구리의 화학ㆍ기계적 연마용 실리카 슬러리의 안정화에 관한 유변학적 연구

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Rheological Study on the Stabilization of the Silica Slurry for Copper CMP

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Introduction

Chemical mechanical polishing is regarded as the most promising technology for the global planarization in microelectric fabrication[1]. In this technology, a slurry containing abrasives and chemicals is utilized to remove unwanted materials from the wafer surface. Copper with its unique electrical properties has been chosen to be a substitute for aluminum in interconnections[2].

Colloidal silica suspension is used as effective CMP slurry. The efficiency of CMP is greatly dependent on the stability of slurry. The particles in stable slurry are well dispersed by overcoming attractive van der Waals forces. To achieve this, repulsive electrostatic and/or steric force is applied. As the magnitude of the van der Waals force is largely determined by the nature of the particles and the solvent, the repulsive force can be modified by organic and inorganic additives. Because the CMP of copper is preferable in acidic media due to the high selectivity, it is not advantageous to use electrostatic method for stabilizing silica slurry of which isoelectric point is about pH 2-3[3]. Polymeric surfactants such as poly(vinyl alcohol) and poly(acrylic acid) can be used as steric stabilizer and their adsorption behavior has been investigated[4].

When inorganic paricles are suspended in solution, their stability can be evaluated from measurement of rheological characteristics and interpreted in terms of polymer adsorption behavior. Rheology was very useful to understand the characteristics of silica suspension, and several results have been reported for various inorganic particles in aqueous media[5,6].

In this paper, the stability of silica slurry is investigated with rheological method. The effect of various volume fractions, and pH were investigated. PVA and PAA were chosen as polymeric stabilizer and the stabilizing effect of the amount added was studied. And the effect of molecular weight of PAA added was observed.

The goal of the present work is to find the optimum conditions of silica slurry for Copper CMP.

Experimental

Material

Amorphous fumed silica, Aerosil MOX 80 (Degussa Co.) was used in this study. The primary size was 40nm and the specific surface area was 250m^2/g. The pH of the slurry was adjusted with nitric acid (Junsei) and potassium hydroxide. Poly(vinyl alcohol) (MW=13,000, Aldrich) and poly(acrylic acid) (MW=250,000~450,000, Aldrich) were used. Another additive to the slurry was hydrogen peroxide which is frequently used as an metal oxidizer in the CMP process.

Method

Fumed silica was dispersed in deionized water. The PVA were added to the silica suspension and stirred overnight to reach the equilibrium. Then the slurry was centrifuged with the frequency of 8000rpm for 2hrs (SUPRA 22K). The amount of PVA adsorbed to the silica particle was determined by measuring the PVA concentration in the supernatant, which was detected from absorbance of the supernatant in a UV-visible spectrophotometer. All the adsorption experiment were performed as suggested by Tadros[7]. And the PAA adsorbed to the silica was measured via TOC(total organic carbon) method.

The rheological behaviors of the slurry were investigated with an ARES rheometer (Rheometric Scientific). In the Steady Rate Sweep test, shear stress and kinematic viscosity were measured according to the shear rate variation (1~1000 sec^{-1}). In the Dynamic Frequency Sweep test, storage and loss modulus were measured according to the frequency variation (0.1~100Hz).

Result and Disscussion

Effect of silica volume fraction and pH

Figure 1(a) shows the changes of viscosity according to shear rate. When shear rate increased, the decrease of viscosity was observed which is called "shear-thinning" effect, indicating an unstable aggregated structure. At relatively low volume fraction (2~5vol%) the shear-thinning effects were weak, that is, almost Newtonian. As the volume fraction increased, both the viscosity at low shear rate and the shear-thinning effect increased. Figure 1(b) shows storage modulus(G′) and loss modulus(G″) of each slurry of 10, 15, 18 vol%. (Others were omitted for the clarity of the graph.) Slurry with higher volume fraction has smaller gap between storage and loss modulus and the smaller modulus line slopes than that of the slurry with lower volume fraction.

These also indicate that as the volume fraction increases, the slurry becomes more non-Newtonian.
Figure 2(a) and (b) shows the effect of pH with the volume fraction 2% and 4%, respectively. These two graphs consistently show that as the pH of the slurry becomes lower, the shear-thinning effect becomes stronger.

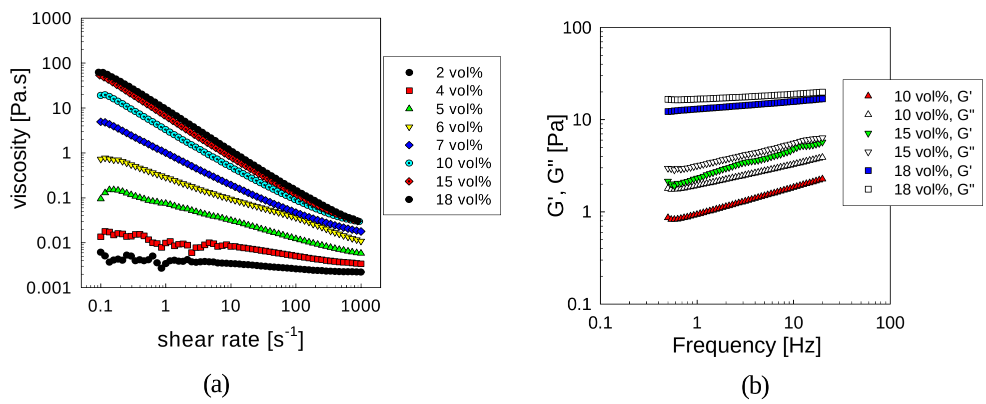

Figure 1.(a) As the volume fraction increases, both the viscosity at low shear rate and the shear-thinning effect increase. (b) Slurry with higher volume fraction has smaller gap between storage modulus and loss modulus and the smaller modulus line slopes than that of the slurry with lower volume fraction.

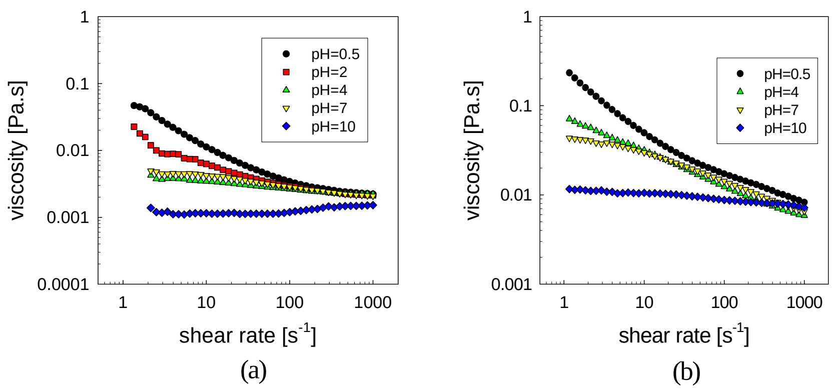

Figure 2. Effect of pH at silica volume fraction (a) 2%and (b) 5%.

Effects of Poly(vinyl alcohol) addition

The relationship between the stability of the slurry and the amount of PVA added is complex. Figure 3 shows the viscosity changes according to the changes of shear rate with various amounts of PVA added. The volume fraction of silica was 5% and the pH was fixed to 4. When relatively smaller amount of PVA was added, the shear-thinning effect decreased and the viscosity at lower shear rate became smaller as the amount of PVA increased. When over 3wt% of the PVA was added, the slurries began to show almost Newtonian behavior but became very viscous. In the case of volume fraction of 10%, addition of PVA to the amount of 0.1wt% increased the shear thinning. Stability was achieved by further addition from 0.5wt% to 2wt%. Newtonian behavior, when over 3wt% of the PVA was added, was the same as in the case of silica volume fraction 5%.

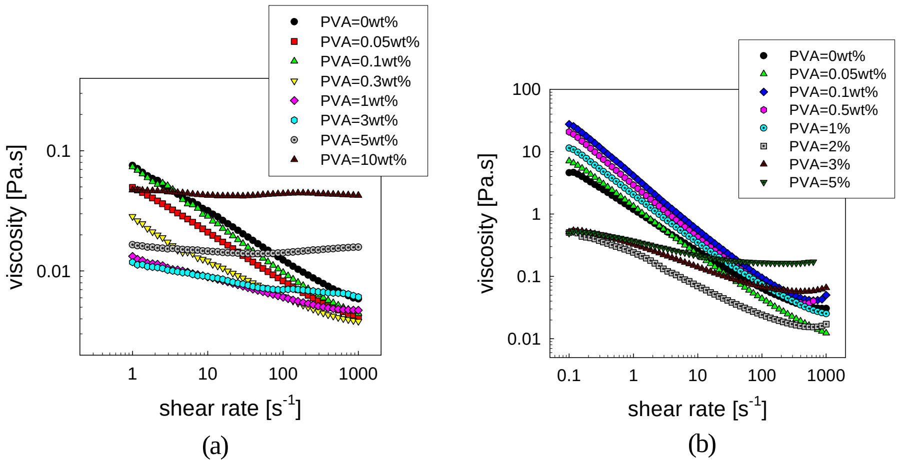

Figure3. The effects of various PVA amount added to the slurry with volume fraction (a) 5% and (b) 10%.

Effects of poly(acrylic acid) addition

Poly(acrylic acid) of five different molecular weights were added to the silica slurry and the rheological behaviors were observed(Figure4.). The silica volume fraction was 5%, and the amount of PAA added was 0.1wt%. PAAs with molecular weights of 250,000 and 450,000 show weak effect. In the case of molecular weights of 750,000, addition of PAA resulted in rather strong shear-thinning effect. But further increase of the molecular weights of PAA added induced the stable slurry.

The optimum amount of PAA addition for the stability of the silica slurry was also investigated. The silica volume fraction was 5%, and the molecular weight of PAA added was 450,000. As shown in the Figure 5(a), addition of PAA less than 0.1wt% showed little effect to the slurry stability. When 0.1wt% of PAA was added the slurry showed little shear thinning effect (Fig. 5(b)). Figure5(c) shows that further addition of PAA resulted in increase of the shear thinning effect.

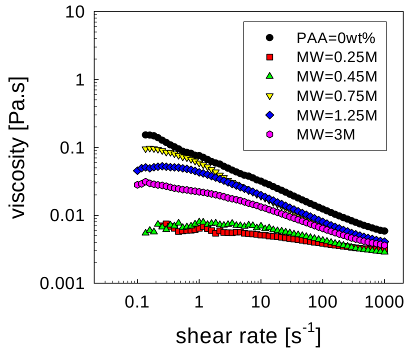

Figure 4. The effects of molecular weight of PAA added to the silica slurry.

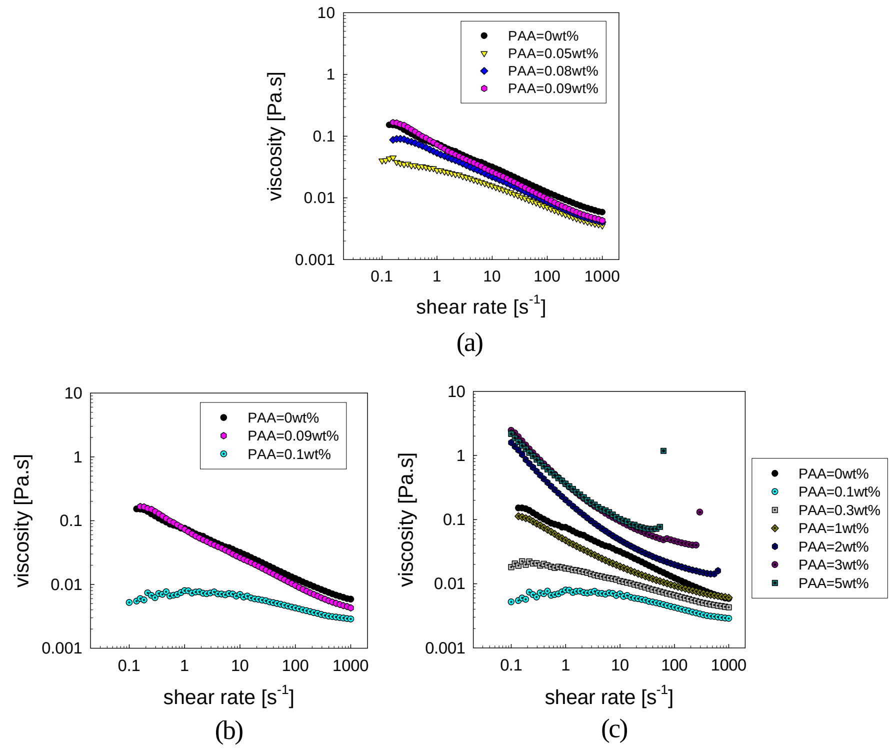

Figure 5. Effects of the amount of PAA added to the silica slurry.

Conclusion

Silica suspension was stabilized by adding polymeric surfactants(PVA and PAA). As the volumetric fraction of silica particle increased, shear thinning effect increased. As the pH is lowered, shear-thinning effect increased. When the small amount of PAA or PVA is added, the initially shear thinning suspension becomes Newtonian. But as the amount of addition is increased, the suspension shows shear thinning behavior again. Surfactant of large molecular weight was found to be inadequate for the stabilizer. The optimalized condition of silica slurry stabilization in this study was addition of 450,000 MW PAA 0.1wt%.

Acknowledgement

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