The Effects of Reductant on the Cleaning Performance for Ceria slurries with Post CMP cleaning

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Introduction

Currently, various ceria-based slurries are applied for semiconductor manufacturing in two kinds of CMP processes: ILD-CMP and STI-CMP; especially in DRAM and NAND flash manufacturing. In these processes, high speed polishing is accomplished by using ceria-based slurries instead of conventional silica-based slurries. Positive-charged ceria slurries have characteristicly high adsorption rates on polished CMP film surfaces, but have more efficient polishing rates compared with silica-based slurries. This is due to effects of both chemical reactions between ceria and silicon dioxide ILD, and the superior mechanical power during CMP polish. However, ceria abrasives frequently remain on polished surface after CMP process due to the formation of chemical bonding "Si-O-Ce" during polish. This bonding makes the post-polish cleaning and removal process difficult. Typically, dHF (diluted HF), SC-1 ($NH_4OH+H_2O_2$), and SPM ($H_2SO_4+H_2O_2$) have been used to remove ceria abrasives from post CMP ILD surfaces. Recent technology node advances in semiconductor manufacturing have required the ILD surface post CMP process to be have a lower remaining ceria concentration.

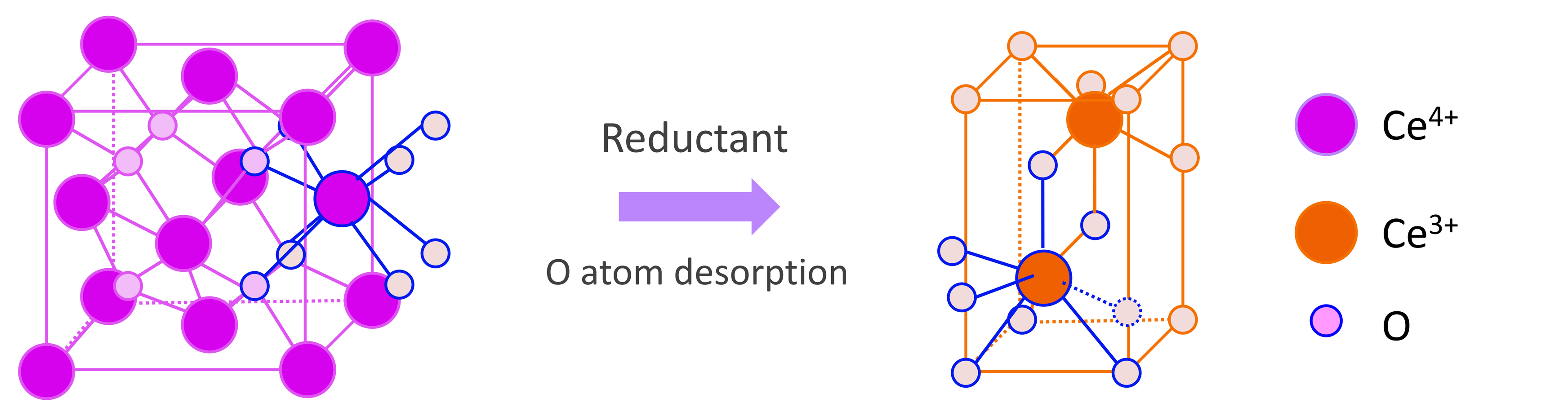
Strategy

Aim — Breaking " Si-O-Ce" chemical bonding.

Approach — Using Reducing agent.
Change Cerium ion valence from Ce^{4+} to Ce^{3+} .
This makes "Si-O-Ce" chemical bonding weaker.

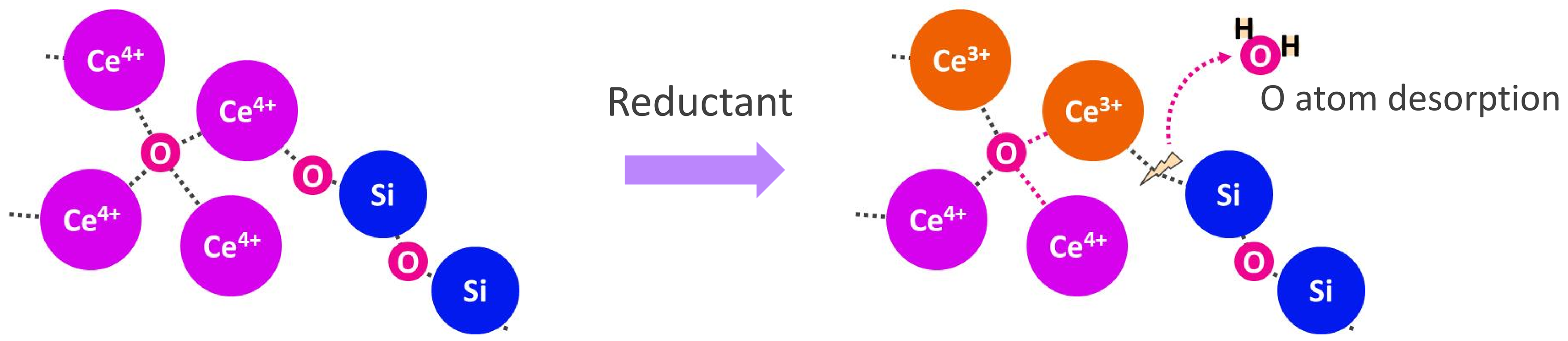
Oxygen defects make chemical bonding weaker

CeO_2: Cubic (Fluorite structure) — Ce_2O_3: Hexagonal (hp5 structure)



The number of O atoms connected in Ce atom. : 8 — The number of O atoms connected in Ce atom. : 7

Surface structural change causes oxygen atom desorption on the outermost TEOS surface

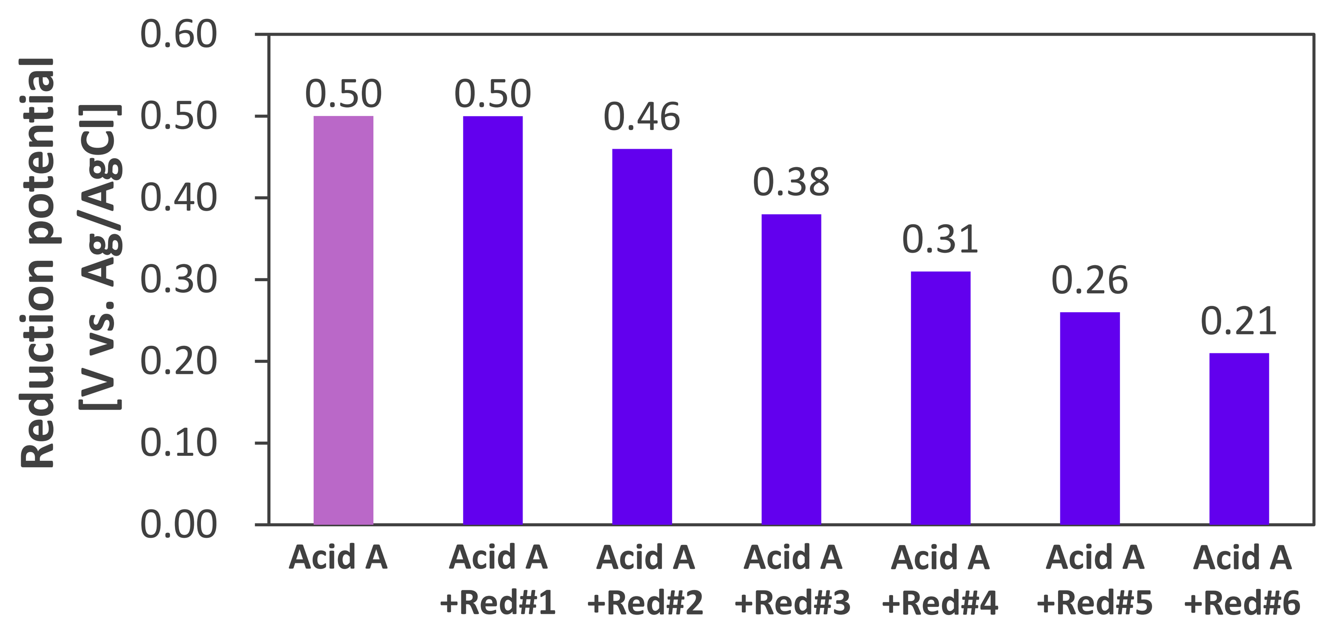


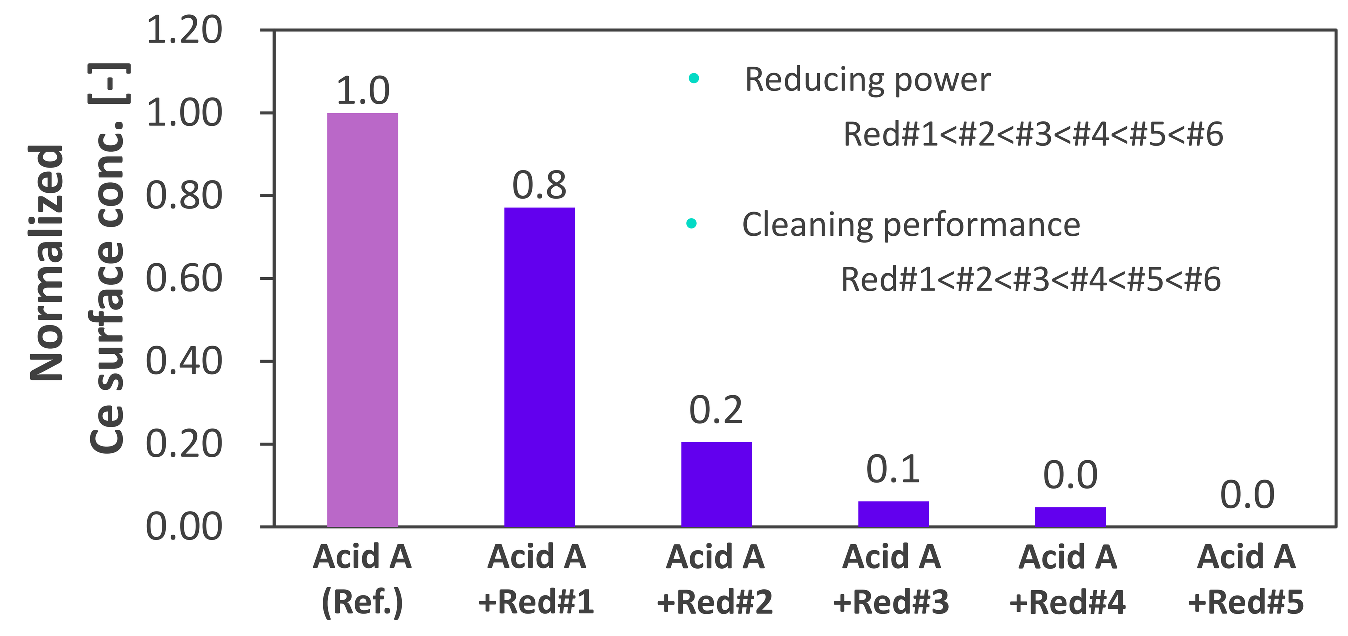
□Ce(IV)→Ce(III) suggests the local structural change from CeO_2 to Ce_2O_3.
This reaction causes an oxygen defect.

□This makes Ce-O-Si bonding on TEOS surface after CMP weak due to the crystal strain.

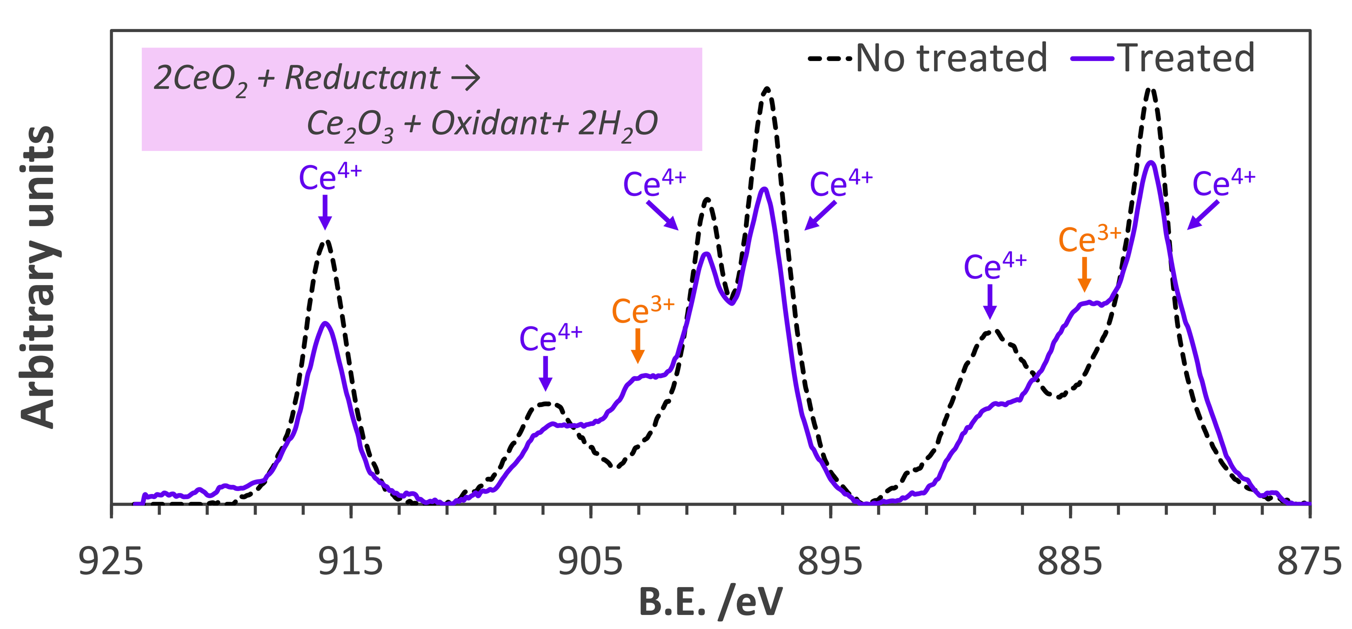
Results and Discussion

(a) Relationship between Reduction potential and Cerium surface concentration after TEOS cleaning

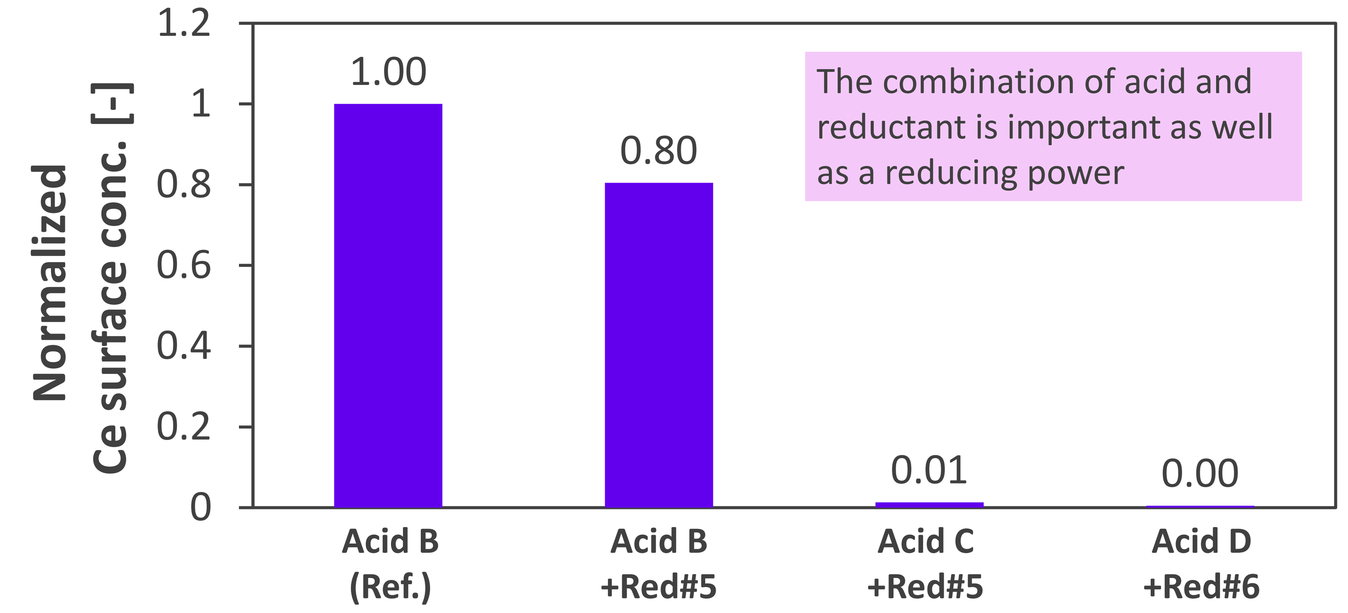




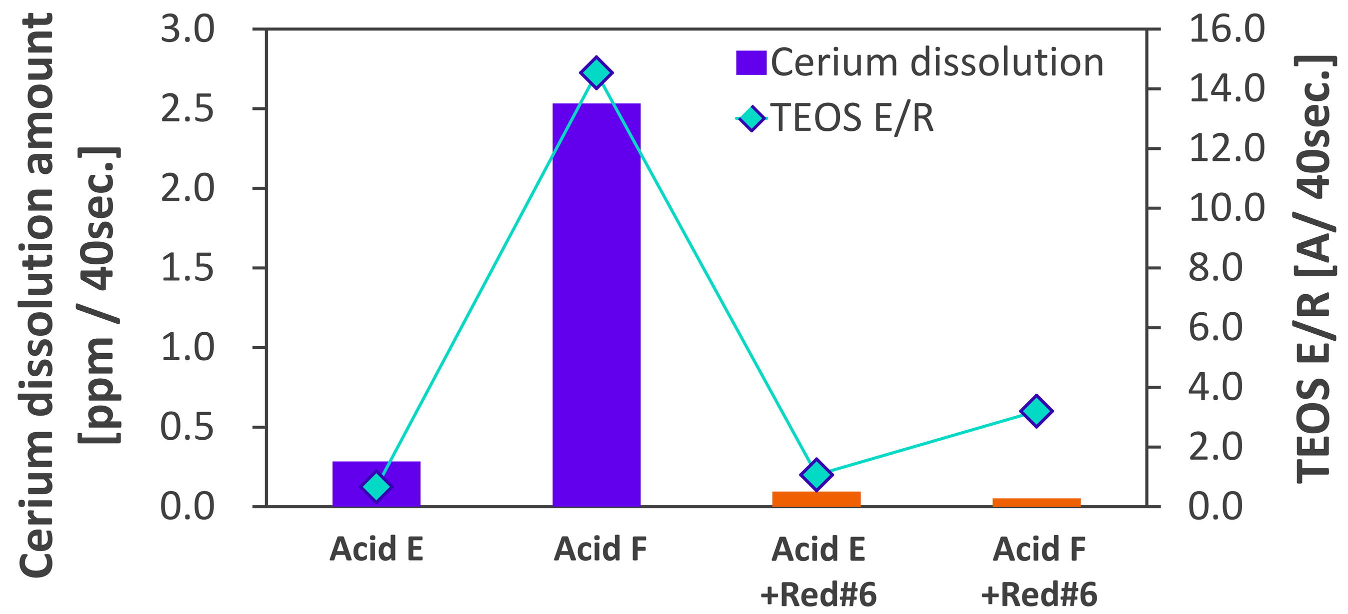
(b) XPS results for CeO_2 films after Reductant dipping treatment



(c) Cerium surface concentration after TEOS cleaning



(d) CeO_2 dissolution rate and TEOS E/Rs



(e) Cerium surface concentration after TEOS cleaning

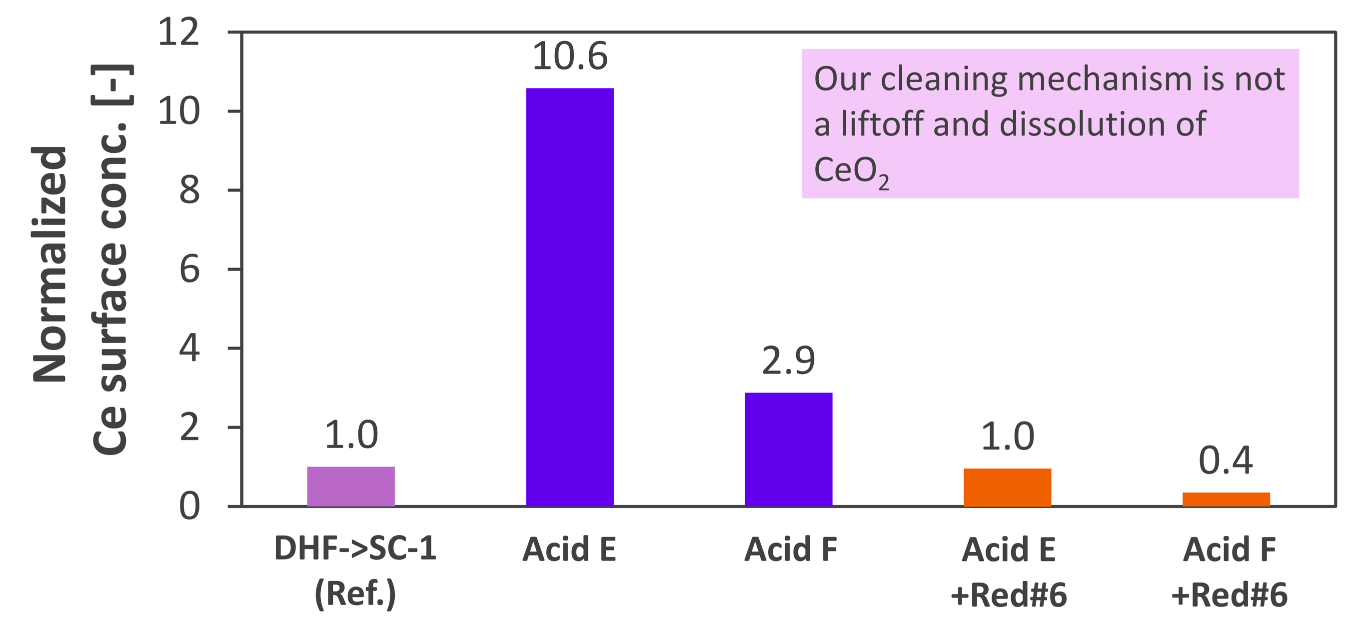


Figure (a) Relationship between Reduction potential and Cerium surface concentration on TEOS after CMP and cleaning.

Figure (b) XPS spectrum (Ce $3d_{3/2}$ and $3d_{5/2}$). We analyzed the surface state of ceria deposited film after a solution treatment including reductant by XPS.

Figure (c) Cerium surface concentration analysis on TEOS by TXRF after CMP and cleaning. We used positive charged slurry made by Hitachi Chemical Company, Ltd.

Figure (d) Cerium dissolution rate and TEOS E/Rs of cleaners. We used cerium powder and ICP-MS when we evaluated cerium dissolution amount.

Figure (e) The cerium surface concentration comparison on TEOS after CMP and cleaning between our cleaners and DHF-> SC-1 continuous process.

Conclusion and Application

Combination of acid and reductant showed significant cleaning performance on TEOS.
We developed cleaner "CMP-B312" based on these techniques. CMP-B312 shows excellent cleaning performance not only on TEOS but also SiN.