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線性 CMP 製程與實驗機台研究

子計畫七：CMP 之化學反應機制研究(I)

Study of Chemical Reactions on Chemical-Mechanical Polishing

主持人:蔡明蒔　　執行機構:國家毫微米元件實驗室

E-mail: mstsai@ndl.gov.tw

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中文摘要：

　　在深次微米半導體製程中，由於元件線幅持續微型化及積極度增高，造成曝光微影景深縮減及需採用多層導線結構。化學機械研磨已成為晶圓上全域性平坦化之關鍵技術。化學機械研磨過程涉及複雜之研磨粉體與研磨受質間之機械性磨耗及化學腐蝕溶解反應，至今仍對其磨耗機制瞭解有限且持續在研究中。其中研磨漿料之組成如研磨粉體及化學反應物對於整體研磨特性有決定性之影響，如移除率、研磨不均勻性，研磨後之表面損傷等。

　　本研究著重於研漿中研磨粉體對研磨特性之影響。以不同之三氧化二鋁粉體，含不同粒徑、晶相，研磨二氧化矽玻璃及鋁銅合金受質，探討粉體與研磨受質間之機械磨耗及化學鍵結作用。結果顯示，當研磨粉體與受質屬同一材質時，如以三氧化二鋁研磨鋁合金受質，研磨主要受粉體之機械性質影響，即移除率與粉體之幾何構形及粒徑大小相關。當粉體與受質屬相異材質時，兩者間之庫倫靜電力為影響移除率的主要因素。當研漿 pH 值介於粉體與受質之等電位點之間時，兩者存在靜電引力促使移除率增加，反之則因靜電斥力而減緩磨除量。研磨後表面粗度則取決於研磨粉體之粒徑大小及研磨墊軟硬，與移除量無關。

## ABSTRACT

In this study, various kinds of alumina abrasives, different particle sizes and crystal phases, were employed in polishing oxide and aluminum alloy substrates to explore their influences on CMP performance, such as removal rates and surface roughness. As the substrates being polished and the abrasives were the same material, it has been found the removal rates would be strongly dependent on the mechanical properties of abrasives. On the other hand, the electrostatic interactions between the abrasives and the substrates would dominate the overall removal rate as the abrasives and the substrates with different isoelectric points (I.E.P.). The maximum removal rate would be obtained as polishing at the slurry pH located between the IEPs of the substrates and the abrasive. In this case, electrostatic attraction exists between abrasives and the substrate, which results in the enhancement the impingement frequency of abrasives on the substrates and the absorption of abraded materials onto the abrasives. The surface roughness after polishing would depend on the abrasive size and the pad hardness. Polishing with larger particle size and harder pad would result in more roughness surface.

## 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 understand-ing 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

still under investigation now. Not only the abrasives are responsible for the mechanical abrasion of the materials being polished, some interactions related to surface charges between the abrasives and the substrate would be considered. In oxide CMP, the removal rate is a strong function of slurry pH[2]. The slurry pH and the I.E.P. of the abrasives would determine which electric polarities would be charged on the surface of abrasives, positive or negative, so that electrostatic interactions would influence the particle agglomeration in the slurry and the interaction between the abrasive and the substrate.

## 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 5wt % alumina abrasive, 3 vol.% $H_2O_2$ as oxidizer, 5 vol.% $H_3PO_4$ and 0.1M citric acid as pH buffer, slurry pH adjusted by adding conc. KOH aqueous solutions.

In the second part, the oxide substrates were polished with various alumina abrasive (A1~A6). The slurry formulation is 5 wt. % alumina abrasives (A1~A6), 0.1 M

ethylene-di-amine (EDA) as pH buffer, the slurry pH was adjusted by adding conc. $HNO_3$ aqueous solutions.

In Kaufman's proposed CMP model[3], a metal oxide passivation film would formed on the surface and dissolved into slurry during CMP abrasion. Cross-refer to the pourbaix diagram of Al-$H_2O$ system, the oxide formed in the metal surface is $Al_2O_3$ 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 $\alpha$-alumina abrasives got the higher removal rates than those with $\theta$, $\delta$-alumina, $\gamma$-alumina. The removal rates of the four types alumina crystalline phase were ranked as follow:

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

Polishing with the larger size and higher hardness of alumina abrasives got higher removal rates of aluminum alloy substrates. Y. L. Wang[4] 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[5] 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 $SiO_2$/ $SiO_2$ and $Al_2O_3$/ $Al_2O_3$ 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[6] 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

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maximum removal occurs at the slurry pH about 6~8 , it located between $SiO_2$ I.E.P. (pH~3) and $Al_2O_3$ I.E.P. (pH~9). The Hogg-Healy-Fuerstenau (HHF) formula[7] 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:

$$V_{HHF}(H) \approx 4\pi\varepsilon_r\varepsilon_0 a_2 \psi_{s1}\psi_{s2} e^{-\kappa H} \quad (1)$$

Where $\varepsilon_r$ 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 $\psi_{s2}$, $\psi_{s1}$, 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[8] 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[1] suggests the penetration depth ($R_s$) of the particle in to the surface is given by:

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

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.

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Table 1   The characteristic of alumina abrasives used in this study

| | A1 | A2 | A3 | A4 | A5 | A6 |
|---|---|---|---|---|---|---|
| Major crystal Phase | Theta (Alpha) | Alpha (Theta) | Alpha | Alpha | Theta Delta | Gamma |
| Phase Content (%) | 50-55 | 85-90 | 90-95 | 95-100 | >90 | >90 |
| Crystal Density of Major Phase (g / cm²) | $\alpha=3.98$ $\theta=3.56$ | $\alpha=3.98$ $\theta=3.56$ | 3.98 | 3.98 | $\theta=3.56$ $\delta=3.2$ | $\gamma=3.2$ |
| Mohs Hardness of Major Phase | 9 | 9 | 9 | 9 | 8-9 | 8 |
| BET Surface Area (m²/g) | 63.56 | 27.45 | 16.30 | 7.72 | 86.12 | 113.64 |
| BET Particle Size (nm) | 23.72 | 54.92 | 92.49 | 195.47 | 17.50 | 13.27 |
| TEM Particle Size (nm) | $\alpha=50{\sim}120$ $\theta=20{\sim}30$ | $\alpha=50{\sim}140$ $\theta=20{\sim}30$ | $\alpha=50{\sim}150$ $\theta=20{\sim}30$ | $\alpha=60{\sim}140$ $\theta=20{\sim}30$ | $\theta=20{\sim}30$ | $\gamma=10{\sim}20$ |
| XRD $\alpha$ Phase Size (nm) | 59.88 | 48.03 | 46.03 | 52.30 | | |
| Aqueous Dispersion Particle Size (nm) | 282.5 | 264.2 | 233.8 | 270.1 | 362.4 | 390.3 |
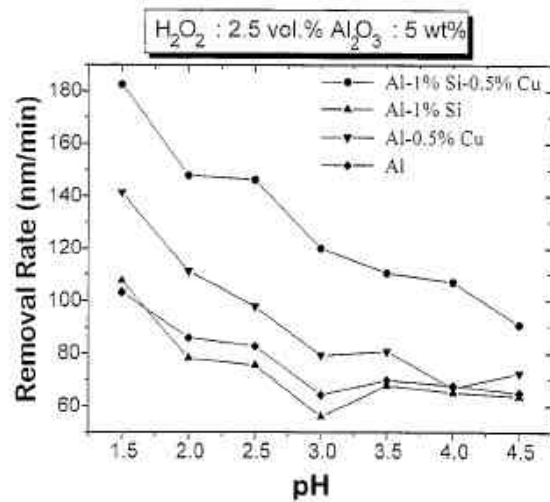


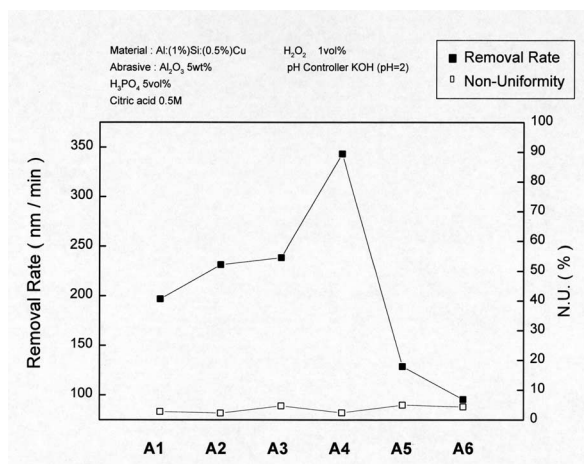Fig. 2 The removal rates of polishing Al alloys films with various slurry pHs.



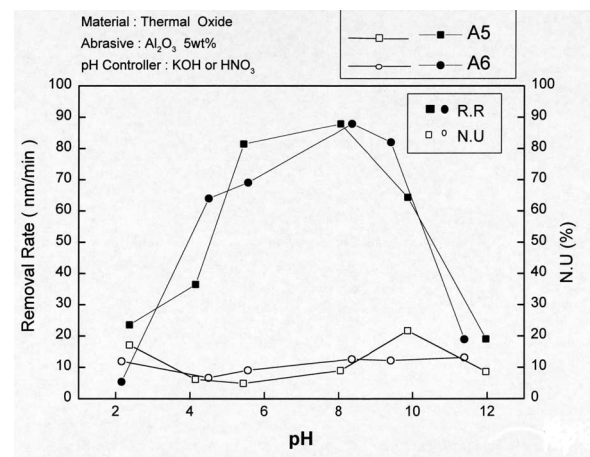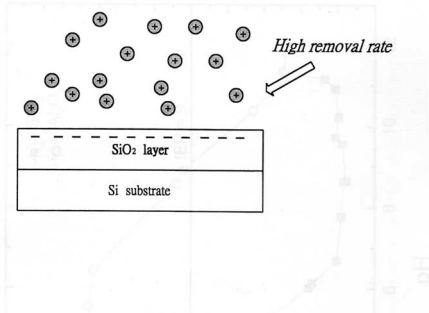Fig. 1 The remvoal rates of polishing AlSiCu substrates with various Al$_2$O$_3$ abrasives.



Fig. 3 The remvoal rates of polishing thermal SiO$_2$ substrates with various Al$_2$O$_3$ abrasives and slurry pHs.

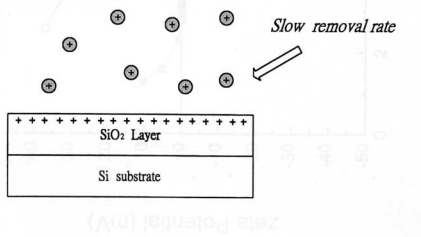(a) Attraction

**IEP (SIO2 layer) < pH < IEP (abrasive)**



*High removal rate*

(b) Repulsion

**pH < IEP (SiO₂ layer)  or
pH > IEP (abrasive)**

*Slow removal rate*

Fig. 4 Schematic of electrostatic interactions between the abrasives and the substrate being polishing.



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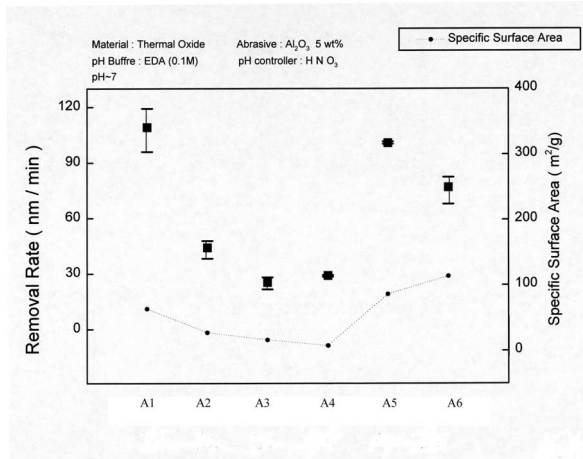


Fig. 5 The relationship between the surface area of the abrasives and the removal rates of polishing oxide substrate with Al₂O₃ slurries
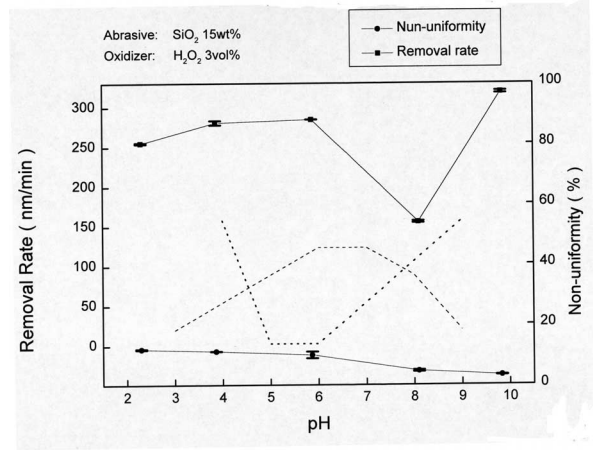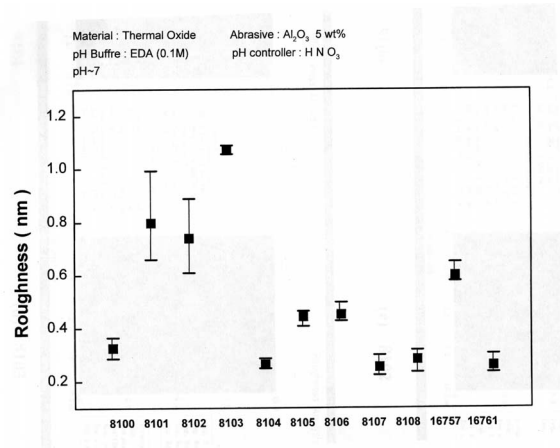


Fig. 7 The surface roughness of the oxide films polished with various Al₂O₃ abrasives.