Development of New Batch-type Plasma Assisted NOR (Native-Oxide-Removal) Dry Cleaning Equipment

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\textbf{Keywords:} Batch-type Process, NOR(Native Oxide Removal), Dry Cleaning

\section*{Introduction}

The more accumulative electronic devices are required, the smaller features, whose smallest size is measured by lithography half-pitch, should be achieved for semiconductor fabrication. Unexpected design and fabrication difficulties should be also overcome as devices shrink. One of difficulties is contact resistance by unforeseen native oxide layers in junction areas. An even so thin native oxide layer may make contact resistance drastically higher and therefore brings about VLSI chip operation fails. Other problems by native oxide include current leakage at gate oxide and insufficient silicidation formation on a device. To resolve these issues, surface cleaning process becomes very critical to make super-clean silicon surface on contact areas and thus semiconductor industry has developed various native oxide removal methods to obtain better chip productivity. We, in this paper, present a new and more effective cleaning way by an efficient batch type apparatus with a dry process to achieve super-clean silicon surface on very small contact holes of semiconductor chips.

\section*{Why dry cleaning for NOR}

Cleaning process indispensability is presently understood. As seen in Fig. 1, wet chemical etchant diffusion into contact holes becomes more difficult as advanced device design rule goes down to nanometer scale. By the reason, longeretch time is required to achieve satisfied-clean silicon surface. However, long time wet etching may be able to cause undesirable wall profiles by different etch selectivity for each material, i.e. Si\textsubscript{3}N\textsubscript{4} and SiO\textsubscript{2}. Other wet etch shortcomings include watermarks, instability with silicides and low-K materials, leaning and broken-up of DRAM structures (see Fig. 2) and so forth [1-4]. However, dry cleaning is able to properly overcome those most shortcomings of wet cleaning, easily control etch selectivity, and compose etchant stagnation-free process. Thus, dry cleaning may be a substitution process to deal with wet cleaning disadvantages.

\section*{Overview of NOR process}

Fig. 3 describes the NOR process which is composed of two steps - chemical reaction and then vaporization. To compose NOR etchants, two chemical reactants are required: hydrogen radicals that are generated by ammonia plasma and, NF\textsubscript{3} gas which is highly reactive with poly-silicon, SiO\textsubscript{2} and Si\textsubscript{3}N\textsubscript{4} and also has almost similar selectivity on three of them. NOR etchants, NH\textsubscript{4}F and NH\textsubscript{4}F:HF, are produced by the mixture of hydrogen radicals and NF\textsubscript{3}. Compounded NOR etchants adsorb in surface and then react with SiO\textsubscript{2} but not with non-polar poly-silicon or weakly polarized Si\textsubscript{3}N\textsubscript{4}. Especially, surface adsorbed NH\textsubscript{4}F and NH\textsubscript{4}F:HF prohibit further reaction. Dissociated oxygen radicals by reaction with etchants form water molecules. NH\textsubscript{4}F based etchants with silicon atoms make (NH\textsubscript{4})\textsubscript{2}SiF\textsubscript{6}[5]. Composed (NH\textsubscript{4})\textsubscript{2}SiF\textsubscript{6} product is then vaporized with a certain increased temperature.

\section*{Batch type equipment optimization}

\textbf{Batch type equipment:} There are several main reasons based on production efficiency why batch-type equipment is more advantageous than clustered single type equipment. At first, it is
compatible with other batch processes: one of examples is LPCVD. NOR is the pre-cleaning process of an LPCVD deposition step. LPCVD uses a batch type furnace and thus it is more efficient to control pre- and main deposition process as a whole by batch type apparatuses. Other advantages include that the NOR batch step is more productive, easy to confirm wafer to wafer uniformity, smaller footprint and cost-low. Fig. 4 compares clustered single type and batch type equipments. Fig. 5 describes the schematic of new batch-type dry cleaning equipment. A vertical type furnace contains 50~100 wafers at one time. The mixture of nitrogen and ammonia composes plasma with 2.45 GHz microwave. Plasma with two gases generates hydrogen radicals which are supplied to the furnace. Hydrogen radicals with NF3 in the furnace will make NOR etchant, NH3F and NH3F:HF.

**Experimental measurements:** Table 1 summarizes experimental optimization to obtain proper parameters to satisfy process requirement. This optimization process was based on thermal oxide as a standard film. Process targets are described in the table: etching amount should be more than 30Å, uniformities in wafer and wafer to wafer should be 10% and 5% respectively. Fig. 6 shows etching amount and in wafer uniformity through optimized experiments. Total etching amount indicates around 33Å and uniformity gives around 5% in average. The data are surely acceptable to the process condition. Fig. 7 presents atomic force microscopy (AFM) surface measurement. Just before evaporation, surface is pretty rough because (NH4)2SiF6 and its compounds still stay on surface. However, after followed evaporation of them, the surface becomes clean than the former surface. The reason is that compounds evaporate from the surface with a certain high temperature and thus they don’t exist any more on the surface. RMS surface roughness by AFM indicated around 0.2nm after etching and evaporation. Fig. 8 shows surface composition analysis results by Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS). NOR left more fluorine on wafer surface than HF wet cleaning as shown in Fig. 8(a). In addition, Fig. 8(b) describes silicon dioxide counts by NOR on wafer surface are less than by normal HF cleaning, which means dry NOR has more excellent capability than HF wet cleaning. Fig. 9 presents an X-ray photoelectron spectroscopy (XPS) result just after the NOR process ends. Before evaporation, XPS shows (NH4)2SiF6. However, cleaned silicon surface is observed after evaporation in Fig. 9.

**Numerical simulation:** Fig. 10 presents numerical simulation of gas flow, heat transfer and gas concentration in a process chamber. The simulation was performed to improve wafer to wafer and in-wafer etch uniformity with a commercial simulation package, FLUENT. Fig. 10(a) depicts a temperature field on wafers in a batch chamber through the evaporation process. 50 wafers are loaded on the boat which rotates at 10 rpm. Two grey structures are heater-installed shrouds. Wafer temperature is higher at the wafer edge than at the wafer center because the wafer edge is closer to heating sources: the brighter indicates higher temperature in Fig. 10(a). Temperature distribution is not axi-symmetric because the boat slowly rotates. Fig. 10(b) and (c) express gas velocity and concentration distribution contours above a wafer. As shown in Fig. 10(b), velocity may be only seen near etchant gas nozzles and exhaust. Wafer rotation makes gas velocity asymmetry. Over the whole wafer, gas velocity is mostly released and thus fluid flow may be dominant by diffusion. Fig. 10(c) shows that gas concentration has gradient near gas nozzles but is almost uniform over the whole wafer. Diffusion may be also dominant on concentration distribution because the chamber is at a low pressure.

**Contact resistance:** As a result, Fig. 11 compares contact resistance measurement distribution data between normal HF wet and dry batch-NOR cleanings. Dots by HF spread more than those by Batch-NOR and overall average values of contact resistance by HF are pretty much higher than those by batch-NOR. Contact resistance was reduced by batch-NOR to 30~50% of wet HF cleaning cases.

**Summary**

We presented batch-NOR as a new dry cleaning process: Batch-NOR is composed of the two-step process, etching and evaporation. It showed excellent native oxide removal efficiency and
compatibility with other batch type processes such as LPCVD. Contact resistance reduced also to around 50~80% of that of wet cleaned surface.

Acknowledgement
We would gratefully appreciate to cooperation by ULVAC Inc. Japan and its personnel, Y. Ono, E. Mizuno, S. Takahashi, H. Hayashi, S. M. Jung, Y. J. Kim, and J. W. Min with Samsung Electronics Co. Ltd.

References
Table 1: Experimental optimization guideline.

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<thead>
<tr>
<th>Process Target</th>
<th>Value</th>
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<td>Etching Amount</td>
<td>&gt; 30 A</td>
</tr>
<tr>
<td>(on Thermal Oxide)</td>
<td></td>
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<tr>
<td>Uniformity</td>
<td>In Wafer 10 %</td>
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<tr>
<td>Wafer to Wafer</td>
<td>5 %</td>
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<tr>
<td>Selectivity</td>
<td>Si₃N₄ 7 ~ 10</td>
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<tr>
<td></td>
<td>BPSG 3 ~ 5</td>
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<tr>
<td></td>
<td>Poly-silicon 5 ~ 7</td>
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Figure 7: AFM measurement after etching and evaporation.
(a) After etching
(b) after evaporation

Figure 8: ToF-SIMS comparison.
(a) Fluorine
(b) SiO₂

Figure 9: XPS analysis after etching and evaporation.
(a) Temperature, (b) Velocity, (c) Concentration

Figure 10: Numerical simulation contour

Figure 11: Experimental result of contact resistance