Solutions to ammoniacal nitrogen presence in CMP effluent from oxide process

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Abstract—In wafer fabrication industry, liquid ammonium hydroxide is commonly used as a cleaning solution. The use of this solution at Chemical Mechanical Planarization (CMP) process has resulted in the presence of ammoniacal nitrogen in CMP’s wastewater effluent. In view of new environmental pollution control, Malaysia Department of Environment (DOE) has introduced ammoniacal nitrogen as a new parameter to be regulated under Environment Quality (Industrial Effluents) regulations with maximum allowable concentration of 20 parts per million (ppm) effective from 1st January 2015.

This paper focuses on evaluating cleaning efficiency of Buffing and Cleaning steps at CMP Oxide process. This is to formulate best chemical and cleaning recipe in minimizing ammonium hydroxide solution usage. The challenge to this change is to ensure the cleaning efficiency at post CMP Oxide process is not compromised.

The authors have found that Buffing process has effectively removed almost all particles on wafer surface after polishing steps. This allows Cleaning process to focus in eliminating residues and metallic contaminants to enhance cleanliness of wafer surfaces. At Cleaning stage, the test using high flow of ultra pure water (UPW) and acids with peroxide mixture named SCS shown a comparable particle removal result with diluted ammonia solution. Methods to evaluate effectiveness of these media in removing residues and metallic contaminants are still under development by the authors.

Keywords—CMP cleaning, ammoniacal nitrogen, environment

I. INTRODUCTION

Chemical Mechanical Planarization (CMP) is one of the most important processes in wafer fabrication because of its superior planarization process. Ammonium hydroxide solutions or its mixtures have been used since 1980s after polishing process for removal of particles and contaminants. RCA chemical known as Standard Clean (SC) solution prepared by mixing water, hydrogen peroxide and ammonium hydroxide is called SC1 whereas water, hydrogen peroxide and hydrochloric acid mixture is known as SC2. Kern and Puotinen developed these RCA solutions in 1965. A study conducted on CMP process using megasonic and SC solutions concluded that lower concentration of SC chemicals resulted better cleaning efficiency [1]. SC solutions are widely used till now as cleaning agents for removing organic and metallic contaminants on silicon based surfaces because of their volatility and low reactivity with silicon compounds [2]. Apart from SC solutions, particles removal by means of creating electrical repulsion using diluted ammonium hydroxide is commonly adopted in semiconductor industry [3]. This paper presents the study conducted on alternative solutions that are non-ammonia based. This study in view of new controlled parameter, ammoniacal nitrogen incorporated into parameters for compliance under industrial effluent limit per Table 1. The allowable limit in industrial effluent is set at 20 parts per million (ppm) for Standard B facility located downstream of water catchments area. This requirement is being enforced by Malaysian environmental regulatory body, Department of Environment (DOE) under Environmental Quality (Industrial Effluent) regulations 2009 effective from January 2015.
TABLE I. AMMONIACAL NITROGEN LIMIT OF INDUSTRIAL EFFLUENTS

<table>
<thead>
<tr>
<th>Trade/ Industry</th>
<th>Existing Industrial Effluent Treatment Systems</th>
<th>Standard A</th>
<th>Standard B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Semiconductor</td>
<td>Ammoniacal Nitrogen</td>
<td>10ppm</td>
<td>20ppm</td>
</tr>
</tbody>
</table>

Substitution of ammonium hydroxide particularly at CMP process has become a necessity since ammonia treatment at waste treatment facility is very challenging due to a high amount of water used in CMP process. High flow of Ultra Pure Water (UPW) and a mixture of acids and peroxide developed by SilTerra called SCS (pending patent) being evaluated at post-CMP process to study the effectiveness of these alternative solutions in replacing ammonium hydroxide with the aims of better or comparable cleaning efficiency. This alternative solution does not contain ammoniacal nitrogen and economical for use at production scale.

II. BACKGROUND

In CMP oxide process, a wafer being polished using a polyurethane pad and polishing takes place when silica based slurry containing abrasive particles introduced to the polishing unit as shown in Figure 1 below. The slurry usually blended with UPW and continuously circulated in facility line. Then, slurry dosed to the polisher as per requirement configured in the process recipe. The CMP oxide mechanism is illustrated in Figure 2. The polishing pad presses these abrasive particles to polish the wafer surface and the polishing process shall uniformly occur in the entire surface of the wafer. Since slurry is rich in potassium ions and particles, an effective removal of these residues after polishing is crucial. Buff Station and OnTrack Cleaner are integrated together to ensure contaminants are removed effectively from polished wafers.

Fig. 1. Schematic view of CMP polisher

Fig. 2. CMP Oxide Mechanism
The three steps of CMP process flow namely Polishing, Buffing and Cleaning are demonstrated in Figure 3. After polishing process, the wafers shall be subsequently processed through a buff station using either Ultra Pure Water (UPW) or chemical solutions. The wafer surface comes in a direct contact with a soft PVA (Polyvinyl Alcohol) pad, which removes contaminants by rotational torque when spinning takes place. Efficiency of buffing process can be influenced by type of flow rate, pad compliance, the pressure between the pad and the wafer, the rotational speed and the buffing time [4]. Photo of the Buff station is shown in Figure 4.

Upon completion of Buffing process, the wafer shall then moves to cleaning process using OnTrack Cleaner. The cleaner consists of a pair of roll brushes positioned on top and bottom of the wafer that rotates during cleaning step with continuous flow of UPW or chemical solutions. Photos of OnTrack Cleaner and Brush Box are given in Figure 5. Both buffing and cleaning processes use combination of mechanical forces and chemical reactions during cleaning.
III. THE EXPERIMENT

SpeedFam IPEC (SFI) AvantGaard™ 776 polisher tool was used to polish wafers in all the experiments conducted in this study. This SFI polisher (refer Figure 6) provides a complete dry-in and dry-out CMP wafer processing by integrating the multi-platen CMP with Buff station using Politex Prima Hi pad and Ontrak DSS200 Synergy.

The experiments were carried out using new prime-grade eight-inch diameter silicon wafers (Si P-type Epi). Wafers were polished using oxide slurry with commercial name of SS25E by the polisher and these wafers were sent for buffing process to evaluate cleaning efficiency. Standard buffing process was applied to evaluate particles removal efficiency of Buffing process after polishing. During Buffing test, media used was Tungsten slurry manufactured by Cabot Microelectronic which being pre-blended with hydrogen peroxide at a fixed concentration. In the second set of experiments, polished wafers were sent directly to OnTrack Cleaner. Buffing process was intentionally skipped and two KJF brush double-sided brushes scrubber made by DSTec were used to hold and rotate the wafer at a prescribed pressure and speed for cleaning process. The number of particles on wafers before and after Buffing process were counted using Tencor Surfscan SP1 Tbi (refer Figure 7 on photo of the measuring equipment).
IV. RESULTS AND DISCUSSION

In the experiment of Buffing efficiency test on 25 wafers, it was found that 99.1% of particles were removed based on difference between number of particles on wafer surfaces before and after buffing process. This implies that the buffing step is an effective technique in removing particles. This finding is quite similar to study conducted by Gale and Busnaina which demonstrated that complete particle removal could be achieved using combination of megasonic cleaning with UPW at optimum conditions without the need of chemical [5]. However, the tool used for this experiment was not equipped with megasonic cleaning capabilities. Nevertheless, it can be concluded that buffing technique alone has successfully removed almost all particles left on wafer surfaces after polishing process. One of wafer maps taken from this experiment is shown in Figure 8 below.

![Photo of a wafer map showing particles before (left) and after (right) buffing step](image)

Next, evaluation of cleaning efficiency using three different media solutions namely high UPW flow, 2% ammonium hydroxide solution and SCS were then conducted. In this test, UPW high flow and SCS being evaluated in comparison to ammonium hydroxide as the standard media at the Cleaner. Upon completion of polishing step, wafers were taken directly for Clean step without Buffing process. This skip-buff process was done because capability of Buffing in removing almost all particles after polishing as demonstrated in the earlier experiment. Result shown in Figure 9 indicates that particles removal efficiency for all these solutions are comparable at an average particle removal rate between 96.6 to 97.2%.

![Oneway Analysis of Column 2 By Column 1](image)
Figure 10 illustrates superiority of Buffing technique during Oxide process in removing particle compared to Cleaning process. Other similar study at Cleaner step found that combination of tetra methyl ammonium hydroxide (TMAH) and chelating agent ethylene-diamine-tera-acetic acid (EDTA) results in best cleaning efficiency[3]. TMAH acts as a surfactant while EDTA enhance the electric double layer repulsion between particle and wafer surface for metallic contaminants remover especially Calcium (Ca) and Iron (Fe) ions. However, the above solution is not suitable for application in Malaysia because TMAH is an ammonia-based chemical.

![Oneway Analysis of Particle Removal Efficiency By Process](image)

**Fig. 10. Particle removal efficiency (Buffing & Cleaning)**

However removal efficiency of other contaminants such as metallic impurities and organic residues are not known from experiments presented in this paper. Methods to measure cleaning efficiency in removing organic residues and metallic contaminants on wafers are still being explored for comparative studies of different medias in comparison to 2% diluted ammonium hydroxide that currently used. There was a study suggesting that a mixture of sulfuric acid and hydrogen peroxide is an excellent agent for removing surfactants or contaminants from wafer surface [6]. The use of hydrofluoric (HF) acid in rinsing during post-CMP is also a common practice in wafer fabrication industries since HF is capable of removing metallic impurities that left over on wafer surface during polishing process [7]. Based on literature reviews, the formulated SCS mixture has the capability to match or improve cleaning efficiency compare to ammonium hydroxide solution.

**V. CONCLUSION**

It is evident that Buffing process has effectively removed particles on wafer surfaces after polishing process. Understanding the capability of cleaning at various process steps is crucial in determining the best cleaning recipes for CMP process optimization. Cleaning process conducted after Buffing stage should be formulated to maintain wafer cleanliness or remove organic residues and metallic impurities for a better cleaning result. However method to evaluate cleaning effectiveness in organic and metallic removal is being fine tuned for this comparative study. This is very important in deciding the best media to replace ammonium hydroxide without compromising quality of cleaning at post CMP process.

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