation, two anionic surface-active polymers were synthesized to study their performance in CMP. A nonionic siloxane copolymer was used as a cosurfactant and the colloidal behavior of these polymers in aqueous solution and their dispersing ability towards fumed silica were studied before using these experimental silica slurries in CMP. Finally the CMP performance of the silica slurries made of these anionic surface-active polymers and the blend of anionic–nonionic surface-active polymers was investigated and compared with a commercial CMP slurry.

**Experimental**

**Materials**

The starting polymers for our present synthesis, siloxane copolymer (SG, with backbone composition x:γ = 60:40) and acrylic copolymer (PMGMMA, with backbone composition m:n = 70:30), with pendant epoxide rings were synthesized in our laboratory following methods described elsewhere [11, 12]. The nonionic siloxane copolymer (SHE) was also synthesized in our laboratory by epoxide ring-opening of SG copolymer with diethanol amine [13]. For this research SG having \( M_w = 2.98 \times 10^5 \) with polydispersity \((M_w/M_n)=2.1\) and PMGMMA having \( M_w = 2.57 \times 10^5 \) and \( M_w/M_n = 1.33 \) were used [13] to obtain the final hydrophilic polymers SHE, SHS and CHS with comparable molecular weights. However, the molecular weights of SHE and SHS would be the same as both polymers were derived from one SG copolymer.

Anhydrous sodium bisulfate, sodium hydrogen carbonate and sodium dihydrogen phosphate were purchased from Tedia and were used without further purification. Disodium hydrogen phosphate and pyrene from Merck were also employed as received. The solvents used in this study were purified following standard methods.

The fumed silica Aerosil 90G with an average primary particle size of 20 nm and a surface area of 90 m²/g was kindly supplied by Nippon Aerosil Co. (Japan).

**Synthesis**

**Synthesis of siloxane copolymer SHS**

SG copolymer (20 g) and ethanol (80 g) were charged in a 500-ml three-necked flask and stirred at 70 °C. An aqueous solution of sodium bisulfite (14.34 g in 120 g water) was then added dropwise (about 1.0 g/min) into the reactor. After completion of this addition, stirring was continued for a further 96 h with a mild reflux at 70 °C. The reaction mixture was then concentrated by evaporating about 70% of solvent with a rotary evaporator and the residual mass was taken for purification by dialysis (cutoff molecular weight of 1,000) for 24 h. The solvent was then completely distilled off under reduced pressure to obtain the SHS copolymer and finally the polymer was dried in a vacuum oven for 48 h at 60 °C.

**Synthesis of acrylic copolymer CHS**

PMGMMA copolymer (20 g) and 1,4-dioxane (80 g) was added to a 500-ml three-necked flask and stirred at 70 °C. An aqueous solution of sodium bisulfite (14.34 g in 120 g water) was then added dropwise (about 1.0 g/min) and stirring was continued for a further 96 h under a gentle reflux at the same reaction temperature. Then, the CHS copolymer was extracted, purified and dried by following the same methods as described for the SHS copolymer.

**Characterization of SHS and CHS**

The structures of the SHS and CHS copolymers (Fig. 1) were characterized by \(^1\)H NMR and \(^13\)C NMR spectra (Bruker AMX-400).

**SHS**: \(^1\)H NMR (D₂O, δ): 0.1–0.3 (–Si–CH₃), 0.35–0.6 (–Si–CH₂–), 1.4–1.7 (–Si–CH₂CH₂–), 3.0–3.15 (–CH₂–SO₃Na), 3.4–3.6 (–CH₂OCH₂).

**CHS**: \(^1\)H NMR (D₂O, δ): 0.9–2.5 (–Si–CH₃), 14.4 (–Si–CH₂–), 24.0 (–Si–CH₂CH₂–), 55.5 (–CH₂SO₃Na), 68.0 [–CH(OH)], 74.9 [–CH₂CH(OH)], 75.3 (–Si–CH₂CH₂CH₂–).

**SHS** (x : y ≈ 60 : 40)

\[
\text{CH}_3\ \rightarrow\ \text{Si}^{13}O\ \rightarrow\ \text{CH}_3
\]

\[
\text{CH}_3\ \rightarrow\ \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{SO}_3\text{Na}^+\ \rightarrow\ \text{OH}
\]

**CHS** (m : n ≈ 70 : 30)

\[
\begin{align*}
\text{CH}_3 & \rightarrow \text{C}(	ext{O})\text{CH}_2 \rightarrow \text{C}(	ext{O})\text{CH}_2 \rightarrow \text{C}(	ext{O})\text{CH}_2 \rightarrow \text{C}(	ext{O})\text{CH}_2 \rightarrow \text{C}(	ext{O})\text{CH}_2 \rightarrow \text{C}(	ext{O})\text{CH}_2 \\
\text{OCH}_3 & \rightarrow \text{OCH}_2\text{CH} \rightarrow \text{CH}_2\text{SO}_3\text{Na}^+ \rightarrow \text{OH}
\end{align*}
\]

**SHE** (x : y ≈ 60 : 40)

\[
\text{CH}_3\ \rightarrow\ \text{Si}^{13}O\ \rightarrow\ \text{CH}_3
\]

\[
\text{CH}_3\ \rightarrow\ \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{OH} \rightarrow\ \text{OH}
\]

**Methods and Measurements**

The surface tensions of all the polymers were measured by using a commercial ring tensionmeter (model TE1C, Lauda, Germany) as a function of concentration and the equilibrium surface tensions were then obtained from the long-time asymptotes at 25 °C. Fluorescence measurements were conducted by using a fluorescence spectrophotometer (model F-4010, Hitachi, Japan) using pyrene as a probe and at a fixed pH of 7.0. The intensity

**Fig. 1 Structures of the surface-active polymers**