Analytical approaches to clarify mechanism and improve performance of ceria slurry clean

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ABSTRACT

Cleaning ceria or cerium is one of the toughest issues in post CMP clean field. In this paper, we present two distinctive methodologies that can be applied to clarify mechanism and improve cleaning performance. Firstly, we focus on evaluating reducing power of candidate materials by electrochemical technique. Secondly, we report how cerium is removed at the elemental level by surface analysis. In addition, we report the performance verification of our cleaning chemical formulations in wafer tools.

INTRODUCTION

Ceria slurries are widely used for oxide CMP because they show high removable rate, high selectivity, and low scratches. In contrast to these benefits, cleaning is very difficult because ceria abrasives strongly adhere to oxide surface. Thus, strong bulk chemicals such as dHF and SPM are mostly used for ceria-based slurry clean. However, using strong chemicals may damage surface and increase process complexity. It is ideal that there are dedicated formulated chemicals for ceria that can be used in CMP built-in cleaning units.

It is said that cerium atoms make chemical bonds with silicon oxide like Ce-O-Si, which makes hard to remove ceria particles. Typically, abrasive particles are removed by physical force by PVA brush in post CMP cleaning process. But only applying physical force is inadequate for ceria particle removal. We need "chemical" interaction between ceria particles and cleaning ingredients to secure better performance.

Figure 1 shows two possible approaches to rip off strongly attached ceria particles. The first one is to undercut oxide film. This way is effective but causes oxide film loss or increases surface roughness. Instead, we are investigating the second way, that is, to break bonds between cerium and oxide atoms. In this approach, we can keep oxide film surface rather intact. If we follow this strategy, how to break or weaken the Ce-O bond by chemicals is a key issue to design ceria slurry clean.

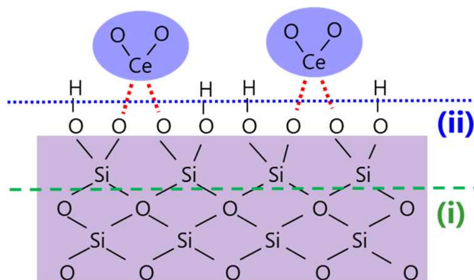

Figure 1 Two different paths to remove CeO_2 particles: (i) Undercut (ii) Break Ce-O bond

There are several potential ways to break or weaken Ce-O bonds. We tested many materials such as oxidants, reductants, surfactants, and dispersants. Among these materials, we have found reductants are frequently effective for ceria cleaning. Thus, reductants seem to play an important role in cleaning process.

In this paper, we analyzed reduction behavior in cleaners by electrochemical technique. We also used surface analysis to obtain direct evidence for bond formation and break between Ce and O atoms. These results are discussed with cleaning performance data taken with 300 mm wafer tool.

EXPERIMENTAL

(a) Electrochemical analysis:

A glassy carbon (outer diameter 6 mm, inner diameter 1.6 mm) was used as the working electrode, platinum was used as the counter electrode, and Ag/AgCl(Saturated KCl) was used as the reference electrode. The test solution was prepared by dissolving 10 mM of the reducing agent in a pH 2 standard

solution; potassium trihydrogen dioxalate dihydrate. 15 ml of the test solution was put into a cell and nitrogen (1 L / min) was blown for 10 minutes before measurement. Electrochemical analyzer ALS620B (BAS Inc.) was used as a potentiostat. All measurements were conducted at 25℃. In cyclic voltammetry(CV), the initial potential was set to the natural potential, the end potential is set to 1.5V, the folding potential is set to -0.25V. Potential was scanned as natural potential -> 1.5 -> -0.25 -> 1.5V and scanning speed was 0.2 V/s. In normal pulse voltammetry (NPV), rectangular pulses were repeatedly applied to the electrodes at regular intervals (0.2s). The pulse width was 50 ms, the pulse height increment was ΔE = 5 mV, the potential was started at −0.2 V and ended at 1.5 V. (Figure 2). The current was sampled after a certain period of time (10 to 45 ms) from the start of application of each pulse.

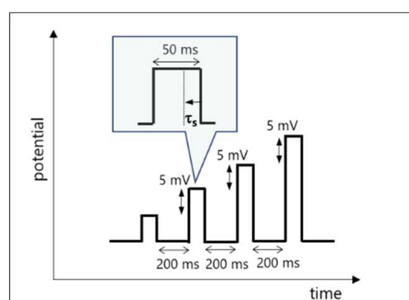

Figure 2 Applied potential(voltage) pulses in normal pulse voltammetry (NPV)

(b) Surface analysis

We analyzed two types of samples by ToF-SIMS. The first sample was simple mixture of SiO_2 and CeO_2 powder. Two powders were well mixed with mortar and pestle before analysis. The second sample was wafers after polishing with ceria slurry and cleaning with cleaners. Wafer surface was SiO_2 prepared by PE-CVD. ToF-SIMS was conducted by ToF-SIMS IV(IONTOF GmbH).

(c) Cleaning performance test

Cleaning performance evaluation was conducted with Ebara F-REX 300X. Slurry was negatively charged ceria and we polished and cleaned blanket SiOx and SiN wafers. Inspection was carried out by SP5 and eDR7380 (KLA-Tencor). Residual Ce was analyzed by both TXRF and VPD-ICP-MS. After CMP clean, we applied additional cleaning process with wet tool (single wafer process) for comparison.

RESULTS and DISCUSSION

(a) Electrochemical analysis of reductants

Figure 3A shows voltammogram of Ingredient A solution. We observed the current originated from reduction reaction around 0.5 V, which is equivalent to 0.7 V (NHE). Since redox potential for $Ce^{4+} + e^- \rightarrow Ce^{3+}$ is 1.6 V (NHE), Ingredient A can potentially reduce Ce(IV) to Ce(III). We obtained CV curves for different reductants that are candidate ingredients for ceria slurry clean (Figure 3B). From this chart, we can specify the reduction behavior as follows: A is more easily oxidized than B. For C, oxidized species cannot recover to original molecule due to the following reaction. D does not work as a reductant.

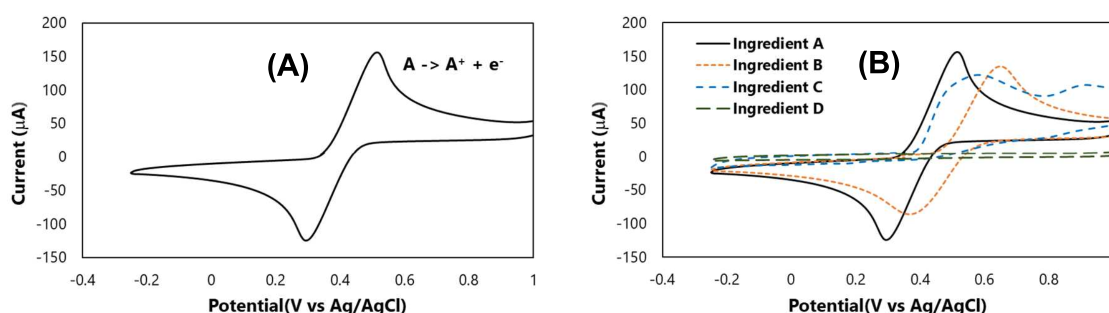

Figure 3 (A) CV curve for Ingredient A solution. **(B)** CV curves for various reductants.

Next, we applied NPV measurement to the same Ingredient A solution. Figure 4A shows NPV curves when we changed τ_s values defined in Figure 2. The detail procedures for analysis of NPV signals are described in the literature [1, 2]. In short, we can calculate diffusion constant of oxidate (D_o) from Cottrell plot (Figure 4B),

$$I_d = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}\tau_s^{1/2}}$$

where n is number of electrons to reduce/oxidize one molecule of analyte, F is Faraday constant, A is area of the electrode, C_o^* is initial concentration of the reducible analyte.

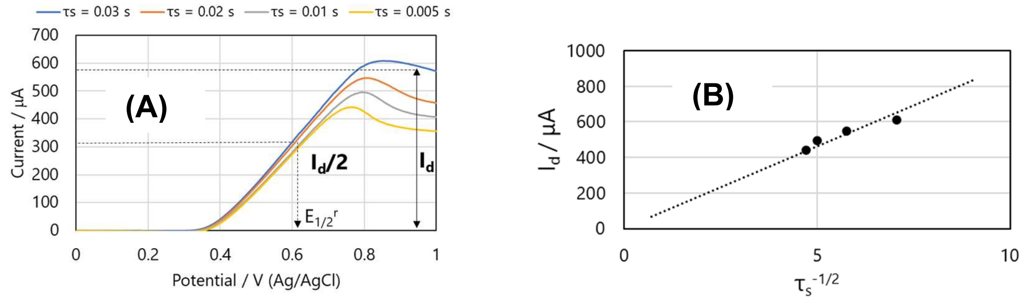

Figure 4 (A) NPV curves for Ingredient A solution for four different τ_s parameters. **(B)** Cottrell plot.

After we determine D_o from Cottrell plot, we can estimate α (cathodic transfer coefficient) by changing NPV curves to the next formula.

$$E = E^* + \frac{2.303RT}{(1-\alpha)nF}\log\left\{\chi\left[\frac{1.75+\chi^2}{1-\chi}\right]^{1/2}\right\}, \chi = I/I_d$$

Here we can obtain E* and (1-α) from intercept and slope of the right-side vs E (potential) plots. Then we can determine k^0 (standard rate constant) by the following relationship.

$$E^* = E_{1/2}^r - \frac{2.303RT}{(1-\alpha)nF}\log\left[\frac{4}{\sqrt{3}}\frac{k^0\tau_s^{1/2}}{D^{1/2}}\right], D = D_O^{1-\alpha} + D_R^{\alpha} \sim D_O$$

where $E_{1/2}^r$ is half-wave potential that is obtained from NPV curve (figure 4A).

We measured NPV for other reductants used in ceria slurry cleaner (signal not shown) and calculated D_o and k^0. Results were summarized in Table 1. Ingredient A and B have relatively large D_o and k^0, which means these materials are promising candidate reductants.

Table 1 Comparison of D_o and k^0 between four reduction species

	Do /cm^2 s^{-1}	k^0 /cm s^{-1}
Ingredient A	1.7×10^{-5}	7.4×10^{-3}
Ingredient B	1.1×10^{-5}	7.2×10^{-3}
Ingredient C	1.2×10^{-6}	2.0×10^{-3}
Ingredient E	1.1×10^{-6}	1.4×10^{-3}

(b) Surface analysis

When we analyzed polished and cleaned surface by ToF-SIMS, we detected many ion species because it is highly sensitive for residue on the surface. We also measured ToF-SIMS for blank SiOx film and simple mixture of of SiO_2 and CeO_2 particles. Figure 5A shows signal intensity of selected negative ion species for these three samples. (We observed signals from many other species, but intensity only for 8 selected species are shown.) “HSi_2O_7Ce(-)” was uniquely stronger in polished and cleaned SiOx film than simple mixture of SiO_2 and CeO_2 particles and blank SiOx film. This indicates HSi_2O_7Ce(-) is originated from “polishing process” and contains the Ce-O-Si bond. We can use this signal as a cleaning indicator.

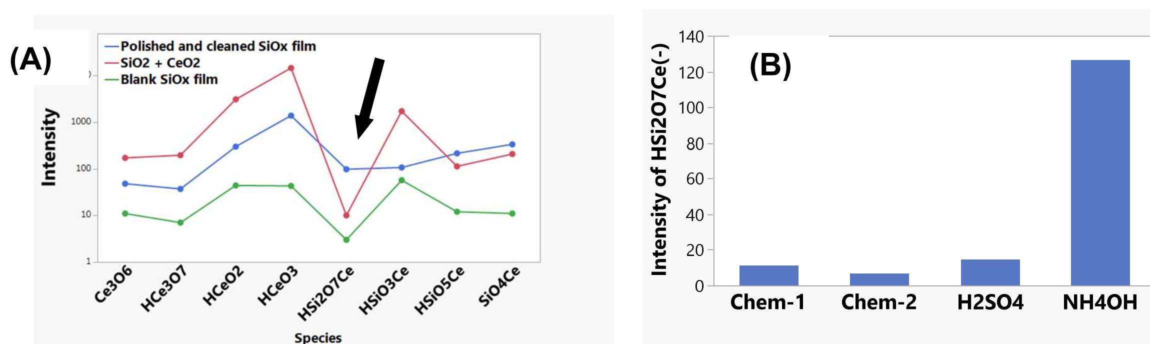

Figure 5A ToF-SIMS: Comparison of signal intensity for selected species between three samples.
Figure 5B Remaining of Ce-O-Si related residue after cleaning different cleaners.

How to break or weaken the Ce-O-Si bond by chemicals is a key issue to design ceria slurry clean. After screening many candidate materials and formulations, we have discovered some reductants and dispersants in acidic condition are effective for this purpose. Figure 5B shows signal intensity of $HSi_2O_7Ce(-)$ by ToF-SIMS for SiOx film after polished with ceria slurry and cleaned with four different cleaners. Chem 1 and 2 – specifically selected chemicals gave smaller intensity than dilute NH_3 and H_2SO_4.

(c) Cleaning performance verification

Finally, we verified the performance of our formulated chemicals with 300 mm wafers and tools with the support of IMEC team. Formulated Chem-A showed far better performance than NH_4OH, its performance was near to NH_4OH followed by diluted HF (Figure 6).

		F-CVD SiOx Blanket			
Clean Chemical	CMP Tool	NH_4OH		Formulated Chem-A	
	Wet Station	-	dHF	-	dHF
Defect Counts and Mapping by SP5 > 60 nm		80	68	66	43
Residual cerium atoms/cm^2	TXRF	1.7 x 10^{12}	< 1 x 10^{10}	2.0 x 10^{10}	< 1 x 10^{10}
	VPD-ICP-MS	3.0 x 10^{12}	1.3 x 10^{10}	6.4 x 10^{10}	9.2 x 10^{9}

Figure 6 Cleaning performance of Chem-A evaluated in 300 mm wafer tools with ceria slurry.

SUMMARY

We applied two unique methods to analyze function of ingredients in ceria slurry clean. By electrochemical analysis we calculated key parameters that explain reduction speed. We also elucidated that Ce-O-Si bonds are broken by some chemicals from ToF-SIMS measurement. Based on these results, we designed effective formulated cleaners for ceria. We demonstrated the performance of our cleaner by 300 mm wafer platform.

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