Effects of Polymer Adsorption on Stabilities and CMP Performance of Ceria Abrasive Particles

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In this paper we present that the effects of polymer adsorption on stabilities and CMP performance of ceria abrasive particles. Characterization of ceria abrasive particles in the presence of poly(vinyl pyrrolidone) (PVP) was performed by the measurements of adsorbed amounts of PVP, average sizes, and the back scattering intensities of the ceria abrasive particles as functions of PVP molecular weight and PVP concentration. The ceria abrasive particles in the presence of PVP were used to polish SiO_2 and Si_3N_4 films deposited on Si wafers in order to understand the effect of PVP adsorption on chemical mechanical polishing (CMP) performance, together with ceria abrasive particles without PVP. Adsorption of PVP on the ceria abrasive particles enhanced the stability of ceria abrasive particles due to steric stabilization of the thick adsorbed layer of PVP. Removal rates of the deposited SiO_2 and Si_3N_4 films by the ceria abrasive particles in the presence of PVP were much lower than those in the absence of PVP and their magnitudes were decreased with an increase in the concentration of free PVP chains in the dispersion media. This suggests that the CMP performance in the presence of PVP could be mainly controlled by the hydrodynamic interactions between the adsorbed PVP chains and the free ones. Moreover, the molecular weight dependence of PVP on the removal rates of the deposited films was hardly observed. On the other hand, high removal rate selectivity between the deposited films in the presence of PVP was not observed.

Keywords : Polymer adsorption, CMP, Ceria abrasive particles, Poly(Vinyl pyrrolidone), Steric stabilization

1. INTRODUCTION

Chemical mechanical polishing (CMP) technique has been intensively developed with along the advanced semiconductor device manufacturing utilizes and it is a key technology in the present ULSI (ultra large-scale integrated circuit) fabrication. The CMP technique contains two effects, such as a chemical effect from the sub-micrometer abrasive particulate slurry and a physical effect from the pressed pad and abrasive particles. Among the abrasive particle slurries used in the CMP technique, ceria has a good selectivity in polishing rates between the SiO_2 and Si_3N_4 deposited films in comparison with other abrasive slurries[1]. Moreover, ceria slurries in the presence of some polyelectrolytes such as poly(methacrylate acid) and poly(acrylic acid), which adsorb on the ceria surfaces, and often play a role in stabilization of the ceria slurries, have been usually used in the CMP technique and they have high oxide-nitride removal rate selectivity[2-7]. Several research groups have proposed some mechanisms for achieving a higher selectivity with their ceria slurries in the presence of polymers than that without polymers in terms of polymer adsorption. However, it is not sufficient for our knowledge about the mechanisms of removal rate selectivity between the SiO_2 and Si_3N_4 deposited films and the role of the added polymer chains in the CMP process. Thus, careful characterization of abrasive particles in the presence of polymer chains is necessary and essential in understanding and improving of the

CMP technique.

In this study, we present results of the stability of ceria particles adsorbed by poly(vinyl pyrrolidone) (PVP) in water as functions of PVP molecular weight and adding PVP concentration in terms of the measurements of the average sizes and back scattering intensities of the ceria particles. Moreover, we will discuss the effects of PVP adsorption on both changes in the removal rates and the oxide-nitride removal rate selectivity determined from the CMP tests of the SiO_2 and Si_3N_4 films deposited on silicon wafers using various ceria particles.

2. EXPERIMENTAL

2.1 Samples

Water was purified by a Milli-Q Academic A10 ultra-pure water system.

One PVP sample purchased from Tokyo Kasei Co. was separated into several fractions in a water-acetone mixture at 25 °C. We chose three fractions of PVP with the molecular weight of 308×10^3 (PVP-308), 600×10^3 (PVP-600), and 886×10^3 (PVP-886).

Ceria particles kindly supplied from Shin-etsu Chemical Co. were suspended in water and they were fractionated by sedimentation. The resulting original ceria slurry contains a ceria concentration of 4.27 wt%. The original ceria slurry was mixed with water and aqueous solutions of PVP with given concentrations to prepare ceria slurry (without PVP) and ceria dispersion (with PVP), respectively, their ceria content was usually fixed at 2.14 wt% during this study.

2.2 Dynamic light scattering

The dynamic light scattering measurements of the ceria slurry and ceria dispersions were performed as a function of time using a Fiber-Optics Particle Analyzer FPAR-1000. The resulting scattering data were analyzed by the photon correlation spectroscopy technique and an average size of the ceria particle was calculated.

2.3 Measurements of intensities for back scattering and transmission

The measurements of back scattering intensities of the ceria slurry and ceria dispersions were performed using a TURBISCAN MA2000[8]. The back scattering intensity was monitored as a function of the height from the bottom of the glass tube at various times elapsed after mixing the sample. It is capable to detect changes in the progress of sedimentation of the ceria particles as a function of time.

2.4 Measurements of the adsorbed amounts of PVP

The amounts of PVP adsorbed on surfaces of the ceria particles were determined as follows. After the ceria

dispersion was agitated during a desired time in the dosing concentrations of 0.0275, 0.55, 0.11, and 0.22 g/100 mL, it was centrifuged to sediment the ceria particles. The concentration of PVP in a supernatant was determined from the flow rate of the corresponding supernatant in a viscometer at 25 °C using a calibration curve of the flow rates of aqueous solutions of PVP as a function of PVP concentration

2.5 CMP tests

SiO_2 (oxide) films deposited on silicon wafers with the diameter of 8 inches by the plasma-enhanced tetra-ethylortho silicate method were purchased from Advantec Co. Si_3N_4 (nitride) films formed by low-pressure chemical-vapor deposition on silicon wafers with the diameter of 8 inches were supplied from Advantest Materials Technology Co. The original thicknesses of the deposited oxide and nitride films were measured to be 1020 and 210 nm, respectively using a NanoSpec/AFT 5100 spectroscopic reflectometer. Such silicon wafers were cut to square samples of 2×2 cm^2 and their deposited films were polished on a lapping machine FACT-200 equipped with a single polishing head and polishing platen using the ceria slurry and the ceria dispersion in the dosing PVP concentrations of 0.0275, 0.055, and 0.11 g/100 mL. Polishing tests of the deposited films have been usually performed with a commercial urethane IC-1000 XY-grooved pad supplied from Nitta Haas Co. for 1 min under the following conditions: the actual polishing pressure of 30 kPa, the rotation speeds of both the head and the table with 80 rpm, and the flow rate of 15 mL/min for the ceria abrasives. The respective removal rates of the films were calculated from the thicknesses of the oxide and nitride films deposited on silicon wafers before and after the polishing.

3. RESULTS AND DISCUSSION

3.1 Stability of ceria slurry

The pH of the ceria slurry was maintained to be ca. 5.6 and its pH is lower than the point of zero charge of 8. 1 ± 0.1[9]. The surface charges of the ceria particles should be positive and the electrostatic repulsive forces could lead to stabilization of the ceria particles. Stability of the ceria slurry was monitored both by the measurements of back scattering and by the dynamic light scattering intensity. Thus, a decrease in the back scattering intensity should occur at the upper layer of ceria slurry. The back scattering was monitored as a function of an elapsed time after the mixing and the resulting back scattering intensity at the upper layer in the tube showed an increase with increasing the elapsed
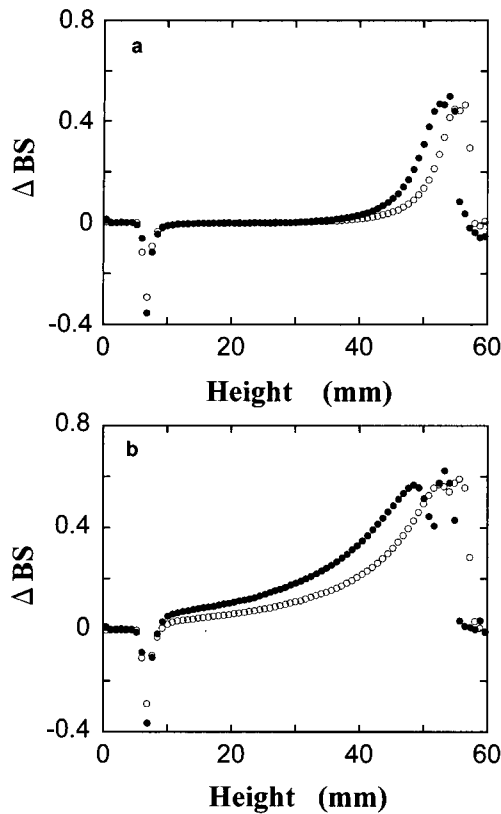
Fig. 1. Plots of the back scattering intensity differences ΔBS for the ceria slurry (●) and the ceria dispersion in the presence of PVP-600 (○) for the elapsed times of 6 (a) and 24 h (b) after the mixing as a function of the sample height.

Fig. 2. Adsorption isotherms of PVP-308 (□), PVP-600 (○), and PVP-886 (◆) on the ceria surface at 25 °C.

time, indicating that the ceria particle gradually sediments[8]. Thus, the difference ΔBS between the back scattering intensity at a given elapsed time and that at time where the initial measurement was performed, should be decreased with an increase in time. Typical plots of ΔBS for the elapsed times of 6 and 24 h after the mixing as a function of the sample height are shown in Figs. 1(a) and (b), respectively. A longer elapsed time causes a larger increase in the ΔBS value at the lower layer in the tube. This means that ceria particulates partially sediment and their packing become compact.

On the other hand, the measuring time for the dynamic light scattering measurements is usually less than 10 min to obtain reproducible data: little sedimentation effect of the ceria slurry influenced the determination of the average size of the ceria slurry and the average diameter of a ceria particle was determined to be 260 ± 10 nm.

3.2 Adsorption of PVP on ceria particles

The pH of ceria dispersions was almost the same as the ceria slurry even if in the presence of PVP. The adsorbed amounts of PVP are almost independent of the
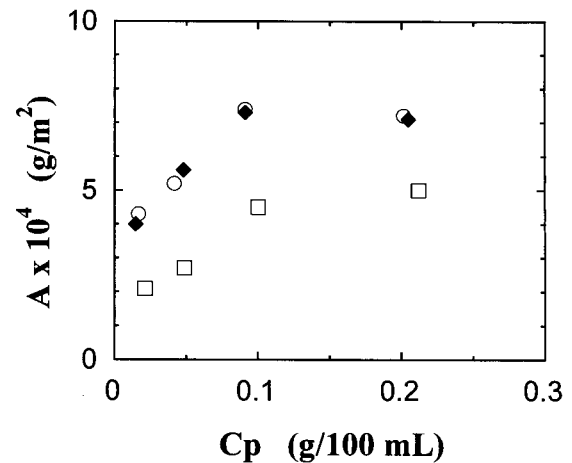
measuring adsorption time. Thus, it can be regarded to be enough for one day adsorption time to determine an equilibrium adsorbed amount of PVP and then adsorption isotherms of PVP on ceria particulates were obtained. Such an adsorption time period is common in many systems for polymer adsorption[10].

Adsorption isotherms of PVP-308, PVP-600, and PVP-886 own the plateau region beyond at the dosing PVP concentration of ca. 0.11 g/100 mL as shown in Fig. 2, irrespective of the molecular weight of PVP. The plateau adsorbed amount of PVP-308 is smaller than those of two higher molecular weights of PVP. Such plateau adsorbed amounts of PVP are almost the same as those at polystyrene lattices[11] and at silica surfaces[12] from water.

Since any flocculation of the ceria particles by PVP adsorption in the ceria dispersion was not observed, adsorption of PVP on the ceria surfaces should cause the larger average size of the ceria particles than that in the ceria slurry and it also should enhance the stability of the ceria particulates due to the steric stabilization effects between the adsorbed PVP layers even if the partial suppression of the electrostatic repulsive forces. The dynamic light scattering measurements of the ceria dispersions give a larger average size of ceria particle than that in the absence of PVP as shown in Fig. 3, where the average diameters of a ceria particle in the presence of PVP-308, PVP-600, and PVP-886 are plotted as a function of the equilibrium PVP concentration. The resulting average sizes increase with an increase in the equilibrium PVP concentration. Moreover, the average sizes at the respective dosing concentrations in PVP solutions increase with increasing the molecular weight of PVP. The difference between the average radius of the ceria particle in the presence of
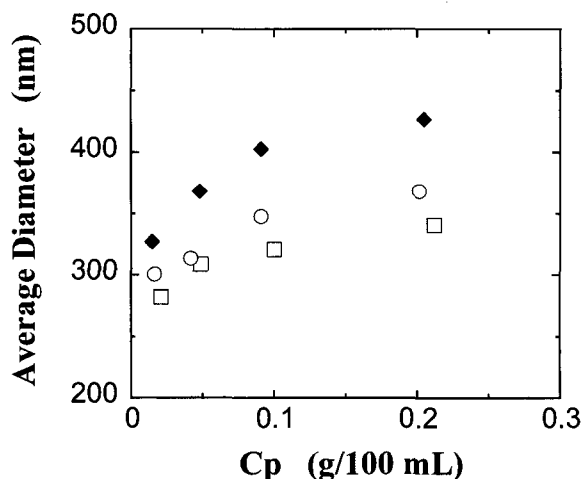
Fig. 3. Plots of the average diameter of a ceria particle adsorbed by PVP-308($\square$), PVP-600 (o), and PVP-886 ($\blacklozenge$) as a function of the equilibrium PVP concentration, Cp at 25 °C.

PVP and that in the absence of PVP corresponds to a thickness of PVP layer adsorbed on the ceria surface and such an adsorbed layer thickness should increase with an increase in the molecular weight of PVP. The respective adsorbed layer thicknesses of 35, 45, and 80 nm for PVP-308, PVP-600, and PVP-886 at the highest dosing concentration of PVP are somewhat larger than the sizes of the corresponding PVP chains in bulk. This means that the conformation of PVP chains adsorbed on the ceria particles consists of larger loops and extended tails [10,11,13], suggesting that such a conformation of the adsorbed PVP chain should play a role in the stabilization of the ceria particles.

Thus, clear stabilization of the ceria particles by adsorption of PVP should be confirmed by the measurements of changes in ΔBS as a function of time by comparison with those of the ceria slurry. The data of ΔBS for the ceria dispersion in the presence of PVP-600 for the elapsed times of 6 and 24 h after the mixing are plotted as a function of the sample height in Figs. 1-(a) and (b). At the fixed sample heights the ΔBS values in the presence of PVP are lower than those in the absence of PVP and this means that the sedimentation of the ceria particles is suppressed by adsorption of PVP.

3.3 CMP tests

The free PVP chains in the dispersion media of the ceria dispersions should adsorb on the deposited SiO_2 and Si_3N_4 films. Such adsorbed PVP chains could be expected to control the CMP technique, namely the achievement of good performance of the CMP. As mentioned above, a conclusive agreement for the CMP

technique by ceria particulates in the presence of polymers has been not yet obtained, however there are some interesting experimental suggestions and conclu-sions[3-9]. Tateyama et al. suggested that for achieving good performance in the CMP the polymer adsorption on oxide film surfaces was not important, while polymer adsorption on ceria particulates was dominant[2]. On the other hand, Kim et al. concluded that adsorption of polymer on deposited films was important to determine oxide-to-nitride removal rate selectivity in the CMP performance by ceria abrasives due to a higher suppression of the removal rate of nitride films than that of oxide films[5]. Thus, in order to investigate the effects of the free PVP concentration in bulk solution on polishing of the oxide and nitride films as well as oxide-to-nitride removal rate selectivity, we employed the ceria slurry and the ceria dispersions, where the free PVP chains remain.

Figures 4 and 5 display the removal rates of the oxide and tirade deposited films by the two different ceria abrasives as a function of the dosing PVP concentration of PVP-308 and PVP-886, respectively. The oxide-to-nitride removal rate selectivity by the ceria slurry was obtained to be 3.6, which is close to the low removal rate selectivity ca. 4 of conventional slurries between the SiO_2 and Si_3N_4 films[5]. In the presence of the free PVP chains the removal rates of both the oxide and nitride films decrease with an increase in the free PVP concentration. Unfortunately, the oxide-to-nitride removal rate selectivity in the presence of free PVP-886 was decreased 3.6, 3.4, and 1.8, while that in the presence of free PVP-308 was also decreased 3.6, 2.8, and 1.8 in the order of the free PVP concentration. Thus, the effect of molecular weight of PVP on the CMP tests was not clearly observed in this study. Moreover, the oxide-to-nitride removal rate selectivity was not enhanced by an increase in the concentration of the free PVP chains, which should adsorb on the surfaces of the oxide and nitride deposited films. This suggests that the removal rates of the oxide films more markedly decrease than those of the nitride ones with an increase in the free PVP concentration. The result is opposite to the previous reports using ceria abrasive particles in the presence of polyacrylates[2-7], which adsorb on the Si_3N_4 films.

Moreover, we performed a primary CMP test of the oxide and nitride deposited films by the re-dispersed ceria particles, which were prepared as follows: after the sedimented ceria particles adsorbed by PVP were rinsed with water to remove the free PVP in the dispersion medium, they were dried and then they were re-dispersed in water; however, any desorption of PVP from the ceria particles was not detective and the adsorbed amount of PVP was not changed by rinsing water. The resulting
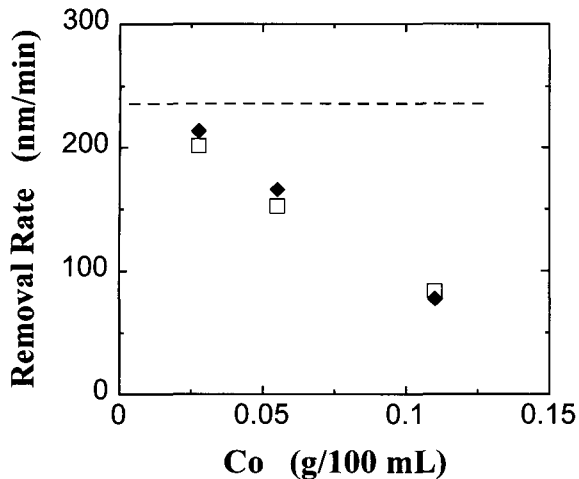
Fig. 4. Plots of the removal rates of the SiO_2 deposited films by the ceria particles adsorbed by PVP-308 (□) and PVP-886 (◆) as a function of the dosing PVP concentration. The dashed line in the figure indicates the removal rate of the SiO_2 deposited films by the silica slurry.

Fig. 5. Plots of the removal rates of the Si_3N_4 deposited films by the ceria particles adsorbed by PVP-308 (□) and PVP-886 (◆) as a function of the dosing PVP concentration. The dashed line in the figure indicates the removal rate of the Si_3N_4 deposited films by the silica slurry.
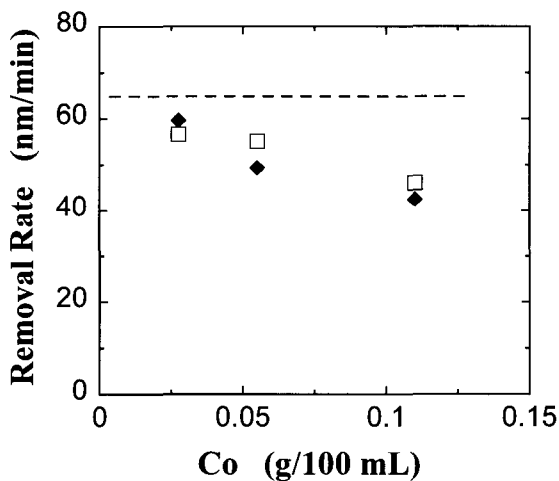
removal rates of the oxide and nitride deposited films were almost the same as using the ceria slurry. This suggests that the pre-adsorbed PVP chains on the ceria particles may not be able to control the CMP performance. Thus, it can be concluded that the presence of the free PVP chains in the dispersion medium plays an

important role in the CMP technique: the free PVP could hydrodynamically interact with the PVP chains adsorbed on the ceria particles and on the deposited films, which may cause to be hard to directly contact the ceria particles with the deposited films. Moreover, such a hydrodynamic interaction could be maintained by the fact that the free PVP chains could provide new comers to adsorb on the ceria surfaces and the deposited films if the pre-adsorbed PVP chains were desorbed under shearing during the CMP.

4. CONCLUSION

When ceria slurry was mixed with aqueous solutions of PVP, no flocculation of ceria particles occurred and adsorption of PVP stabilized them due to the thick layer of PVP adsorbed on the ceria surface. Such a steric stabilization of ceria particles was confirmed by the measurements of back scattering intensities of them. A decrease of the removal rates of the SiO_2 and Si_3N_4 deposited films with an increase in the free PVP concentration could be mainly attributed to the hydrodynamic interactions between the adsorbed PVP chains and the free ones. However, the removal rate selectivity between the deposited films in the presence of PVP was not higher than that in the absence of PVP.

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