Abstract:

Thin wafers have become a basic need for a wide variety of new microelectronic products. Thinner die are being required to fit into thinner packages. Wafers that have been thinned using a final wet etch process on the backside have less stress compared with standard mechanical backgrinding. Isotropic wet etching of silicon is typically done with a mixture of nitric and hydrofluoric acids along with the addition of chemicals to adjust for viscosity and surface wettability for single wafer spin processing. As the silicon is etched and incorporated in the etching solution the etch rate will decrease with time. This variation has been modeled. The focus of this paper is to compare the process control techniques for maintaining a consistent etch rate as a function of time and wafers processed. The models allow for either the time to be extended, chemicals to be replenished or a combination of these.

Silicon Etching:

The chemistry most commonly used for isotropic wet etching of silicon is a combination of nitric acid and hydrofluoric acid. It is very often referred to as the HNA system (HF:Nitric:Acetic) with Acetic acid is added as a buffer for wet bench applications. The nitric acid acts as an oxidizer to convert the surface into silicon dioxide and then the HF etches (dissolves) the oxide. The reaction proceeds as shown below and has been well documented in the literature.\textsuperscript{i}

\[
\begin{align*}
\text{Si} + 4\text{HNO}_3 & \rightarrow \text{SiO}_2 + 4\text{NO}_2 + 2\text{H}_2\text{O} \\
\text{SiO}_2 + 6\text{HF} & \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O}
\end{align*}
\]

Although the above equations are quite simple, the actual etch rates of silicon are dependent upon the ratios of the chemicals in the mixture and also upon many processing parameters.\textsuperscript{ii} A single wafer spin processor provides the capability to etch one side of the wafer while protecting the other side. For use in a single wafer spin processor, the addition of chemicals with higher viscosities is needed to provide a more uniform etch over the wafer surface. The Acetic acid in the above solution is replaced by a combination of Phosphoric and Sulfuric acids. These thick viscous acids do not chemically participate in the etching reaction and therefore do not alter the chemical kinetics, but do increase the mass-transfer resistance as a result of the increase in the viscosity. It has been reported in the literature\textsuperscript{iii} that the addition of a few viscous acids to the mixture of HF and Nitric will decrease the roughness of the wafer more efficiently for the same removal rate. In addition, the ratios of the HF and Nitric can affect the etch rates and surface roughness. At high HF and low nitric concentrations the process is very temperature dependent and reaction rate controlled resulting in unstable silicon surfaces. At low HF and high nitric content, smooth polished surfaces result due to the more diffusion limited reaction. The rate of chemical reaction along with the spin process parameters have significant effect on the overall uniformity and surface finish that results from the process. Therefore it is of utmost importance to keep the chemical mixture consistent from wafer to wafer and batch to batch in order to obtain repeatable silicon wafer etching results.

\textsuperscript{i} Laura Mauer, Herman Itzkowitz, John Taddei | Solid State Equipment Corporation
Experimental:

The experiments were conducted on an SSEC 3300 Series single wafer spin processor system. The chemistry employed was a mixture of Hydrofluoric, Nitric, Sulfuric and Phosphoric acids in the ratios of 1:6:1:2. Recirculation of the chemistry was done using SSEC’s Collection Ring technology. There are many process parameters that can be varied during the etching process and from previous work an optimized process was selected for this study.

Silicon wafer thickness and TTV measurements were done on the MTI Proforma 300SA using MTI’s exclusive Push/Pull™ capacitance technology. Automated scans across the complete wafer surface provided complete mapping of the wafer thickness before and after etching.

As silicon wafers are etched for a constant amount of time we see a gradual decrease in the depth of the etch (decreasing etch rate). The graph below shows an expanded scale in order to take a close look at the data along with a trendline. This change in etch depth (etch rate) with wafers processed is unacceptable for a manufacturing process.

![Figure 1: Silicon etch depth for constant etch time.](image)

Model:

If we look at a physical interpretation for the silicon etching and decreasing etch rate we come up with the following equation as a possibility.

\[ S = \frac{a}{bA} (1 - e^{-bAt}) \]

where

- \( S \) = silicon removed in µm
- \( a \) = initial etch rate
- \( b \) = parameter
- \( A \) = wafer area

Using this equation and comparing with the data we see good agreement. It should be noted that the above equation and resulting decrease in etch rate is dependent upon the wafer size (area of silicon being etched). For this investigation, wafer size was 150mm. For larger wafers the decrease in etch rate will be greater.
Process control of wet etching for silicon wafer thinning

Time vs. Chemicals

To eliminate the variation in etch rate as wafers are processed we have two obvious options: increase the etching time or spike/replenish the active chemicals. Using the model and data we have acquired we see the following comparison.

The above data and model indicates that our etch rate is decreasing by 2.5% every 10 wafers. This translates into a 1 second increase in etch time after 4 wafers. The resulting etch rate is more consistent however the etch time and therefore tool throughput decreases. For a tool with an initial throughput of 25 wph, this would decrease to 15 wph after 16 hours (and 400 wafers) of processing.

In the changeover from etch to rinse we close the collection cup and stop collecting the chemical in order to avoid the addition of water into the chemistry. The amount of chemical lost during this brief time (less than a second) is approximately 30ml at the flow rate we are using. Therefore, after processing 400 wafers we would have depleted the chemical supply by 12 liters and it would need to be refilled. Also at some point the amount of silicon in solution will be at a maximum and the chemistry will need to be replaced.

Another way to maintain a constant etch rate is to either spike the chemical mixture with the active ingredient (HF) or to continuously remove and replenish the chemical solution or some combination of these.
Our calculations are based on the 25 liter volume within our recirculating chemical system. The cost for filling the system with chemicals based on the chemical mix of 1:6:1:2 (Hydrofluoric, Nitric, Sulfuric and Phosphoric) is $163.95. Option one is to replace (remove and add) a percentage of the solution for every wafer. A second option is to spike with HF based on 10% of the initial solution volume and the 0.25% decrease in etch rate observed. However, this could not be done indefinitely due to some minimal loss of chemical during the switchover to water rinsing as mentioned above. The spiking with HF can be combined with adding enough of the chemical mixture to make up for the amount lost during changeover to the rinse cycle.

The graph below shows the results of adding 30 ml of chemical after every wafer where the chemical being added is a mixture of 5 ml of HF along with 25 ml of the 1:6:1:2 mixture.

![Silicon Etch Depth](image)

**Figure 4:** Addition of chemicals to maintain constant etch rate.

Continuing this addition of chemicals out to 400 wafers we see the ability to maintain the etch rate.

![Silicon Etch Depth](image)

**Figure 5:** Comparison of increasing time or addition of chemicals.

Although both techniques will maintain a more stable etch rate, increasing the etch time will decrease the wafer throughput and require periodic shutdown for chemical disposal and refill resulting in lower system utilization. Chemical replenishment will maintain the wafer throughput, provide continuous chemical disposal and replenishment resulting in higher system utilization and overall lower cost of ownership.
Summary:

As silicon wafers are etched a decrease in etch rate is observed. Spiking with HF provides a means to replenish the active component. At the same time, silicon is building up in the solution in the form of hexafluorosilicic acid. The only way to remove the silicon is to throw away some solution with each wafer. The wafer size will determine the spiking, removal and fresh make-up quantities for a stable equilibrium to be reached where the solution is self-replacing. This is the lowest cost of ownership in terms of chemical costs and system down time and will result in a constant etch rate with time.

---


\(^2\) D. Kendall, R. Shoulz, Wet Chemical Etching of Silicon and SiO2, and Ten Challenges for Micromachiners”, Handbook of Microlithography, Micromachining and Microfabrication” p.41-97 (1997)  

\(^3\) ibid

\(^4\) L. Mauer, J. Taddei, R. Youssef “The Role of Wet Etching in Silicon Wafer Thinning” Compound Semiconductor.net, January 11, 2010