Colloids and Surfaces A: Physicochem. Eng. Aspects 411 (2012) 122–128

Contents lists available at SciVerse ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

Influence of anionic polyelectrolyte addition on ceria dispersion behavior for quartz chemical mechanical polishing

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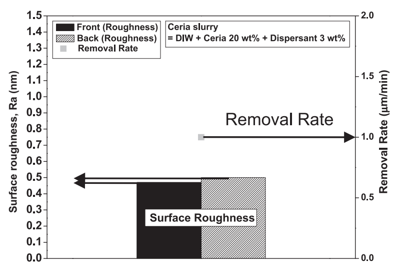
HIGHLIGHTS

- ► New ceria chemistry with additive (PAMS) is proposed for quartz CMP.
- ► We report the adsorption behavior of PAMS on ceria and slurry stability behavior.
- ► The viscosity and electro kinetic behavior is different from other common additives.
- ► The mechanism explains ceria suspension behavior at various additive concentration.
- ► The desired surface quality of quartz could be achieved with the proposed chemistry.

GRAPHICAL ABSTRACT

Surface roughness and removal rates after quartz substrate polishing at an optimized ceria slurry condition.



ARTICLE INFO

Article history:
Received 27 April 2012
Received in revised form 19 June 2012
Accepted 6 July 2012
Available online 20 July 2012

Keywords:
Ceria
Poly(acrylic acid-co maleic acid) sodium salt
Dispersion
Quartz
Chemical mechanical polishing

ABSTRACT

In this study, the effect of anionic dispersant, poly(acrylic acid-co maleic acid) sodium salt on ceria (CeO_2) slurry stability was investigated for quartz chemical mechanical polishing (CMP) applications. The properties of the ceria slurry, including pH, viscosity, and stability behavior as a function of dispersant concentrations (0.1, 1, 3 and 5 wt%), were characterized to identify optimized conditions for the polishing process. With the addition of dispersant, the pH of ceria slurry increased to an alkaline regime which is compatible for quartz CMP processing while the viscosity sharply increased at 5 wt%. The stability results show that the slurry is stable only at 3 wt%, whereas the particles become agglomerated and settle quickly at all other dispersant concentrations. Adsorption and electrokinetic behavior of the ceria slurry were measured to understand the ceria slurry behavior at various dispersant concentrations. At low concentrations, the dispersant does not protect the particles enough to overcome the van der Waals attraction forces, whereas, at higher concentrations, particle agglomeration occurs due to bridging flocculation. At the optimum concentration, the dispersant provides enough steric hindrance to overcome the attractive force. In addition, the presence of sodium ions in the dispersant also strongly influences the settling behavior of ceria particles. The polishing test showed that the desired removal rate and surface quality could be achieved with the optimized slurry.

1. Introduction

In semiconductor processing, lithography technology enables the formation of micro or nano patterns on substrates by specific optical sources. Photomasks with original patterns play a key role in the lithography process, which determines the performance of devices [1,2]. As such, stringent conditions must be met to

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http://dx.doi.org/10.1016/j.colsurfa.2012.07.009

produce blank masks [3,4]. Blank masks are produced from quartz substrates, as quartz has high transmittance and a low thermal expansion coefficient. Chemical mechanical polishing is an essential process for producing smooth surfaces to minimize diffuse light scatter and surface plasmon effects [5].

Both silica and ceria have been used as abrasive particles in conventional quartz CMP processing [6]. However, among these, ceria has been widely preferred in quartz CMP as it offers high removal rate and generates relatively few scratches [7]. Usually, in quartz CMP process, the desired material removal rate is quite high and hence, a high concentration of ceria slurry (10–20 wt%) is used. The ceria particles tend to agglomerate more easily and hence affect the surface quality of the surface being polished. Scratch generation and surface roughness increase during polishing are the main problems encountered during polishing as a result of particle agglomeration. Since for commercial mask, the surface roughness should be minimal, the particle agglomeration should be prevented in the slurry during quartz CMP process. Generally the agglomeration of the particles could be prevented by adding suitable dispersants. There are two basic mechanisms that can keep particles in suspension without agglomeration; electrostatic stabilization and steric stabilization [8]. In electrostatic repulsion, the net charge on the particle surface is increased due to the adsorption of ionic surfactant, and this increases the electrostatic repulsive forces between two particles, whereas in steric stabilization, the dispersant adsorbed on the particle surface act as a physical barrier that prevents the particles from attraction by overcoming the van der Waals attractive forces between particles.

Numerous studies have been reported in the literature regarding ceria suspensions with various additives such as sodium hexametaphosphate (SHP) and sodium dedecylbenzenesulfonate (SDBS) [9], poly(acrylic acid) [10–12] and poly(vinyl pyrrolidone) [13] for various applications such as STI CMP, etc. Among these, the most commonly used additive with ceria particles in STI CMP is poly(acrylic acid). However, the main purpose of adding poly(acrylic acid) is to enhance the selectivity between Si_3N_4 and SiO_2 film polishing rate. Wei et al. [9] reported the slurry stability behavior of nano ceria abrasive by using various surfactants such as SHP and SDBS. They evaluated the ceria stability behavior with these surfactants from viscosity and zeta potential measurements. They further reported that dispersant is necessary for stable ceria dispersion as mechanical ultra-sonication alone could not provide stable dispersion. However, there are no detailed studies in the literature yet on ceria dispersions with respect to quartz CMP processing.

Thus, in the present study, we evaluated poly(acrylic acid-co maleic acid) sodium salt (PAMS) as a dispersant for ceria slurries for quartz CMP process. Poly(acrylic acid-co maleic acid) sodium salt has been used for the dispersion of barium titanate in liquid medium and in the assembly of ZnO nanorods [14,15]. However, it is not typically used for ceria dispersions, and there have been no detailed studies regarding its adsorption behavior on oxide particle surfaces. In the present work, the effect of PAMS dispersant on ceria stability is characterized as a function of concentration.

2. Materials and methods

A 20 wt% ceria slurry (SHOWA DENKO, Japan) was used for all experiments with various concentrations of dispersant (0, 0.1, 1, 3, 5 wt%). The primary particle size of ceria is 1 μm. The dispersant used in this study was poly(acrylic acid-co maleic acid) sodium salt (34%, LION Corporation, Japan), which is anionic in nature. The chemical structures and properties of the dispersant are given in Fig. 1 and Table 1, respectively.

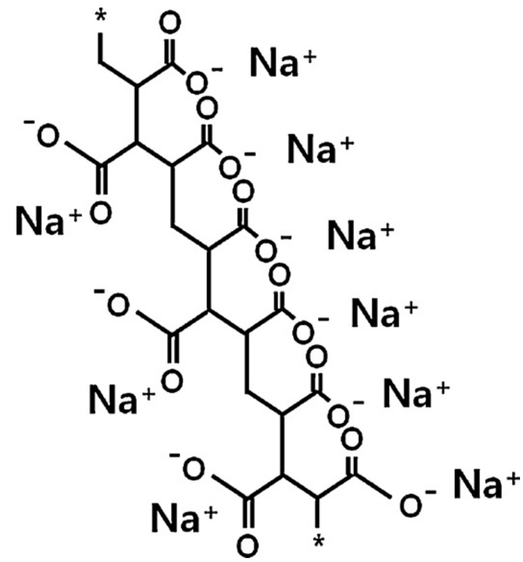

Fig. 1. Chemical structure of the dispersant, PAMS.

Table 1
Properties of dispersant, poly(acrylic acid-co maleic acid) sodium salt (PAMS).

Properties	
Viscosity (cP, 25 °C)	50–170
Melting Point (°C)	0 to −10
Boiling Point (°C)	100–105
Specific gravity	1.26–1.30
pH	9–10
Solubility	Water soluble

Slurry viscosity was measured using a viscosity meter (LVDV-1, Brookfield, USA) while a zeta analyzer (ELS-Z, Otuska, Japan) was used for the measurements of mean particle size and zeta potential of the ceria slurry. The adsorption isotherms were measured by the following procedure: The ceria dispersions of desired concentration (20 wt%) were prepared and then, the dispersant of desired concentrations was added to the ceria dispersions. The mixture was stirred continuously in a magnetic stirrer for 24 h [13]. Subsequently, the dispersions were centrifuged at 5000 rpm for 30 min, and the supernatant was filtered by using syringe filters (0.45 μm, NORM-JECT, USA) and then analyzed for conductivity. The conductivity values were converted in to dispersant mass using experimentally determined calibration curve. The adsorption isotherms are then derived from the difference between the amount added and the amount remaining in the supernatant. During these experiments, we did not notice any adsorption of polymer on the filter. In CMP experiments, a porous Ce Pad (Nitta Haas, Japan) was used to polish the tetragonal quartz substrate (152 mm × 152 mm × 6.35 mm) with the ceria slurry. All CMP experiments were conducted in a double side polishing machine (12B Double Side Polishing Machine, Speedfam, Japan) that can polish both sides of the quartz substrate. In the CMP test, the pressure was 100 g/cm^2 with 7 rpm and 20 rpm upper/lower plate speeds.

The internal and sun gear rpms were 9 and 1, respectively and the polishing time was 60 min. Fig. 2 shows a schematic of the polishing machine and process. The removal rate was calculated using a micrometer and the roughness was measured by a scanning probe microscopy (Veeco, USA).

3. Results and discussion

In the SiO_2 CMP process, the pH value of the slurry is critical as it affects both the abrasive particle size distribution and the surface