A new removal rate model which is a modification to the Preston equation is developed to re-account the dependence of removal rate on the down force (pressure) and rotation speed during the chemical-mechanical polishing (CMP) process. The removal rate is first expressed as a linear function of both normal and shear stresses. The analogy of the CMP removal process to traveling indenters is considered and the stresses acting upon the abrasive particles (indenters) are formulated using previous models based on principles of elasticity and fluid mechanics. An expression is then derived which predicts the (pressure)$^{5/6}$ and (speed)$^{1/2}$ dependences of the removal rate. Experimental results with thermal oxides are consistent with the predictions.

Chemical-mechanical polishing (CMP) has been widely recognized as the most promising method that achieves both local and global planarization for ultralarge scale integrated circuit (ULSI) manufacturing processes. The polishing (material removal) mechanism is still obscure however and the process control and basic understanding of this technology remain essentially on the empirical level. So far most CMP users and researchers adopt Preston's equation to monitor removal rate. This equation incorporates the pressure ($P$) and speed ($V$) as the main contributors to removal rate ($R.R.$).

$$ R.R. = C_0P^aV^b $$ [1]

Or more generally it can be expressed as

$$ \Delta T/\Delta t = C_0(F/A)(\Delta s/\Delta t) $$ [2]

where $\Delta T/\Delta t$ is the change in thickness over time $t$ (i.e., removal rate); $F/A$ is the total applied force $F$ over area $A$ on which the polishing (abrasion) occurs; $\Delta s$ is the relative travel distance between sample surface and pad; and $C_0$ is the Preston coefficient related to chemical erosion processes and material characteristics. Both Eq. 1 and 2 suggest that the removal rate depends equally on pressure and speed.

Originally proposed for glass polishing, the Preston equation is also of experimental nature and no analytical work has been published to verify or to challenge it. Runnels and Eyman took into account the normal stress ($\sigma_n$) and shear stress ($\tau$) acting on a point during polishing.

$$ R.R. = C_0\sigma_n \tau $$ [3]

The normal stress acting on the abrasive particles against the samples originates from the pressure imposed by the polish arm while the shear stress arises from the slurry flow across the sample surface activated by relative motion between the rotating pad and carrier. Further development of Eq. 3 requires the determination of stress distributions, which involves delineation of several active mechanisms including fluid flow and solid deformation. The contribution of fluid flow to stresses and erosion during CMP operations have been analyzed. Nevertheless a more general model combining fluid flow and solid deformation (wearing) is still lacking.

Cook perceived the removal process as a traveling indenter plowing across the wafer surface. The abrasive particles transported in by the turbulent slurry encroach upon and indent into the wafer surface. The indentation process is considered Hertzian and the resulting stresses can be calculated from principles of elastic mechanics. The force $F$ acting on a spherical particle of diameter $d$ in the particle/wafer contact can be calculated as

$$ F = \frac{3Pd^2}{2K} $$ [4]

where $K$ is particle fill fraction which is unity for a fully filled closed packing, and $P$ is the pressure. The normal stress $\sigma_n$ can then be expressed as the force $F$ divided by the contact area between the polishing particle and the sample surface $\pi r_c^2$.

$$ \sigma_n = \frac{F}{\pi r_c^2} $$ [5]

The radius of contact $r_c$ can be determined from theories of contact mechanics

$$ r_c = \left[ \frac{3}{4} F \left( \frac{d}{2} \right) \left( \frac{1 - \nu^2}{E} + \frac{1 - \nu'^2}{E'} \right) \right]^{1/3} $$ [6]

where $\nu$, $\nu'$ are the Poisson's ratios of sample surface and the particle and $E$ and $E'$ are elastic moduli of the sample and particle, respectively. Runnels related the feature-scale erosion model to the Preston equation and formulated the stresses due to slurry flow. In his model, the shear stress $\tau$ can be approximated as

$$ \tau = C \left( \frac{\mu}{\sqrt{\mu V PA}} \right) = C \mu \sqrt{VPA} $$ [7]

where $\mu$ is the dynamic viscosity, $A$ is the sample surface area being polished, and $C$ is a constant related to the chemical aspects of the process. Equation 7 is derived based on the tribological approximation for slider bearings and the shear stress $\tau$ repre-
The removal rate data are plotted against carrier speed in Fig. 1 under varied pressure. The data are fitted to Eq. 8 with constant \( P \). As illustrated, the agreement with the prediction in Eq. 8 is excellent. Removal rate exhibits a \( V^{1.2} \) dependence over a wide pressure range. The calculated \( M \) values from the fitted curves using Eq. 8 are listed in Table I. \( M \) increases as more pressure is being applied on the wafers. This implies that the chemical erosion process is accelerated under high pressures. This acceleration may not be infinite however, since, under a high enough pressure, the pad surface feature flattens and the slurry holding capability deteriorates, which slows the chemical erosion process, leading to a drop in removal rate.

Figure 2 shows the pressure dependence of removal rate. Pressure was varied from 4 to 11 psi while carrier speed was set at 10, 20, 30, 40, and 50 rpm. The data are fitted to Eq. 8 with constant carrier speed. At high pressure and high carrier speed, removal rate does exhibit a \( P^{5.6} \) dependence. However, at low pressure and high carrier speed, removal rate is lower than that predicted from Eq. 8. This may result because under the above situation, the stress corrosion is known to occur in most metals. Under 7 psi (4960 Pa), the normal stress acting on a 0.3 mm silica particle in SC-1 slurry is ca. 46 MPa (--6672 psi), which falls within the range where stress corrosion of metals occurs. Additionally, the speed \( V \) may exert certain influences on the chemical erosion rate as erosion corrosion is known to depend strongly on the flow of slurry.

The expression for removal rate in Eq. 8 is markedly different from that in Eq. 1. While the \( P^{5.6} \) dependence of \( RR \) in Eq. 8 is close to Preston’s prediction, the \( V^{1.2} \) term in Eq. 8 apparently suggests a much weaker dependence of removal rate on speed \( V \). Notice that, on a particle scale, the \( V \) term in Eq. 8 should correspond to the speed that a fixed point on the wafer experiences relative to slurry flow. It is directly associated with the relative motion between pad and carrier.

To verify the validity of Eq. 8, CMP experiments are performed with 1 \( \mu \)m thick thermal dioxide samples grown on 200 mm silicon wafers using IC1000/Suba IV pads mounted on a polishing platen. SC-1 slurry consisting of fumed silica suspension dispersed in aqueous potassium hydroxide (\( pH \sim 10.3 \)) is distributed across the pad at a flow rate of 200 scm. Pad conditioning is performed between each wafer to rejuvenate the pad surface features. Pad speed is fixed at 20 rpm while pressure and carrier speed are varied to examine their respective effects on removal rate. Oxide thickness is measured by Nanospec at 17 points across wafers and the removal rate is calculated from thickness differences averaged over the 17 points before and after each polish.

The removal rate data are plotted against carrier speed in Fig. 1 under varied pressure. The data are fitted to Eq. 8 with constant \( P \). As illustrated, the agreement with the prediction in Eq. 8 is excellent. Removal rate exhibits a \( V^{1.2} \) dependence over a wide pressure range. The calculated \( M \) values from the fitted curves using Eq. 8 are listed in Table I. \( M \) increases as more pressure is being applied on the wafers. This implies that the chemical erosion process is accelerated under high pressures. This acceleration may not be infinite however, since, under a high enough pressure, the pad surface feature flattens and the slurry holding capability deteriorates, which slows the chemical erosion process, leading to a drop in removal rate.

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### Table I. Calculated \( M \) parameter from the fitted curves in Fig. 1 based on Eq. 8.

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<th>( P ) (psi)</th>
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Potentiometric Investigation of Silicon Electrode Immersed in Alkaline Hydrogen Peroxide Solution Containing Trace level of Iron

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ABSTRACT

Sensing electrodes derived from the regular silicon wafer were shown to respond sensitively to the part-per-billion level of iron impurities in alkaline hydrogen peroxide solution (frequently referred to as standard clean-i solution). The potentiometric results clearly indicate that the large positive shift of silicon open-circuit potential mainly originates from the adsorbed iron impurities on the surface oxide layer. Acid treatments by HCl or HF effectively regenerate the iron-contaminated silicon sensing electrode.

Introduction

Alkaline hydrogen peroxide solution (NH4OH/H2O2/H2O) was first developed by Kern in 1967 to remove absorbed organic contaminants from silicon wafer surfaces.1 Although the exact formulation may vary, this frequently referred standard clean-1 (SC-1) solution is still widely used in large quantity as an effective organic cleaning solution for the preparation of ultraclean silicon substrates for microelectronic device fabrication. The organic cleaning function is achieved through a dynamic balance between oxide formation and etching which simultaneously takes place on the wafer top surface in alkaline hydrogen peroxide solution. The adsorbed organic (especially particles) can be detached during these face-lifting oxidation/etching cycles and effectively removed from the silicon surface. However, there are two major drawbacks arising from the SC-1 treatment. First, the nonuniform chemical etching can enhance undesirable microscopic scale surface roughening. Second, a trace level of metal impurities (especially iron) from NH4OH/H2O2 aqueous solution can easily contaminate the silicon wafer surface to strongly degrade the minority carrier lifetime and cause premature breakdown of gate oxide.2,3

Recently, we reported that direct open-circuit potential measurements on a silicon-based sensing electrode provide a sensitive method for directly monitoring ultratrace [part per billion-part per trillion (ppb-ppt)] metallic impurities in HF-related solutions.4 The unique feature of this new detection methodology is that the sensing electrode was derived directly from the regular silicon wafer. Consequently, the Si-based sensor was designed to respond selectively only to contaminants which react with the silicon wafer surfaces. We report here the potentiometric investigation of the silicon electrodes immersed in various NH4OH/H2O2 solutions. Our potentiometric data demonstrate that detection of part-per-billion level of iron impurities is feasible in the highly basic and oxidizing SC-1 solution using a silicon wafer-based sensing electrode. In contrast to the direct metal deposition on the silicon surfaces in HF solution,5 our data demonstrate that the observed positive silicon potential shift originates from the trace level of iron impurities adsorbed by the thin surface chemical oxide layer formed during the NH4OH/H2O2 cleaning treatment.

Experimental

All the potentiometric measurements were carried out using previously described procedures.5 Briefly, a computer interfaced, high impedance potentiometer was used in conjunction with a double-junction standard Ag/AgCl reference electrode to measure the open-circuit potential of the silicon electrodes immersed in various SC-1 solutions. The silicon electrodes were prepared from boron-doped Czochralski (CZ) wafers. The electrical contact was made to the back side of the silicon chip using GaIn eutectic (99.99%, AESAR). Prior to each potentiometric experiment, the silicon electrode was etched by hydrofluoric acid (4.9%, electronic grade) and immersed in the SC-1 solution for 30 min to cover the silicon surface with chemical oxide. A followup HF etching (5 min, 4.9%) was employed if the hydrogen terminated silicon surface is required. The Fe2+/SC-1 solutions were prepared in polymerized Teflon labwares through dilution of a concentrated Fe3+ IC standard solution (Aldrich) with electronic grade SC-1 solution (NH4OH/H2O2/H2O, 1:1:30). A typical potentiometric experiment involves measuring the base line potential for 60 min in the clean

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REFERENCES