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High-selectivity damascene chemical mechanical polishing

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Abstract

In this study, multi-step chemical mechanical polishing (CMP) with different copper removal rates and polishing pads is used to eliminate topography efficiently and to reduce micro-scratches on copper films. In colloidal-silica-based slurry, the polishing behaviors of copper, tantalum and silicon dioxide are found to relate to that kind of alkaline additives. The size of cations from alkaline additives influences the zeta potential of slurries, so as to vary the material removal rate. The addition of small-sized K^+ from KOH provides high removal selectivity of tantalum/copper and oxide/copper, so as to benefit the reduction of copper dishing.
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1. Introduction

In copper (Cu) damascene processes, chemical mechanical polishing (CMP) has been a promising method for achieving a globally planarized surface and defining interconnection areas [1–5]. CMP needs to produce a planarized Cu line with an intact surface because the quality of Cu surfaces directly contributed to the adhesion of dielectric films, the continuity of multilevel interconnection, and even stress reliability [6–11]. Chemical effect is particularly important in Cu-CMP because Cu is easily corroded and oxidized. Various abrasives have been developed to remove Cu oxides or passivation films, however, scratches are usually generated on Cu surfaces after CMP due to complicatedly tribochemical behaviors of Cu in different slurries and polishing conditions. Abrasives should be small or soft enough to avoid scratching while large or hard abrasives are needed to maintain a significantly removal rate. Ideally, the Cu-CMP process should remove the excess Cu from barrier surfaces without losing Cu metals in trenches. A higher removal rate of Cu is required for the phase 1 Cu-CMP to efficiently eliminate the step height of the Cu films, whereas a lower removal rate of Cu is necessary for the phase 2 Cu-CMP to precisely control the end-point over the barrier metals. To guarantee the formation of the isolated interconnection lines, overpolishing is usually carried out to remove residual metals on the field surface outside of patterns. A major issue that remains is the severe dishing of Cu lines and erosion of dielectric films in high pattern density areas during the overpolishing step. To reduce the amount of Cu dishing, various slurry chemistries are investigated in this study. Colloidal silica is adopted as the abrasive in the second-step CMP, considering its high suspension stability in slurries with a wide pH range and its sphere shape with less damage on polished substrates. The polishing behaviors of Cu, tantalum (Ta), and silicon dioxide (SiO_2) films in the colloidal-silica-based slurries with hydrogen peroxide (H_2O_2) and alkaline additives are discussed. Also, the formulation of slurries is optimized to improve the removal selectivity of different materials.

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2. Experimental details

All polishing experiments were performed with (100) oriented, 6-in.-diameter p-type Si wafers. The polishing sample was stacked with 900-nm-thick Cu and 50-nm-thick Ta, which was sputtering deposited on a 550-nm-thick thermal grown SiO_2 wafer. For CMP analyses, the thicknesses of the Cu and Ta films were calculated by dividing the film resistivity with its measured sheet resistance. A Tencor M-gauge was used to measure the sheet resistance of the Cu and Ta films before and after CMP processes. The thickness of thermal SiO_2 film was measured by a Nanospec 210XP-thickness measurement system. Cu-CMP was performed with a Westech Model 372M polisher using a Politex Regular E. pad. Polishing parameters, such as down force, platen/carrier rotary speed, back pressure and slurry flow rate were set to be 5 psi, 42/45 rpm, 2 psi and 150 ml/min, respectively.

The polishing slurries under investigation were formulated with 10 wt.% diluted colloidal silica (<50 nm in size), 10 wt.% H_2O_2 (30 wt.% semiconductor grade) and adjusted slurry pH value by adding various alkaline additives. Three types of alkaline additives, including potassium hydroxide (KOH), ammonium hydroxide (NH_4OH) and tetra-methyl-ammonium hydroxide (TMAH) were used as slurry pH adjusters. All chemical constituents mentioned above were added to the solution of de-ionized water with rigorous string.

In a colloidal dispersion of particles, there will generally be a net charge at the particle–liquid interface. The existence of the surface charge gives rise to the formation of the zeta potential. The zeta potential of the colloidal silica in the formulated slurries was measured by an electro-acoustic instrument, model DT1200. A laser diffraction particle size analyzer, UP-150 was used to measure the aggregation size of abrasives in slurries.

3. Results and discussion

The removal of Cu is contributed from both mechanical and corrosive (chemical) wears. In this study, the effects of slurry pH and added alkaline ions on the polishing behaviors of Cu, Ta and SiO_2 are discussed. The planarization performance of Cu-CMP is related to the properties of polishing pads. A soft pad, which has a smaller hardness and a larger compressibility, is usually used to prevent surface scratching, while a hard pad is usually used to reduce Cu dishing because its limited compressibility has a higher Cu removal rate on the feature tops. Fig. 1 shows the polishing behavior of Cu, Ta and SiO_2 for various pH values. The slurry formulation contains 10 vol.% H_2O_2, 10 wt.% colloidal silica, and adding KOH to adjust slurry pH ranged from 2 to 10. In acidic aqueous medium, Cu tends to be corroded and then the removal rate of Cu is faster than those of Ta and SiO_2 on which stable native oxide is present. The maximum

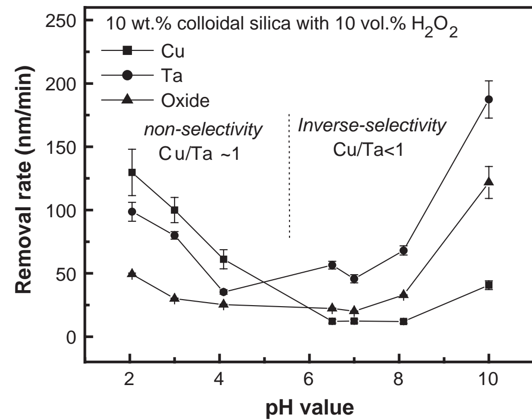


Fig. 1. Removal rates of Cu, Ta, and oxide with various pH adjusted by KOH in the slurry with 10 wt.% colloidal silica slurry and 10 vol.% H_2O_2.

removal rate of Cu is above 130 nm/min at pH 2. As slurry pH increases into neutral regime, the removal rate of Cu drops as the dissolution rate of Cu is dramatically reduced by formation of Cu oxide passivation (Cu_2O, CuO). The solubility of Cu oxide becomes large as the slurry pH in the alkaline regime due to the formation of soluble Cu hydroxides or the decline of the hydrogen peroxide (H_2O_2) activity in the strongly alkaline solution. Competing with the passivation behavior of Cu, the foregoing reactions result in few Cu removal rate increase (~40 nm/min), as shown in Fig. 1.

In order to achieve global planarization, there should be high removal selectivity between metal, diffusion barrier and dielectric layer. So the polishing behavior of Ta and SiO_2 should be noticed. For polishing Ta, it is found that higher removal rates occur at both strongly acidic (pH 2) and alkaline (pH 10) slurries, as shown in Fig. 1. The Pourbaix diagram of the Ta–water system indicated the formation of tantalum pentoxide (Ta_2O_5) in a wide pH range. The formation reaction of Ta_2O_5 on the Ta surface could be expressed as follows [12]:

$$2Ta + 5H_2O = Ta_2O_5 + 10H^+ + 10e^-. \quad (1)$$

In acidic solution, the oxygen reduction reaction may take place and be written as:

$$O_2 + 4H^+ + 4e^- = 2H_2O. \quad (2)$$

The overall reaction can be rewritten as

$$2Ta + 5/2O_2 = Ta_2O_5. \quad (3)$$

It has been reported that the presence of H_2O_2 plays a crucial role in determining the kinetics of the formation and dissolution of Ta_2O_5. The overall dissociation reaction of H_2O_2 is depicted as

$$2H_2O_2 = 2H_2O + O_2. \quad (4)$$

H_2O_2 is highly unstable in the alkaline solution. The rate of the dissociation reaction of H_2O_2 is enhanced in solutions with high pH. The produced oxygen from the dissociation of

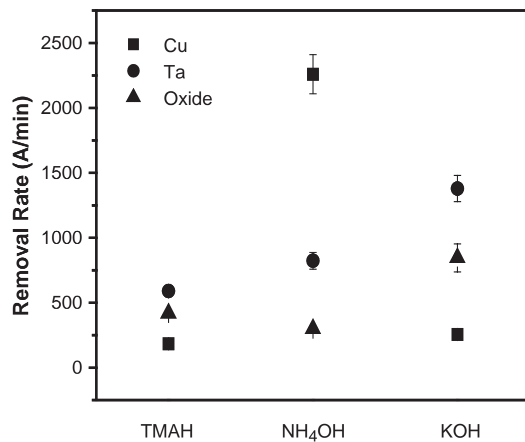
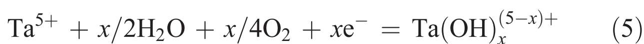
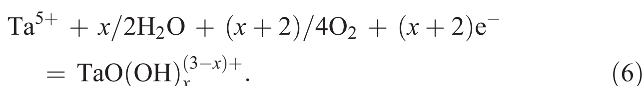


Fig. 2. Polishing rate of Cu in colloidal-silica-based slurry with H_2O_2 using various alkaline additives to adjust pH value at 9.2.

H_2O_2 is suggested to facilitate noble Ta_2O_5 forming soluble hydroxotantalate and oxotantalate as shown in the following reactions [12]:



$$Ta^{5+} + x/2H_2O + x/4O_2 + xe^- = Ta(OH)_x^{(5-x)+} \quad (5)$$



$$Ta^{5+} + x/2H_2O + (x+2)/4O_2 + (x+2)e^- = TaO(OH)_x^{(3-x)+}. \quad (6)$$

In alkaline solutions, therefore, the removal rate of Ta is determined by the dissolution rate of Ta_2O_5 and increased with increasing the pH value of the slurries.

For polishing Ta in solutions with low pH, the mechanical abrasion dominates the Ta removal rate due to the presence of stable Ta_2O_5 films in the acidic solutions. Therefore, the larger secondary ionic particle size of abrasive at pH 2 leads to higher Ta removal rate because the iso-electric potential of colloidal-based slurries was around pH 2 in this study.

The removal behavior of oxide with slurry pH values is similar to that of Ta. As oxide CMP is carried out in acidic and neutral region, the removal of oxide is dominated by the mechanical abrasion, indicating that the larger abrasive at pH 2 induces higher oxide removal rate. In strongly alkaline slurries, the removal rate of oxide increases as the slurry pH increases because the hydrolysis reaction of oxide increases with increasing the slurry alkaline. In addition, adding more KOH into slurry would increase the ionic strength of slurry leading to a dramatic decrease in the thickness of diffusion layer. That means the repulsive electrostatic charges on both the abrasives and the substrate would be neutralized by the excess K^+ cations, so the removal rates would be promoted.

Various kinds of alkaline additives, including KOH, NH_4OH and TMAH, are investigated for their influence on the removal behavior of Cu, Ta and SiO_2 during polishing. Fig. 2 shows the removal rates of Cu, Ta and SiO_2 in the colloidal-silica-based slurries with various alkaline additives (KOH, NH_4OH, and TMAH) to control pH value at 9.2.

It is through ammonium hydroxide that cupric ions would chelate to form soluble $Cu(NH_3)_4^{2+}$ and to increase the Cu removal rate. As a result, polishing in the NH_4OH-containing slurry, the removal rate of Cu is increased to 225 nm/min, as shown in Fig. 2. But the removal rate of Cu in the slurries with the other two alkaline additives (KOH and TMAH) is less than 30 nm. For Ta and SiO_2 polishing in the slurry with KOH, the maximum removal rates of Ta and SiO_2 are about 135 and 85 nm/min, respectively, but only about 55 and 45 nm/min, respectively, in TMAH-added slurry at the same pH value. It implies that cations from the alkaline additives, i.e. K^+, NH_4^+ and $N(CH_3)_4^+$, contribute to the overall removal rate of Ta and SiO_2. In general, electrostatic double layer is within tens of micrometers. For smaller abrasives with a diameter of less than 50 nm, there is an electrostatic repulsive force between the negatively charged silica abrasives and the substrate. According to the theory of Stern layer, counter ions adsorption would decrease the surface potential. The negatively charged colloidal silica abrasives would be neutralized by adsorption of cations from the alkaline additives. If the size of cations is large, there will be less cations adsorbed on the colloidal silica due to the effect of steric hindrance, so as to extend more the diffusion layer thickness. As shown in Fig. 3, the absolute zeta potential (or the repulsive force) of colloidal silica in TMAH-added slurry is larger than that in KOH-added slurry because $N(CH_3)_4^+$ is larger than K^+. The high zeta potential of TMAH-added slurry leads to less impacting frequency of colloidal silica onto the substrate, and then the removal rate decreases.

For the NH_4OH-based slurry, it is different from the other alkaline solutions because NH_3 would dissolve Cu oxide passivation and form $Cu(NH_3)_4^{2+}$ to enhance the removal rate of copper. The removal rate is about 225 nm/min for Cu and 80 nm/min for Ta at pH 9.2. With more NH_4OH added into the slurry, at pH 10, the removal rate would be enhanced to 1490 nm/min for Cu and 100 nm/min for Ta. So

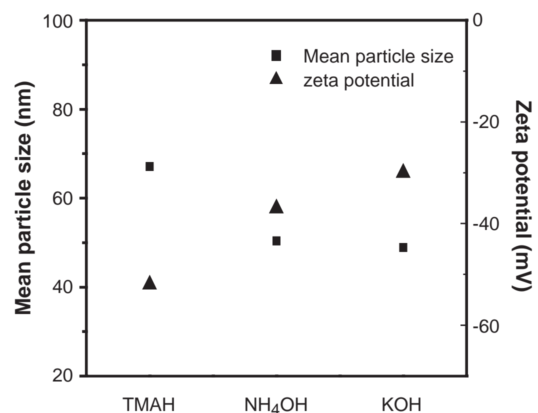


Fig. 3. Mean particle size and zeta potential of colloidal-silica-based slurry with H_2O_2 using various alkaline additives to adjust pH value at 9.2.

the removal selectivity of Cu/Ta and Cu/ SiO_2 gets higher (14.3 and 19, respectively) and that would be suitable for the 1st step of Cu removal but not for the 2nd step of Ta removal.

In order to reduce metal dishing and oxide erosion, it is better to control fast removal rate of Ta and not to remove Cu and SiO_2, respectively. The KOH-added slurry has higher removal selectivity of Ta/Cu and SiO_2/Cu. Furthermore, the Ta removal rate is relatively high (~140 nm/min) in the KOH-added slurry. So KOH is found to be a suitable pH adjuster for the colloidal-silica-based slurry.

4. Conclusions

In this study, the removal mechanism of Cu-CMP on the characteristics of colloidal-silica-based slurry is investigated. It is found that the polishing behavior of Cu, Ta and oxide is deeply dependant on the slurry pH and the surface-charge-related interactions between the slurry and the polishing substrate. The attraction and expulsive force affect the impacting frequency between colloidal silica abrasives and the wafer surface. Large-size cations lead to a less impacting frequency between the abrasives and the substrate, so as to get lower removal rate. Combining the results mentioned above, high or low removal selectivity of Ta/Cu and SiO_2/Cu during the two-step Cu-CMP process can be achieved by modified colloidal-silica-based slurries with proper alkaline additives and pH values.

Acknowledgments

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