Ammonium Salt Added Silica Slurry for Chemical Mechanical Polishing (CMP) of Interlayer Dielectric Film

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Abstract To avoid alkaline metal contamination during chemical mechanical polishing (CMP), a KOH-free silica slurry is found out for the interlayer dielectric film planerization. In this paper, the silica particle agglomeration condition is changed by an ammonium salt addition to the slurries with various pH values. The salt addition to the slurries of pH = 6 - 7 promotes the silica particle agglomeration, and enlarges the effective abrasive particle size. The ammonium salt-added silica slurry reveals a high polishing rate and an excellent particle removal after a post-CMP scrub cleaning.

1. Introduction

Chemical Mechanical Polishing (CMP) is recognized as one of the most promising processes for the global planerization of interlayer dielectric (ILD) films among multi-level interconnections [1]. One of important process parameters in the CMP is the polishing rate, which determines the Turn-Around-Time (TAT) of the ILD film planerization. Generally, a silica slurry with KOH is believed as a desirable slurry for the high speed polishing, because the KOH promotes the Si-OH dissociation of the ILD surface. The issue, however, is the alkaline metal (K+) contamination during CMP. The abrasive silica particle contamination after CMP is also remained unsolved.

The purpose of this study is to find out a KOH-free slurry with a high polishing rate and an excellent silica particle removal by a post-CMP cleaning process. In this paper, a KOH-free silica slurry is found out by controlling the silica particle agglomeration condition, or essentially the effective abrasive particle size.

2. Experimental

2-1. Theoretical background

In case of silica [2], HO- ions in the slurry tend to adsorb on the silica surface, and then the dissociation reaction of SiO2 occurs as the follows:

\[ \text{Si-O-Si} + \text{OH}^- \rightarrow \text{Si-OH} + \text{O-Si}^- \]

Since the silica particle surface has the negative charges (-O' ), the counter ions of the positive charges in slurry surround the particles to neutralize the negative surface charges as shown in Figure 1. This pair of the negative and positive charged layers is called as to the "Electrical Double Layer (EDL)". When the repulsion force between the outer positively-charged layers is strong enough, the silica particles are dispersed in the slurry. According to the Verwey-Overbeek theory [3], the silica particles are agglomerated each other when the repulsion force is decreased by reducing the EDL width. The EDL width decreases with decreasing the HO- ion concentration in the slurry because of lowering the negative surface charge density on the particle. The EDL width also decreases with increasing the electrolyte salt concentration in the slurry because of the charge screening effects.

2-2. Slurry preparation and Polishing experiment

Based on the theoretical background, the slurries were prepared with various pH values and various salt concentrations. In this paper, an ammonium salt was chosen as the adding salt, and an ammonium-hydroxide or an acetic-acid solutions were selected to control the slurry pH value. These chemicals contain no alkaline metal ion such as K+.

Figure 2 illustrates the slurry preparation process. The starting silica slurry was a mixture of water (80%) and high purity silica particles of 40 nm-diameter. An ammonium salt was added to the slurry with the concentration of 0.1 to 0.3 mol/l, and then an aqueous ammonium-hydroxide or an aqueous acetic-acid solutions were introduced to adjust the slurry pH values approximately at 6 (weak-acid), 7 (neutral) or 9 (base). The slurries without the salt were also prepared as pH = 6 to 9.

The slurry composition effects on the polishing rate as well as the particle removal after CMP were
examined as the follows. A silicon dioxide (SiO₂) film on 6" wafer was polished by a rotating polishing pad with the slurry of 50 ml/min. The polishing pressure was 0.4 kg/cm², and the rotation rates both of the wafer and the polishing plate were 35 rpm. After the polishing, the wafer was cleaned by a scrubbing, and then dried. The number of particles with the diameters greater than 160 nm were counted by a laser particle counter. The polishing rate was calculated by the relation between the polished thickness and the polishing time duration.

3. Results

Figure 3 shows the slurry composition effect on the polishing rate. The polishing rate was the functions both of the slurry pH value and the salt concentration. In the case of no salt addition (0 mol/l), the polishing rate for the weak-acid slurry (pH=6) was only 100 A/min. The polishing rate was increased with increasing the pH value. When the slurries with 0.1 mol/l salt were used, the polishing rates were larger than those without the salt irrespective of the pH values. Especially, the salt-added weak acid slurry (pH=6) had the strongest acceleration effect, and the polishing rate was jumped up to 2600 A/min. When the salt was added to 0.3 mol/l, the acceleration effect was slightly weakened regardless of the slurry pH. Namely, it is found that the salt-added slurries of pH = 6 ~ 7 reveal large polishing rates.

Figure 4 shows the slurry composition effect on the particle number on the 6" wafer after the post-CMP cleaning (scrubbing). In case of pH = 9, a lot of particles were remained regardless of the salt addition. By the salt addition to the weak acid (pH = 6) or the neutral (pH = 7) slurries, on the other hand, the particle numbers were extremely decreased. Namely, it is found that the salt-added slurries of pH = 6 ~ 7 have an excellent particle removal property.

In Figure 5 is shown the relation between the polishing rate and the particle number after the post-CMP cleaning (scrubbing). The slurries examined here were classified into three groups; the "Group A" is the no salt-added slurries, the "Group B" is the base slurries (pH = 9), and the "Group C" is the salt-added slurries of pH = 6 ~ 7. The slurries in the "Group A" have the worst properties, the polishing rates were less than 1000 A/min., and the particles more than 10,000 numbers were remained on the 6" wafer. The polishing rate was slightly push up by using the base slurries (pH = 9) in the "Group B" because of the ILD film (SiO₂) dissociation, or essentially the chemical-effect increment of the polishing. A lot of particles, however, were remained after the post-CMP cleaning. In the "Group C", the salt-added slurries of pH=6 ~ 7 had high polishing rates and relatively small numbers of particles remained on the wafer.

4. Discussion

As described in the section 2-1, it is predicted theoretically that the silica particles tend to be agglomerated each other in the slurry compositions of low HO⁻ ion concentrations (pH = 6 ~ 7) or high salt concentrations. So, the particle size distributions for the typical slurries in the "Group A", "B" and "C" were examined by a sedimentation method. By this method, the secondary particle size or the agglomeration size in the slurry was obtained. As shown in Figure 6, it is found that the secondary particle size of the "Group C" slurry is larger than those in the "Group A" and "B" slurries. Since the primary silica particle size was 40 nm, approximately 170 silica particles were agglomerated in the most probable secondary particle of the "Group C" slurry.

Based on the above experimental results, the reason why the salt-added slurries of pH = 6 ~ 7 ("Group C") have the large polishing rates and the excellent particle removal is explained as follows: the silica particle agglomeration is strongly promoted by the salt-addition to the slurries of pH=6 ~ 7, increasing the effective abrasive particle size. Therefore, a mechanical-effect for the ILD film is enlarged, yielding the large polishing rate. The agglomerated silica particles in the salt-added slurries of pH=6 ~ 7 are removed more sufficiently than the small particles in the "Group A" and "B" slurries, since the scrub cleaning is effective to relatively large particles.

Finally, using a silica slurry without KOH, three-level aluminum interconnection on the planerized ILD films was obtained successfully as shown in Figure 7.

5. Conclusion

In conclusion, the ammonium salt addition, instead of KOH, to silica slurry enlarges the effective abrasive particle size by the silica particle agglomeration, thus enabling us a high speed planarization CMP and a less contamination both of the alkaline metal ions and the silica particles after the CMP.

References

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Fig. 1 Schematic illustrations of silica particles of the dispersion or agglomeration conditions. The width of electrical double layer is reduced by the addition of salts to the slurry of $\text{pH} = 6$ - 7, thus promoting the agglomeration of silica particles [3].

Fig. 2 Preparation process of the silica slurries with various conditions of $\text{pH}$ and salt concentration.

Fig. 3 Polishing rate as the function of the salt concentration with various $\text{pH}$ values of the slurry.

Fig. 4 Effect of the salt concentration on the particle number remained on 6" wafer after the CMP and the brush scrub cleaning processes.

Fig. 5 Relation between the polishing rate and the particle number remained after the cleaning process: Group A, no salt addition; Group B, slurry of $\text{pH}=9$; Group C, slurry of $\text{pH}=6$ or 7 with the salt addition.

Fig. 6 The secondary particle size distributions in the typical slurries among Group A ( $\text{pH} = 7$, Salt = 0 mol/l ), Group B ( $\text{pH} = 9$, Salt = 0 mol/l ) and Group C ( $\text{pH} = 7$, Salt = 0.3 mol/l ). The size distribution was examined by a sedimentation method.

Fig. 7 Three level Al interconnects on the interlayer dielectric films planarized by the CMP process using a silica slurry without KOH addition.