INTRODUCTION

Wet etching is widely used in semiconductor device manufacturing and serves various functions: from surface cleaning to etching of mesas and grooves on multilayer semiconductor structures [1–3].

As IC features shrink, requirements imposed on the quality of starting materials and production technology become ever more stringent [4, 5]. Along with material perfection and the density of defects introduced during various process steps, the IC yield depends on the overall process purity, namely, on the purity of gaseous energy suppliers, clean-room environment, deionized water, chemicals, etc. [4–7].

Ultrapure technology (ultrapure process environment, ultrapure wafer surface, and precise control of process parameters) is a key factor in the successful development of ULSI ICs [3, 6, 7].

In [6, 7], the idea of wafer processing in a closed manufacturing system (CMS), where the wafers are transported between reactors in a nitrogen-filled channel without being in contact with air, has been put forward. This idea is based on experimental data according to which such conditions allow a considerable decrease in the Al/n+Si contact resistance.

In this work, we report results on wafer cleaning in equipment that simulates CMS conditions. The additional effect of cavitation in the liquid etchant is discussed [8].

THEORY

When silicon wafers are cleaned by wet etching, they are usually at rest. Reaction products (hence, molecular, ionic, and atomic contaminants [9]) are not entrained by the liquid but are redistributed over the surface. Therefore, even the heated etchant does not sweep them away from the etchant–wafer interface.

The liquid flow rate [8] depends on the liquid properties (such as viscosity, surface tension, and evaporation-related parameters), the presence of (soluble or suspended) solid or gaseous impurities, the interface condition (purity, as well as the presence of gas-filled cracks or scratches), and the crystallographic orientation of the surface.

By heating a liquid at constant pressure or by decreasing the pressure at constant temperature under static or dynamic (i.e., during motion) conditions, one can bring up the liquid to the state where vapor, gas, or vapor–gas bubbles (cavities) begin to grow [8].

The bubble may grow with a moderate rate if dissolved gases diffuse into it or merely if the gas inside the bubble expands with increasing liquid temperature or decreasing liquid pressure.

Bubble growth due to an increase in the liquid temperature is called evaporation; if the driving force of bubble growth is a dynamic decrease in the pressure (with the temperature remaining virtually constant), such a process is called cavitation [8].

If the pressure rises during bubble growth, the growth will be terminated and the bubbles start shrinking. Eventually, they collapse and disappear because of gas dissolution and/or vapor condensation.

Collapse takes place sharply if the bubbles, or cavities, contain a small amount of gas or gradually if the gas content is considerable.

Thus, cavitation involves a variety of processes from bubble nucleation to bubble collapse [8]. It may evolve in both a moving liquid and a liquid during rest. Also, the process may occur both in the volume and at the solid–liquid interface.

Thus, we can conclude that (1) the cleaning efficiency will be improved if the wafers are in a dynamic state, (2) the cleaning efficiency will be improved if contaminants (etching products) are swept away from
The number of bright spots (contaminants) on the wafer surface and the threshold voltage $V_0$ of the MOS structures vs. technology

<table>
<thead>
<tr>
<th>Number of bright spots</th>
<th>$V_0, \text{V}$</th>
<th>Cleaning technology</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–1</td>
<td>0.4–0.5</td>
<td>Suggested</td>
</tr>
<tr>
<td>3–5</td>
<td>0.8–1.0</td>
<td>Conventional (industrial)</td>
</tr>
</tbody>
</table>

the etchant–wafer interface, and (3) cavitation is an unsteady process involving cavity growth and collapse [8].

**EXPERIMENTAL**

We experimented with KEF-20 (phosphorus-doped, resistivity 20 $\Omega$ cm) Si(100) wafers. They were etched in extra-pure grade nitric acid and then rinsed in type-A deionized water following industrial technologies.

The cleaning setup (figure) meets CMS requirements. It consists of an air-tight chamber (bath) into which cassettes with wafers are placed. The bath is covered by a reflecting lid with orifices. A shaft mounted along the axis of the bath forms a semiclosed space that is connected to the rest of the chamber via nozzles with their axes inclined to the horizontal plane. The cassettes are made in the form of two parallel perforated disks attached to the shaft. A fan was mounted on the lower disk.

Cleaning was performed as follows. A cylindrical cassette with ten silicon wafers was attached to the shaft with rings and a nut, and the gas and water inlets were shut.

Concentrated nitric acid was poured into the bath up to a hole through which the waste liquid is removed. Then, the bath was covered by the splash reflector and the upper lid. The gas (nitrogen) inlet was opened, and the nitrogen flow rate was brought to a desired level (the pressure range 1761.2–1956.9 hPa).

Nitric acid was used because it is a strong oxidant attacking most organic and inorganic substances present as atomic clusters on the wafer surface [9]. The nitrogen was heated to 85°C with an electrical heater.

The cassette was a loose fit on the shaft and could rotate and reciprocate by the action of the gas, which was fed to the semiclosed space through the openings and applied pressure on the blades–fins of the fan (the rotational speed of the cassette was 80–90 rpm).

Hot bubbles partially penetrate through the openings in the lower disk, move up, expand, and collapse, striking the wafers and make them vibrate. In these conditions, the gas entraps contaminations and carries them out toward the surface. The angle between the wafers and the cassette is continuously varied to provide thorough mixing of the liquid and uniform etching. The vibration frequency of the wafers due to the heated gas was 500–1500 Hz.

Once the cleaning process in the nitric acid had been complete, deionized water was delivered to the bath under pressure, mixing up with the gas, and forced out the acid through the upper outlet into the drain. The time of cleaning on the acid was 1–3 min.

It should be noted that the cassette rotated and reciprocated throughputs wafer rinsing in the gas-heated water (1–3 min).

Once the rinsing process had been complete, the feed control valve was shut and the water was rapidly (within 2 min) removed through the drain due to the positive pressure of the heated gas. Simultaneously, the gas flow rate was increased (to a pressure of 2739.6–2935.3 hPa) and the temperature was raised to 90°C. The cassette, subjected to the high gas pressure, moved up, and its rotation velocity grew to 1500–1800 rpm.

The wafers were dried due to the centrifugal forces, water evaporation, and vapor removal under the action of the hot gas. The drying time was 20–25 s.

After drying, gas delivery was terminated and the cassette was passed to the next operation. It was made of the homogeneous material that did not contaminate the solution.

A backflow condenser can be mounted, if necessary, on the top of the bath in operating with readily vaporizable liquids like acetone.

The cleaning quality of the silicon wafer surface was estimated directly with an MMU-3 microscope (magnification $\times$ 240) from the number of bright spots in the dark field of the microscope. The bright spots can be identified as solid particles, microdefects, metal ions, or organic contaminants [9–12].

The cleaning quality was also estimated indirectly from the threshold voltage of test MOS structures. The threshold voltage was derived from capacitance–voltage characteristics taken from wafers cleaned by the new (suggested) and industrial techniques.

**DISCUSSION**

The results obtained are summarized in the table. It is seen that our technique improves the cleaning quality and the electrical performance of the MOS structures.

A decrease in the number of bright spots to 0–1 (hence, the overall improvement of the surface quality) can be explained as follows (see the figure).

1. The delivery of the fresh liquid to the wafer surface and its intense stirring (due to low-frequency wafer vibration, wafer rotation in the horizontal plane, reciprocating motion of the wafers in the vertical plane, and passing the heated gas (nitrogen) through the liquid).