Study of Chemical Reactions on Chemical-Mechanical Polishing

Chemical Mechanism, Slurry

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MOTIVATION

Owing to the more server requirements on the DOF of deep submicron lithography and multi-layer interconnect fabrication, global planarization of the wafer is required. Chemical-Mechanical Polishing (CMP) is the only technique known to achieve global planarization(1). Since mid-1980s, IBM introduced CMP into the regime of semiconductor manufacturing, most of the technical parts of CMP came from previous optical glass polishing. The complex interactions of mechanical wearing and chemical dissolution of substrates must be taken into account during CMP, and the process are carried out by mostly experimentalism with little or no understanding of its fundamental mechanisms. Up-to-date, the complex and dynamic interactions between chemical erosion and mechanical wearing during CMP are not well-understood and under development.

Abrasives in the slurry play the very important role during CMP process, but
RESULTS AND DISCUSSION

All test wafers were p-type, (100) oriented, 6" bare silicon wafers. The oxide samples were prepared by thermally oxidation of bare Si wafers and about 5500 Å thick silicon dioxide films were obtained. The aluminum alloy films were obtained by deposition of 550 nm silicon oxide, 20 nm titanium, 20 nm titanium nitride and 900 nm Al-Si(1%)-Cu(0.5%) sequentially.

The characteristics of alumina abrasives used in this study are shown in Table 1. From A1 to A4 alumina series, the alpha-phase contents increase, and A5, A6 are mainly low-temperature alumina transition phase. All polishing experiments were carried out on a IPEC/Westech 372M polisher with Rodel IC 1400 polish pad on the primary platen and a Rodel Politex Regular E post polishing buffering pad on the second platen. The polishing parameters, such as down forces, back pressure, platen/carrier rotation speed, slurry flow rate, were set to be 8 psi, 3 psi, 20/25 rpm, 150 ml/min for oxide substrates polishing, and 5 psi, 2 psi, 45/24 rpm, 150 ml/min for aluminum alloys substrates polishing.

Two part of experiments were carried out. The first one is aluminum alloy substrates were polished with various alumina abrasives (A1–A6). The slurry formulation in the aluminum CMP is 5 wt. % alumina abrasive, 3 vol.% H2O2 as oxidizer, 5 vol.% H3PO4 and 0.1M citric acid as pH buffer, slurry pH was adjusted by adding conc. HNO3 aqueous solutions.

In Kaufman's proposed CMP model(2), a metal oxide passivation film would formed on the surface and dissolved into slurry during CMP abrasion. Cross-reference to the Pourbaix diagram of Al-H2O system, the oxide formed in the metal surface is Al2O3 in the pH range of 4-8. The results of polishing aluminum alloys with various alumina abrasives (A1–A6) are shown in Fig. 1. It shows that polishing with α-alumina abrasives got the higher removal rates than those with θ, δ-alumina, γ-alumina. The removal rates of the four types alumina crystalline phase were ranked as follow:

α-alumina > θ, δ-alumina > γ-alumina

Polishing with the larger size and higher hardness of alumina abrasives got higher removal rates of aluminum alloy substrates. Y. L. Wang(3) found that the removal rates of aluminum alloys decreased with increasing slurry pH from 1.5 to 4.5 as polishing with alumina abrasives (Fig. 2). According to the Pourbaix diagram of aluminum-water system, the acidic corrosion dominates as pH < 4. In the neutral aqueous solution, Al surface becomes corrosion resistant due to the formation of a passivation oxide film. Apparently, the removal rates of Al alloys were dependent upon the solubility of surface aluminum oxide passivation.

According to the SiO2/Al2O3 and Al2O3/Al2O3 polishing system, the removal rate would mainly be controlled by the geometry factors of the abrasives. Polishing with sharp-edge shape, larger size and higher hardness abrasives tends to obtain the higher removal rates. From the tribology point of view, the shape of the abrasive plays the important role on the substrate abrasion. It would determine how the abrasive penetrates into the substrate at the contact load and the transition from elastic to plastic deformation that would contribute to the overall material removal. In this study, it was confirmed that less wear occurs when materials are abraded by rounded, rather than sharp abrasives. Besides, the removal rates would be dependent upon the solubility of material being polished in the solution.

The removal rate of polishing oxide with alumina abrasives, A5 and A6, at various slurry pH were shown in Fig. 3. The
maximum removal occurs at the slurry pH about 6-8, it located between SiO$_2$ I.E.P. (pH-3) and Al$_2$O$_3$ I.E.P. (pH-9). The Hogg-Healy-Fuerstenau (HHF) formula was employed to estimate the electrostatic interaction, $V(H)$, between the abrasives and the polished substrate. The calculation can be simplified as the sphere (abrasive)-plate(oxide film) interaction:

$$V_{HHF}(H) = 4\pi \varepsilon_2 \varepsilon_0 a_2 \psi_1 \psi_2 e^{-\kappa H}$$  \hspace{1cm} (1)

Where $\varepsilon_2$ is the relative permittivity of the solution and $\varepsilon_0$ is the relative permittivity of the vacuum. The spherical particle in an electrolyte solution, having radius $a_2$ and particle and plate surface potentials $\psi_1$, $\psi_2$, respectively, at a closest distance, $H$, between their surface, $\kappa$ is Deby-Hückel parameter.

As slurry pH located between the I.E.P. of the oxide film (about 3) and the alumina abrasive (about 9), the electrostatic attractive force would be maximum and to drive abrasives approaching to the substrate and to bring away the abraded debris. Otherwise a repulsive force and less interactions between the abrasives and the substrate would be obtained. Fig. 4 is the schematic of electrostatic interaction between alumina abrasive and oxide film.

Cook proposed that mass transport during polishing is determined by the relative rates of the following processes, movement of solvent into the surface layer under the load imposed by the polishing particle, surface dissolution under load, adsorption of dissolution products onto the surface of the the abrasive, the rate of back-deposition of dissolution products onto the surface, and surface dissolution which occurs between particle impacts.

It is suggested that polishing compounds such as CeO$_2$ or ZrO$_2$ possess a chemical tooth that expedites both shearing at the glass surface and transport of reaction products away from the surface faster than that of re-deposition. If the abrasives could approach the substrate effectively, both substrate dissolution under load and removal by adsorbed onto the abrasives become faster and higher removal rates would be obtained. As the attractive force exists between the abrasive and oxide film, higher removal rates could be obtained owing to high frequency of abrasives impinging on the surface and good adsorption of dissolved products onto the abrasives. The oxide removal rate concerns with the specific surface area of abrasive deeply. Higher removal rate would be obtained by polishing with the abrasives of higher specific surface(Fig. 5). The removal rates of polishing with four types of alumina abrasives are ranked as follows:

$$\theta, \delta$ -alumina > $\gamma$ -alumina > $\alpha$ -alumina

the removal rates of polishing AlSiCu alloys with silica-based slurry at various slurry pH were shown in Fig11. Higher removal rates could be obtained at slurry pH about 5-6 and 10 because of electrostatic force and alumina solubility. In the pH range 2-7, the removal rate was dominated by electrostatic force between the abrasives and the alumina substrate and increased with slurry pH. In the pH range between 7 and 9, both electrostatic repulsion and low alumina solubility would lead to the minimum removal rate. As slurry pH larger than 10, the removal rate would be enhanced owing to the improved alumina solubility.

**Surface Roughness**

Brown suggests the penetration depth ($R_s$) of the particle in to the surface is given by:

$$R_s = \frac{3}{4} \phi \left( \frac{P}{2kE} \right)^{\frac{2}{3}}$$ \hspace{1cm} (2)

Where $\phi$ is particle diameter, $P$ is pressure (replacing load per area), $k$ is particle concentration (unity for a fully filled close hexagonal packing) and $E$ is Young’s modulus. $\alpha$ -alumina is stale crystalline phase and forms at a temperature of 1200°C. In the TEM images, $\alpha$ -alumina gets a big size because of forming temperature. The particle size of $\theta$, $\delta$, $\gamma$ -alumina is smaller. According to the formula (2) penetration depth is proportional to particle, it means $\alpha$ -alumina is penetration deeper than $\theta$, $\delta$, $\gamma$ -alumina and induces large surface roughness and more scratch. Fig. 7 shows the surface roughness with A1 to A6 abrasive. A4 have maximum $\alpha$ -alumina content and get the largest surface roughness. A5, A6 are all composed by low temperature alumina transition phase, $\theta$, $\delta$, $\gamma$ -alumina, have small surface roughness.

**CONCLUSION**

The abrasives in the polishing slurries play very critical role in CMP processes. In this study, we demonstrate that surface charges,
or zeta potential, on both the abrasives and the polishing substrate would contribute significantly to the overall removal rate. The mechanical and geometrical factors of abrasives would not be the only factor taken into account for the removal rates, but they would influence the surface roughness after polishing.

REFERENCES


Table 1  The characteristic of alumina abrasives used in this study

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<th>A2</th>
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Fig. 1 The removal rates of polishing AlSiCu substrates with various Al₂O₃ abrasives.

Fig. 2 The removal rates of polishing Al alloys films with various slurry pHs.

Fig. 3 The removal rates of polishing thermal SiO₂ substrates with various Al₂O₃ abrasives and slurry pHs.
Fig. 4 Schematic of electrostatic interactions between the abrasives and the substrate being polishing.

(a) Attraction
IEP (SIO2 layer) < pH < IEP (abrasive)

(b) Repulsion
pH < IEP (SIO2 layer) or pH > IEP (abrasive)

Fig. 5 The relationship between the surface area of the abrasives and the removal rates of polishing oxide substrate with Al2O3 slurries.

Fig. 6 The removal rates of polishing AlSiCu substrates with various SiO2-based slurry pHs.

Fig. 7 The surface roughness of the oxide films polished with various Al2O3 abrasives.

Fig. 8