Investigation of Ceria-PAA interactions during STI CMP process leading to brush loading issues

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INTRODUCTION

Ceria-based slurries were used for silicate glasses but over the last few years, it has become popular in semiconductor fabrication for a high polishing rate with better surface quality. Ceria abrasives show a high removal rate and better selectivity than silica-based slurries in STI CMP. Additives to achieve better selectivity at the same polishing rate are being introduced in STI CMP slurry formulation while removal efficiency of ceria particles on oxide surface in STI post-CMP cleaning is difficult. Poly (acrylic acid) (PAA), an anionic polymer is commonly used to improve the dispersion stability of ceria particles and oxide-to-nitride selectivity via adsorbing on the surfaces due to the electrostatic attractive forces between the highly positive charged ceria particles and negatively charged carboxylate group. PAA also acts as a passivating agent for obtaining a high selectivity ratio between oxide and nitride surfaces as it prevents abrasives from polishing the nitride surface by getting preferentially adsorbed on the high positively nitride surface [1-5].

It is reported that the SiO_2 removal rate depends on the availability of Ce^{3+} on the ceria surface and the addition of additives can block active sites on the ceria surface, which may lead to a significant decrease in the SiO_2 removal rate [3]. Adsorption of carboxylic (-COOH) groups present in PAA modifies the ceria surface from positively charged to negatively charged, which improves the dispersion stability and decreases the residual abrasives particles due to the presence of repulsive forces between ceria abrasives and oxide film. Improved dispersion stability will enhance the oxide removal rate with improved surface uniformity. With the increase in the concentration of surfactant in slurry, the abrasive transition from bridging agglomeration to a stable state and then to flocculation was observed. This indicates that there is an optimum concentration at which additives can perform effectively [6]. At low concentrations, additives are not sufficient to cover abrasive surfaces while at high concentrations, free additives which are not adsorbed cause flocculation. It was reported that pH and ionic strength are the two important factors that affect the amount and strength of adsorbed PAA [8]. Studying the adsorption behavior of PAA on the ceria abrasive surface is important to understand the interactions between them. In this paper, we investigated the chemical interaction between ceria, PAA, and PVA brush, and its effect on brush loading at different pH conditions.

BACKGROUND

Chemical mechanical planarization (CMP) is a widely adopted technique to achieve local and global planarity of the wafer during the microelectronic device fabrication process. It plays a significant role in the structural development of front-end-of-line (FEOL) and back-end-of-line (BEOL) processes. STI is one of the critical steps in FEOL where the semiconductor device components are isolated to prevent the leakage current [ref] and it requires selective polishing between silicon nitride and gap filling materials such as silicon dioxide. In the STI CMP process, the ratio of the removal rate of oxide to nitride needs to be high to achieve high selectivity and product yield. In general, CMP slurry consists of abrasive particles, oxidizers, dispersants, passivating agents, etc. Ceria abrasives are mostly used for STI CMP as it shows a high silicon dioxide removal rate due to the formation of Ce-O-Si bonding during SiO_2 polishing. *Cook et al*. proposed that hydrated Ce-OH groups on the ceria surface function as “chemical tooth” to break silica bonds by forming Ce-O-Si bonds by reacting with active $Si\text{-}O^-$ sites [7-8]. It was reported that Si-O-Si is a weaker bond that can rupture, and *Hoshino et al*. suggested the removal of silicon dioxide occurs in form of lumps during polishing [8].

Further, the effective removal of ceria particles from the oxide surface is a major issue in STI post-CMP cleaning due to the strong adhesion of ceria on the oxide surface. During the STI post-CMP cleaning, the ceria particles can also cause contamination at the surface or by penetrating inside the brushes which deteriorates the brush lifetime [9]. The issues related to the ceria removal during the STI post-CMP cleaning can be controlled either by modifying the CMP slurry that reduces the interaction between ceria and oxide surface or by modifying the post-CMP cleaning chemistries that effectively remove the strongly adsorbed ceria particles from the surface. The latter approach has been explored by many researchers by incorporating different additives in the cleaning solutions but is not effective in brush loading.

EXPERIMENTAL

To study the brush loading with ceria particles at different pH conditions (prepared at pH 3, 7, and 10), a single PVA brush (200-mm, AION Co. Ltd., Japan) nodule was dipped in 200 mL ceria slurry suspensions for 1 min and was analyzed using FESEM (S-4700, HITACHI, Japan). Ceria slurries were prepared at 0.1 wt.% concentration in deionized water (DIW) using 100 nm calcined ceria particles (US Research Nanomaterials Inc., USA) at different pH conditions. Slurries were analyzed by using different techniques to evaluate the effect of pH and concentration on PAA-ceria interactions. Zeta potential and particle size distribution of ceria suspensions were measured using a zeta analyzer (ELS-Z, Otsuka Electronics, Japan). An anionic polymer, PAA (Mw= 2000) was added to ceria slurry at different concentrations (1 wt.%, 3 wt%, and 5 wt%) for the same pH conditions to study the variation in brush loading.

DISCUSSION

Figure 1 shows FE-SEM images of ceria brush loading at different pH conditions where the reference image of uncontaminated fresh PVA brush nodule is shown in Fig. 1a. A very high brush loading with ceria particles was observed at pH 3 (Fig. 1b), whereas relatively non-uniform high brush loading was observed at pH 7 (Fig. 1c). At pH 10, relatively low brush loading with ceria particle was observed. To understand the mechanism of brush loading with ceria particles at various pH conditions, the zeta potential of both ceria particles and PVA brush nodules were evaluated (Fig. 2a). Figure 2a shows that the zeta potential of PVA remains negative for all pH conditions studied with a low-negative potential (close to zero) at pH 3 and the potential increases in the negative direction with the increase in pH of the solution. However, ceria particles possess positive zeta potential at pH 3 and 7, and negative potential at pH 10. The opposite surface charges between PVA brush and ceria particles at pH 3 and 7 resulted in high brush loading (Fig. 1b and c). The similar surface charge of PVA and ceria particles at pH 10 resulted in repulsive forces between them which leads to very low brush loading (Fig. 1d). Figure 2b shows the ceria particle size distribution at different pH conditions and it indicates that at pH 7, the ceria particle dispersion is very poor. The low positive surface potential of ceria particles at pH 7 leads to a low repulsive force between them and resulted in particle agglomeration.

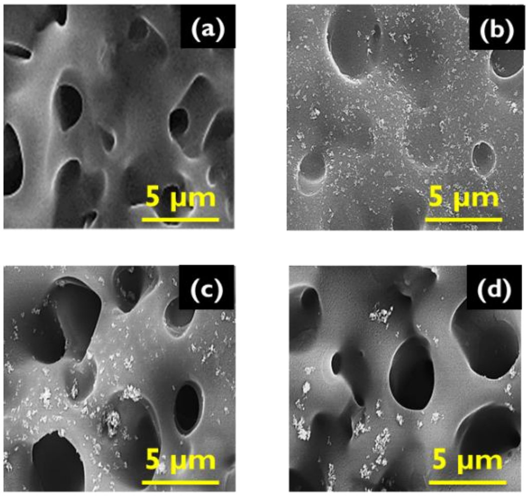

Fig.1 FESEM images (at 10 kx) for (a) Fresh brush surface and the effect of pH on ceria loading at (b) pH 3 (c) pH 7, and (d) pH 10 conditions

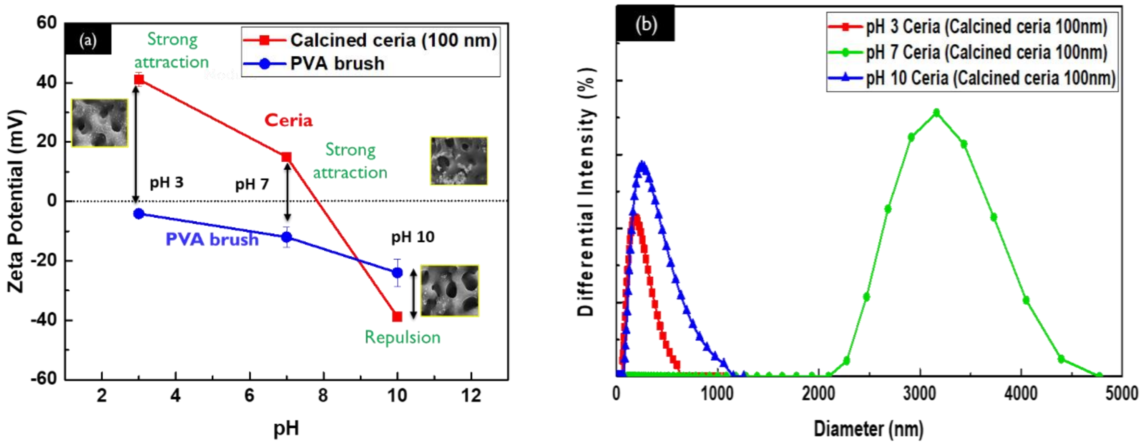

Fig.2 (a) Variation of zeta potential of calcined ceria and PVA brush at different pH conditions and (b) effect of pH on ceria particle size distribution

Figure 3 shows the effect of the concentration of PAA on the ceria brush at different pH conditions. With the increase in the concentration of PAA up to 3 wt.%, the ceria brush loading decreases at all pH conditions. Further increase in the concentration of PAA leads to the rise in ceria particle loading on the brush. This confirms that 3 wt.% is the optimum concentration of PAA to reduce the ceria particle loading. In acidic to neutral region, 1 wt.% PAA is insufficient to get fully adsorb on ceria particles due to low dissociation of the carboxylic groups which decreases slurry stability and leads to brush loading. Above 3 wt.% of PAA, the bridging flocculation phenomena occur and result in high brush loading [6, 9].

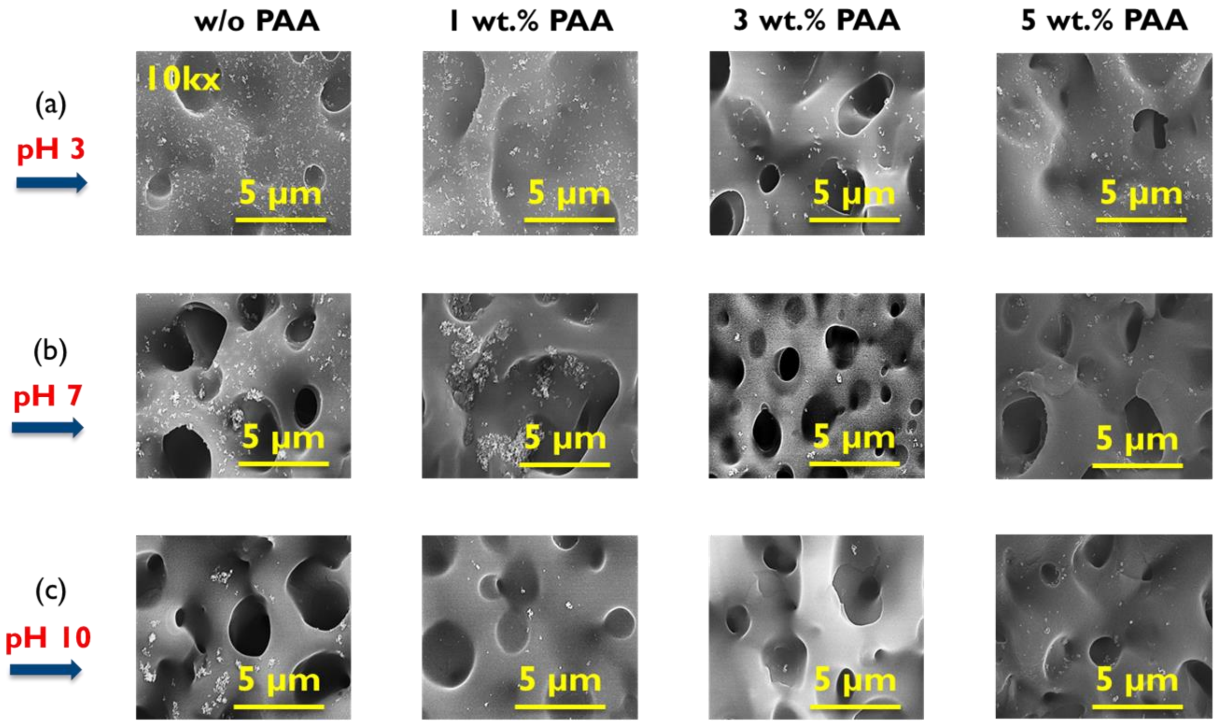

Fig.3 FESEM images (at 10 kX) (a) Fresh brush surface and the effect of pH on ceria loading of the brush surface for different pH conditions: (b) pH 3 (c) pH 7 and (d) pH 10. at different concentrations

With the addition of 3 wt% of PAA, the zeta potential of ceria particles decreases and remains negative value at all pH values (Fig. 4). The strong electrostatic repulsion between ceria particles with PVA brush due to the significantly high negative potential of ceria particles resulted in low brush loading (Fig. 3).

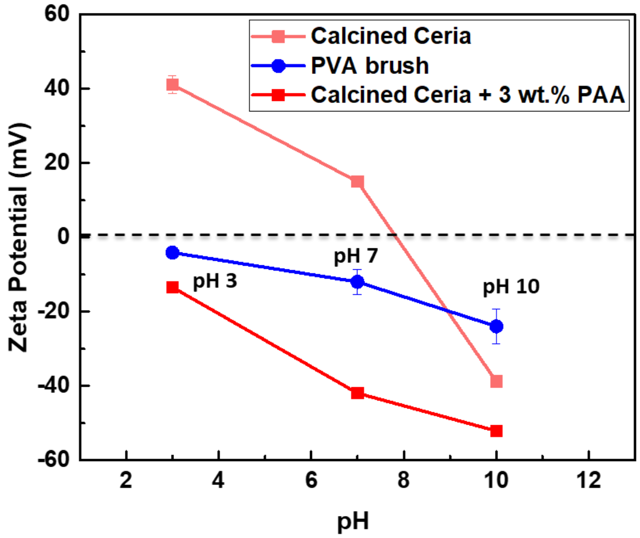

Fig.4 Variation of zeta potential of calcined ceria with the addition of PAA and PVA brush at different pH conditions

CONCLUSIONS

Ceria particle loading on PVA brush was significantly high at acidic-neutral conditions due to the strong electrostatic attractive forces between these two surfaces. The electrostatic repulsive force between PVA and ceria particles at alkaline pH resulted in low brush loading. This study shows that 3 wt.% PAA is the optimum concentration for reducing the ceria particle loading on the brush. Insufficient adsorption of the PAA at pH 3 may induce ceria particles to contaminate the brush surface. For pH >7, sufficient coverage with uniformly adsorbed polymer chains on ceria particles may be responsible for highly stable systems and low brush contamination.

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