

# A modified multi-chemical spray cleaning process for post shallow trench isolation chemical mechanical polishing cleaning application

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## Abstract

Chemical mechanical planarization (CMP) has become widely accepted for the formation of device interconnect structures. Shallow trench isolation technology (STI) utilizes CMP and has been applied to deep-sub-micron processes. Poly Si, CVD Si or SiO<sub>2</sub> can be grown or deposited in the trench and planarized by a CMP process. However, the typical wafer surface is contaminated with slurry particles and metallic impurities after the CMP process. The silica particles may damage the VLSI patterns and the metallic impurities can induce many crystal defects in Si wafers during the following furnace processing. Therefore, the post CMP clean is a very important step for the STI process. However, the wafer for poly-Si surface is hydrophobic, SiO<sub>2</sub> surface is hydrophilic and Si film is very easy to charge up. Thus, the defect can be difficult to remove by a conventional cleaning technique. In this study, we propose the use of a modified multi-chemicals spray cleaning process for post STI CMP cleaning. We used a modified and heated ammonia/peroxide mix (APM) clean with an ammonia pre-soak and an HF step to etch a thin layer for the removal of trapped metallic ions which can be followed by a hydrochloric/peroxide mix (HPM) clean process to assist in the removal of metallic ions. © 1998 Elsevier Science S.A. All rights reserved.

**Keywords:** Chemical mechanical polishing; Shallow trench isolation; Post-CMP cleaning; Multi-chemicals spray cleaning

## 1. Introduction

As device geometrics have continued to shrink and circuit complexity has continued to grow, the device isolation has become a major factor limiting the circuit density. The traditional local oxidation of silicon (LOCOS) has a limitation for sub-half micron generation due to the lateral encroachment of field oxide upon the device active areas, field oxide thinning in sub-micron regions of exposed silicon, non-planarity, and stress-induced silicon defects [1]. In order to increase the device package density for high performance VLSI/ULSI technology, the shallow trench isolation (STI) process becomes attractive. STI improves the isolation between devices where compared to conventional LOCOS-type isolation techniques [2–5]. Although, the CMP process is well recognized as a powerful method for global planarization, several issues associated with CMP including dishing, oxide remaining above nitride and post-CMP cleaning have to be resolved before STI can be fully replace LOCOS.

During the CMP process, the wafer surface is contaminated with silica particles and metallic impurities. These

defects can introduce many crystal defects in Si wafers during furnace processing, since the planarization of STI is carried out at the front-end-of-line. However, the removal of the defects is difficult because the poly-Si or Si substrate surface is hydrophobic and SiO<sub>2</sub> surface is hydrophilic and the surface of silicon nitride is easily charged up [5]. In this paper, we introduce a modified multi-chemical spray cleaning process for post STI CMP cleaning process to assist in the removal of the defects and metallic impurities.

## 2. Experiment

In this paper, all of the data presented was obtained from testing 200-mm wafers. The STI fill was deposited by the sub-atmospheric chemical vapor deposition (SACVD, 450 Torr) technique which was a TEOS base system. Figs. 1 and 2 show the STI process and trench scheme. First of all, the LPCVD nitride deposited 150–200 nm and after pattern define and trench etching, the STI was formed. The depth of the trench is 350 nm and trench density is 36%. The SACVD was deposited 600 nm on pattern wafers and was subsequently polished 200 nm.

The polishing process was performed on Applied Mirra polisher multi-head, multi-platen system. Table 1 shows the

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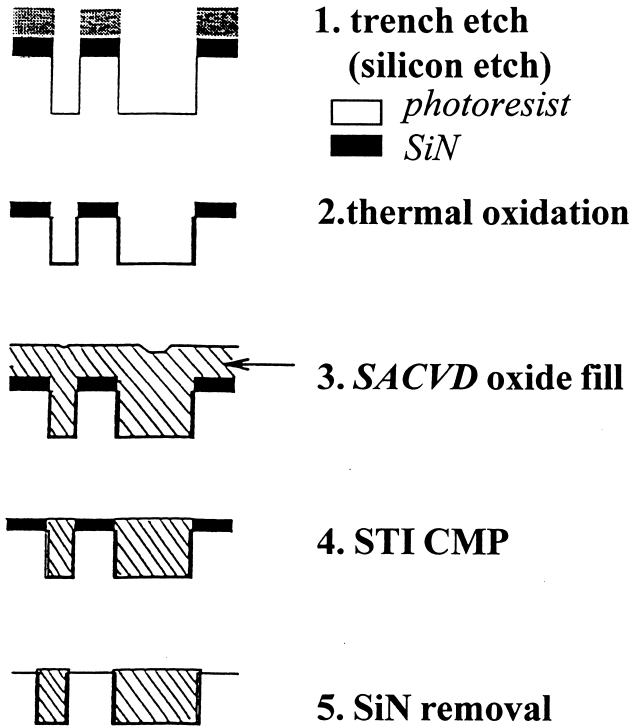


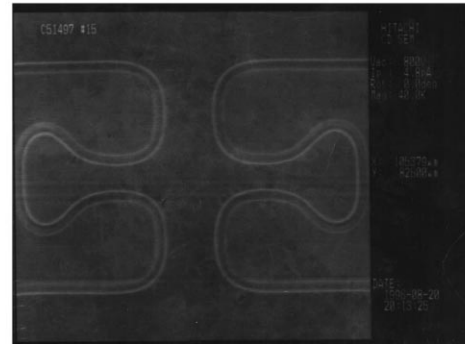
Fig. 1. The STI process scheme.

detail parameters of STI CMP in the Applied Mirra polisher. The polishing pads were IC1000/Suba-IV perforated pads made by Rodel. The KOH-based colloidal fumed silica slurry (SS-12) from Cabot was used for the oxide CMP. The modified multi-chemicals spray cleaner used in this study had a standard FSI MERCURY spray cleaner and a SCREEN AS-2000 Post-CMP processor with PVA brush. The APM (ammonia/peroxide mix) and HPM (hydrochloric/peroxide mix) was heated before being delivered to the chamber in the FSI system. Most of the cleaning recipe was modified and followed the procedure formulated by Kern and Puotieu at RCA, which is often referred to as the RCA method [6]. Table 2 lists the clean recipes used in this study.

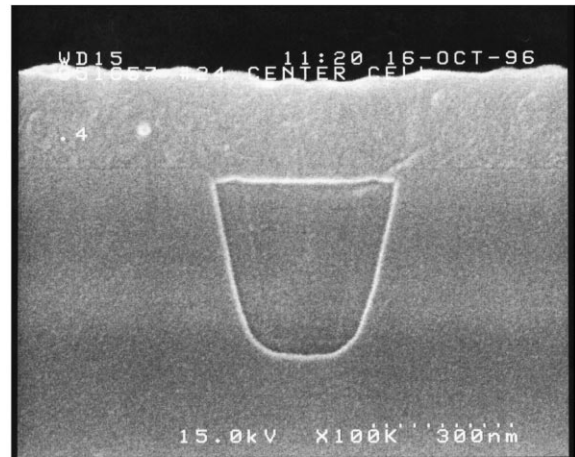
The performance after the cleaning process was examined for both particle defects and metallic contaminates on wafers. The metallic contamination was measured by Rigaku-3630 TXRF and defects on the wafer were

Table 1  
The parameters of the STI recipe in Mirra

|                    | Step 1        | Step 2        | Step 3           | Step 4           |
|--------------------|---------------|---------------|------------------|------------------|
| Plate rev./min/acc | 0/30          | 10/5          | 30/5             | 80/5             |
| Head rev./min acc  | 0/30          | 10/5          | 30/5             | 80/5             |
| Head sweep         | No sweep      | No sweep      | Sinusoidal sweep | Sinusoidal sweep |
| Polish I-tube      | Vented        | Vented        | Vented           | $p=4.0$ psi      |
| Ret ring           | Vacuum        | $p=2.0$ psi   | $p=5.0$ psi      | $p=5.5$ psi      |
| Check membrane     | Vacuum        | Vacuum        | $p=2.0$ psi      | $p=4.5$ psi      |
| Delivery 1         | Slurry=200 ml | Slurry=200 ml | Slurry=200 ml    | Slurry=200 ml    |
| Delivery 2         | No            | No            | No               | No               |
| Time (s)           | 2             | 6             | 4                | By endpoint      |



The SEM picture of STI (a) top view



(b) cross section

Fig. 2. The SEM picture of STI.

measured by a KLA digital comparison system. Surface roughness was examined by atomic force microscopy (AFM). The thickness of oxide loss on the pattern wafer during cleaning was measured by a Nano SPEC 8000 system.

### 3. Results

All of the polished wafers were cleaned in the spray processor using different chemicals. The combined effects

Table 2  
The conditions of the clean recipe

| Cleaning recipe    | Solution                                                                    | Temperature (°C) | Process time |
|--------------------|-----------------------------------------------------------------------------|------------------|--------------|
| APM                | NH <sub>4</sub> OH+H <sub>2</sub> O <sub>2</sub> +H <sub>2</sub> O<br>1:1:5 | 75~80            | 10 min       |
| HPM                | HCl+H <sub>2</sub> O <sub>2</sub> +H <sub>2</sub> O<br>1:1:6                | 75~80            | 10 min       |
| Dilute HF scrubber | HF+H <sub>2</sub> O<br>1:50                                                 | 25               | 10~25 s      |

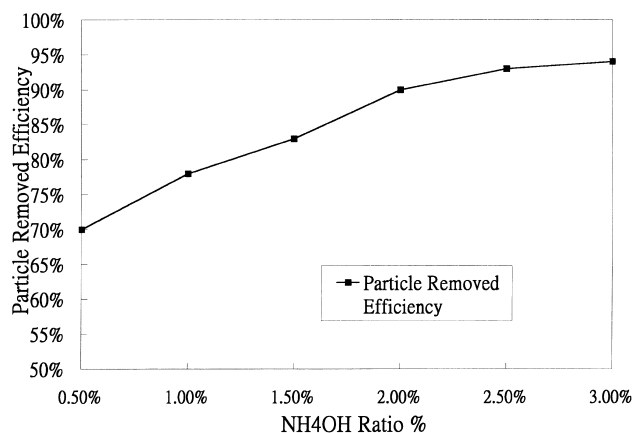


Fig. 3. The relation between NH<sub>4</sub>OH ratio and particle removal efficiency.

of APM, HPM and dilute HF scrubber were evaluated on the surface of wafers. Fig. 3 shows the trend chart of particles removed for different cleaning chemical ratios of NH<sub>4</sub>OH in the APM. From the results, the particle removal efficiency is very sensitive to the NH<sub>4</sub>OH content in the APM. In order to improve particle removal results, the combined effect of APM, dilute HF scrubbing and HPM was also evaluated. In order to eliminate the possibility of poor surface roughness after a HF dip, different dilute HF treatments were also examined. Table 3 lists the results for different combined cleaning recipes.

From the results of Table 3, the combined cleaning recipes for APM, dilute HF scrubber and HPM exhibit an excellent defect level. The metal ion contamination after

CMP polishing can be removed by using a dilute HF scrub. For dilute HF scrubber 15 s is enough for the defect and metallic contamination removal, the HF scrubber 30-s treatment will result in more oxide loss and worse surface roughness. The sequence of 'HF scrubber prior to APM' shows a worse defect and metal level than 'APM prior to dilute HF scrubber'. Figs. 4 and 5 show the comparison picture between 'APM+HF scrubber 15 s+HPM clean' and 'HF scrubber only' on AFM. Figs. 6 and 7 show the SIMS analysis for 'APM+HF scrubber 15 s+HPM clean' and 'HF scrubber only'. In order to eliminate the surface fluctuation for SIMS analysis, we have deposited 0.1 μm low temperature amorphous silicon film on the oxide surface with Applied P-5000 chambers before the SIMS measurements.

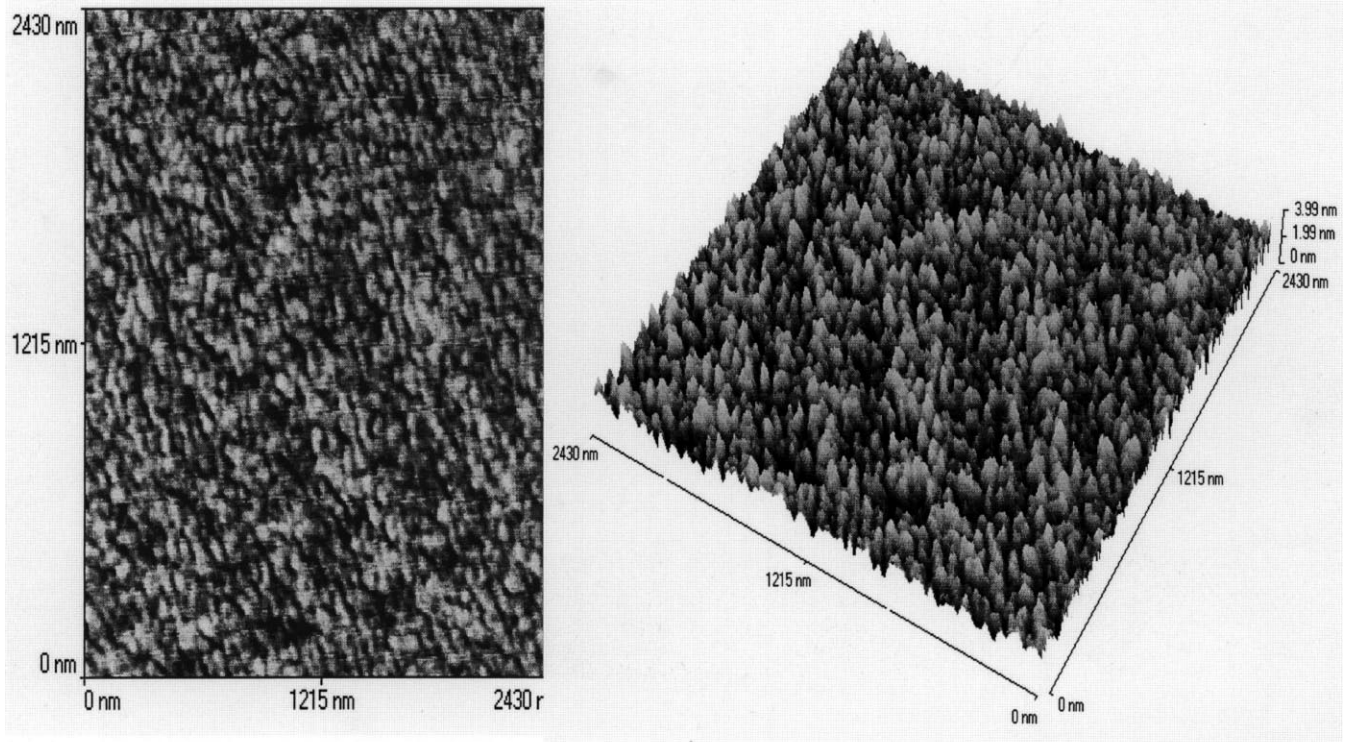
#### 4. Discussion

For STI post-CMP clean results from the above information, there is a concept of zeta potential that could be used to explain the results. The enhanced cleaning ability of NH<sub>4</sub>OH and H<sub>2</sub>O<sub>2</sub> solutions is believed to be explained by a strong relationship that exists between the pH value and zeta potentials of these solutions and other materials present in the cleaning environment. Malik and Zhang [7] studied the relationship between zeta potential and silica, alumina and tungsten. It is believed that when the zeta potential of a silica particle and the oxide surface are the same sign, either positive or negative, defects will be easier removed from the wafer surface due to the electrical repulsive forces. The pH

Table 3  
The clean effect for several combined cleanings<sup>a</sup>

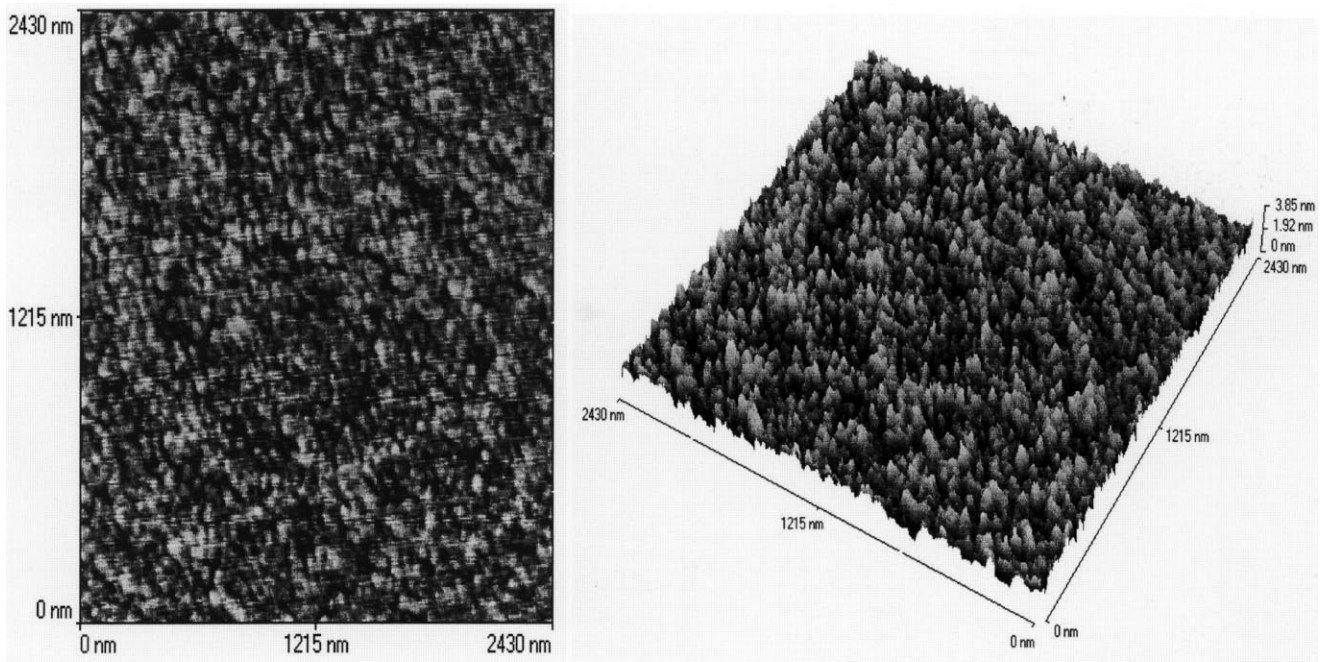
| Clean recipe                 | Defect (>0.2 μm) | Oxide loss (Å) | Surface roughness by AFM (Å) | K    | Fe   | Ca    | Cu   | Mn   |
|------------------------------|------------------|----------------|------------------------------|------|------|-------|------|------|
| APM+HF scrubber 5 s          | 47               | 13.4           | 3.14                         | 2.31 | 1.15 | 3.84  | 1.07 | 1.62 |
| APM+HF scrubber 15 s         | 19               | 37.4           | 3.43                         | 2.79 | 1.07 | 3.38  | 1.08 | –    |
| APM+HF scrubber 30 s         | 8                | 74.2           | 4.85                         | 3.14 | 1.21 | 3.24  | 0.98 | –    |
| HF scrubber 15s+APM          | 89               | 41.8           | 3.52                         | 3.33 | 1.27 | 5.29  | 1.19 | –    |
| APM+HF scrubber 15 s+HPM     | 19               | 43.1           | 3.38                         | 3.12 | –    | –     | 0.92 | –    |
| APM+HF scrubber 15 s+APM+HPM | 11               | 45.7           | 3.47                         | 3.11 | –    | –     | 1.01 | –    |
| Standard HF 15 s scrubber    | 24               | 39.5           | 2.92                         | 3.07 | –    | 6.58  | 1.14 | –    |
| APM only                     | 98               | 4.45           | 2.32                         | 84   | 2.21 | 11.15 | 0.79 | 1.95 |

<sup>a</sup> The metal ion concentrations are measured by TXRF (units: E10 atom/cm<sup>2</sup>); –, below the detection limit.



**(a) Sample, Roughness = 4.55 Å**

Fig. 4. The AFM picture of 'APM+HF scrubber 15 s+HPM clean'.



**(b) Sample-2, Roughness = 4.39 Å**

Fig. 5. The AFM picture of 'HF scrubber only'.

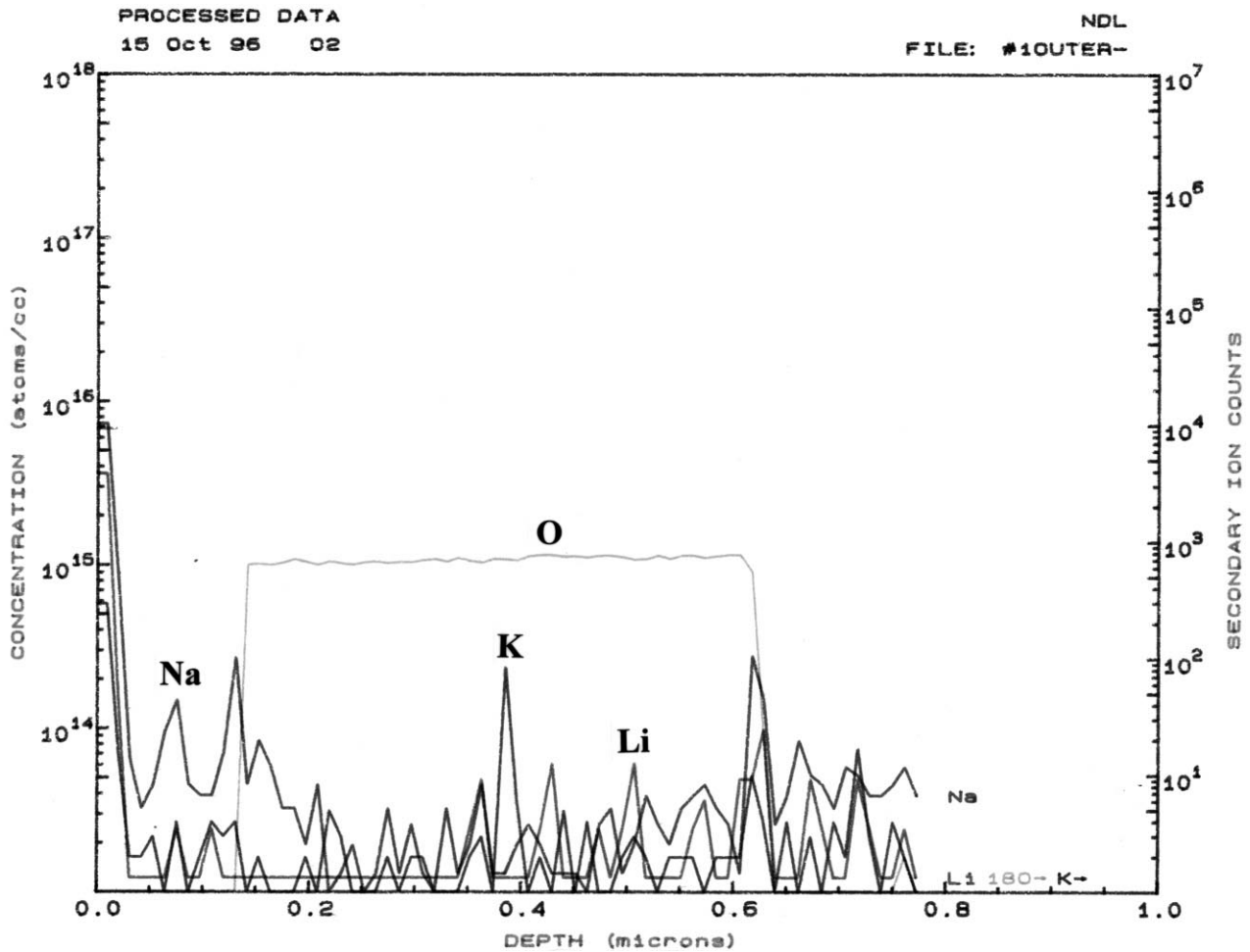


Fig. 6. The SIMS analysis of 'APM+HF scrubber 15 s+HPM clean'.

value of SS-12 is about 12.5–13.5 caused by KOH. APM cleaning is important for the slurry particle removal due to the fact that both the slurry and wafer surface have the same sign of zeta potential (negative). If a HF dip is implemented before APM, the surface will be positive and will gather the negative particle, such as silica. The defect will increase after the attraction occurs. From the above explanation of the zeta potential concept, it could explain the results of Table 2 why the sequence of 'HF scrubber prior to APM' shows the worse defect level and metal than 'APM prior to dilute HF scrubber'.

Implementation of the dilute HF will result in the etching of a thin layer of oxide film. During the CMP process utilizing SS-12 slurry, the metal ion of potassium can penetrate the oxide and nitride film and become 'trapped' in the damaged region caused by CMP. Using dilute HF to etch a thin oxide layer will result in the metal ions being carried away from the wafer surface. There is a significant difference between traditional RCA clean and post CMP cleaning due to the effect of changing the sequence of chemical cleaning steps. It has been widely accepted that a dilute HF cleaning prior to the APM cleaning can provide a very low metal and particle contamination [6]. However, accord-

ing to the results shown in Table 2, when the order of the dilute HF and APM steps are switched, particles and metal levels are decreased by approximately a factor of four or five. It is believed that the challenge for post-CMP cleaning is to remove most of the residual slurry particles with the APM solution in the first step. Then, once slurry particles are removed, the dilute HF in the second step is able to etch the top 30–50 Å of oxide, thereby removing the metallic contamination which has been incorporated in the surface and near surface region. Otherwise, if the HF dip is prior to the APM cleaning, the slurry particles cannot be easily removed during HF dip because the zeta potential between the materials is of different signs. The surface of wafer will gather the slurry particle and the surface region under the slurry particles are not etched and it can be difficult to remove metallic contamination with the following cleaning agents.

The HPM process will remove the sodium, calcium, ferric, aluminum and other metal ions. These ions may come from the polishing machine and slurry flow system, such as polish pads, polish heads, wafer transfer system, diamond disc slurry piping and the slurry itself. This cleaning step for improving the solubility of metal ions results in

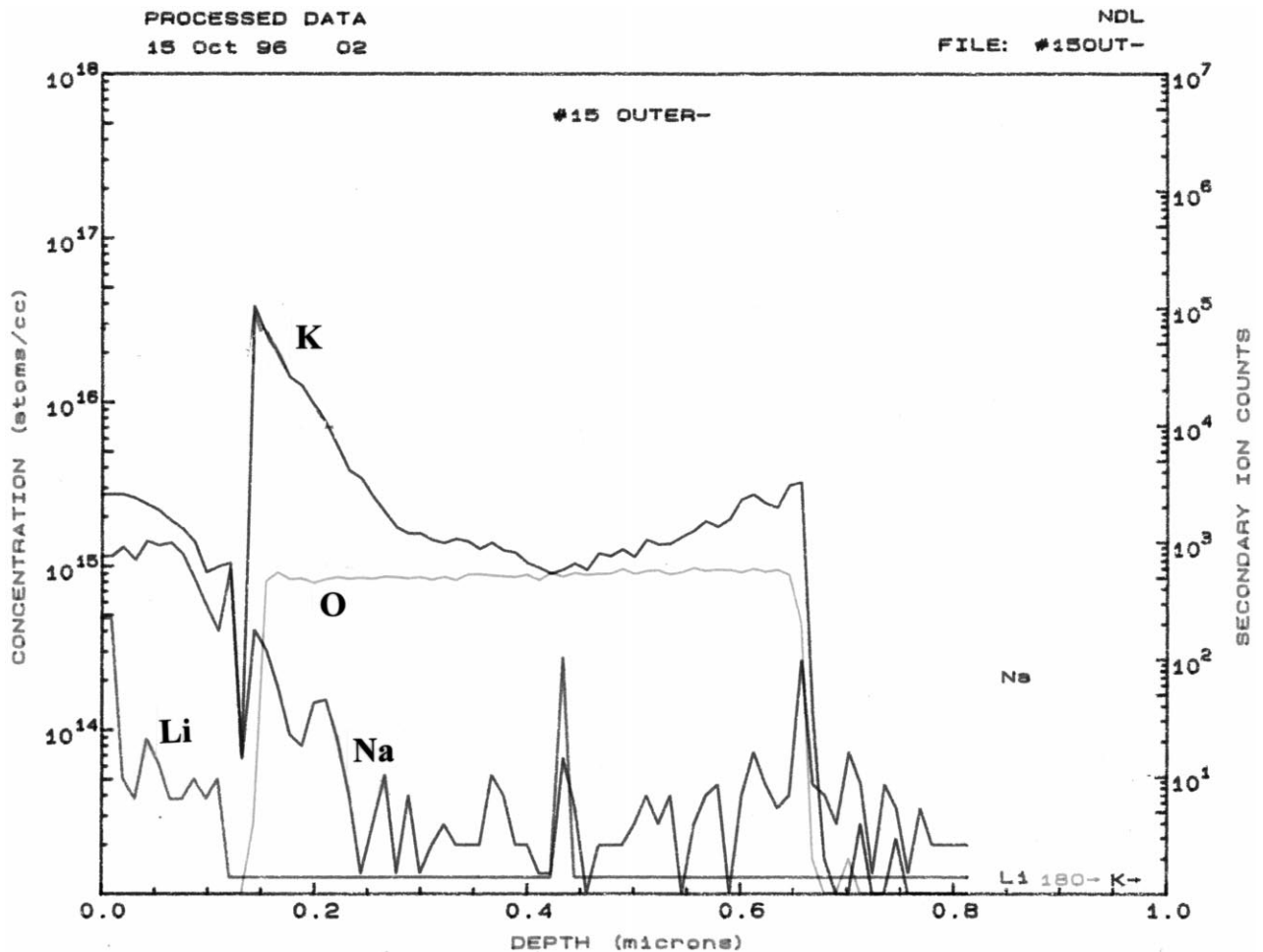


Fig. 7. The SIMS analysis of 'HF scrubber only'.

the formation of soluble complexes. In solution, the  $\text{Cl}^-$  anion is a highly reactive ion and may contribute to the removal of these metal ions. So the HPM cleaning is necessary to implement into the post CMP cleaning process.

The other sequence is evaluated in this study. Adding one step of APM before HPM to compare with the APM/HF scrubber 15 s/HPM process. From the results of Table 2, there is no significant defect and metal ion removal due to the cleaning limitation.

## 5. Conclusions

The wafer surface is contaminated by particles and metallic ions during the CMP process. Since the planarization of STI is carried out within the device formation, it is of great importance to remove the residual particles and metallic impurities for improving device yield and performance. A new modified multi-chemicals spray cleaning process for post STI CMP has been developed. This cleaning sequence provides a lower level defect and metallic contamination than the traditional post-CMP cleaning process. Besides, the addition of a dilute HF dip step to the post-STI CMP

process reduces potassium concentration and other defects significantly. Further addition of HPM can reduce sodium, calcium, ferric and aluminum concentrations. Finally, a total cleaning formula: 'APM+HF dip 15 s+HPM', is capable of removing virtually all major metallic ions down to below the detection limit of TXRF.

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