Semiconductor Technology from A to Z

Wet Chemistry

Wet etching

Principle

The principle of wet etching is the conversion of the solid material of the layer into liquid compounds with the help of a chemical solution. The selectivity is very high, since the chemicals used can be precisely tailored to the layers present; for most solutions, it exceeds 100:1.

The process proceeds in three sub-steps, which must occur one after another:

1. The reactive species travel from the solution to the surface of the layer to be etched.
2. The chemical reaction takes place at the surface, forming a soluble compound.
3. The reaction product detaches from the surface and is transported away into the solution.

Whichever of these steps is the slowest determines the behavior of the entire process. If the actual reaction is the bottleneck, the process is called reaction-limited: the etch rate then depends strongly on temperature and increases roughly exponentially with it, but the process etches uniformly across the entire wafer. If, on the other hand, the transport to and from the surface is the bottleneck, the process is diffusion-limited. The temperature dependence is then weaker, but any non-uniformity in the flow directly affects the removal rate – the edges of the wafer are etched faster than the center.

For practical purposes, this means: reaction-limited processes are controlled through very precise temperature control, while diffusion-limited processes are controlled through movement of the solution, i.e. through circulation, rotation of the wafer, or ultrasound. In narrow trenches and contact holes, every process becomes diffusion-limited, because the solution there is hardly exchanged at all. This is one of the reasons why wet etching is not suitable for fine structures.

Requirements

The following requirements have to be met by the chemical solutions:

- the masking layer must not be attacked
- the selectivity must be high, both with respect to the masking and to the underlying layer
- the etch process must be able to be stopped by dilution with water
- no gaseous reaction products may form, since bubbles can locally shadow certain areas

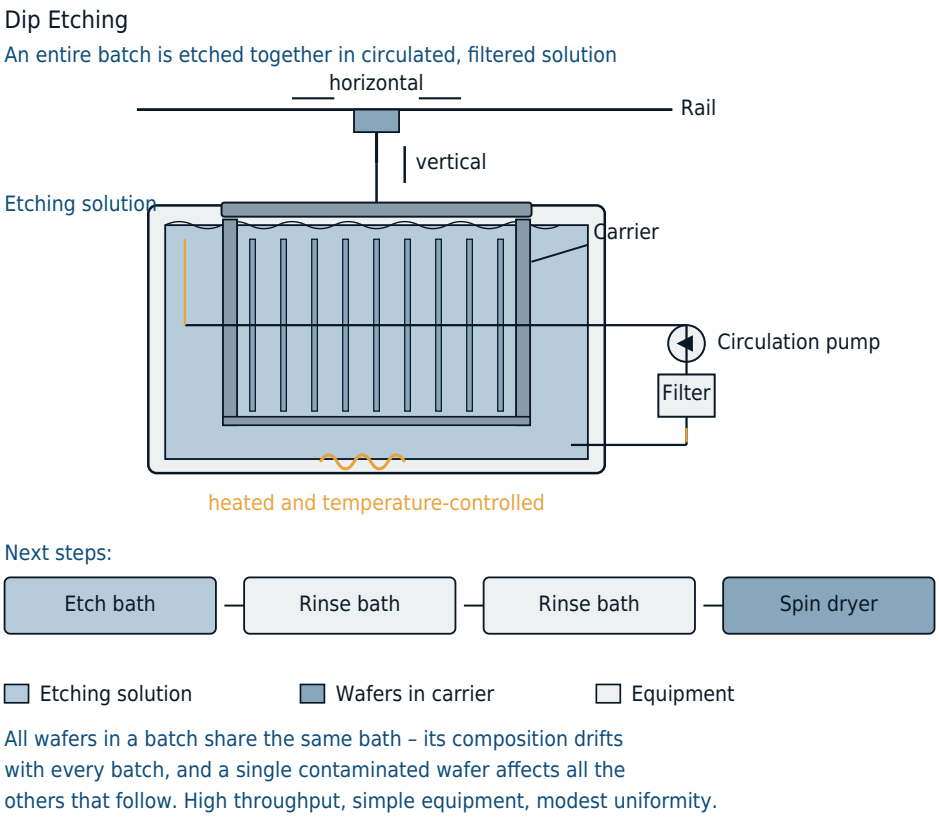
- constant etch rate over a long period
- the reaction products must dissolve directly, so that no particles contaminate the etch solution
- the solution must fully wet the surface; otherwise water-repellent areas and narrow trenches will not be reached
- no introduction of alkali or heavy metal ions, which would enter the oxide as mobile charges and render devices unusable
- good environmental compatibility and easy disposal

The last requirement is the most difficult one in practice. The most effective etch solutions are also the most hazardous, and some of the chemicals used cannot be replaced by more benign alternatives. The effort required for exhaust air, wastewater, and occupational safety therefore accounts for a considerable share of the operating costs of a wet chemical facility.

Dip etching

In the dip etch process, an entire batch of wafers is processed at once in a bath containing the etch solution. Filters and circulation pumps keep particles away from the wafers. Since the concentration of the etch solution decreases as more wafers are processed, it often has to be renewed.

The etch rate, i.e. the material removal per unit time, has to be precisely known in order to achieve reproducible etch results. Precise temperature control of the etch solution is required, since the etch rate of most chemical solutions increases with temperature.



The lifting mechanism can transport the batch both horizontally and vertically. After the wafers have been etched, the etching process is stopped by rinsing in several dip baths; the wafers are then dried in a spin dryer.

The advantages of dip etching are the high wafer throughput and the relatively simple construction of the etch equipment. However, the uniformity of layer removal is low.

A fundamental problem of the process is the bath itself: every wafer in a batch sees the same solution, which changes over time. Its composition shifts with every batch processed, dissolved material accumulates, and a single contaminated wafer can affect the entire batch as well as all subsequent ones. The concentration is therefore continuously monitored and replenished, and the service life of a bath is limited.

For critical steps, dip etching has therefore largely been replaced by single-wafer processing. It has, however, persisted wherever long etch times at high temperatures are required and the uniformity requirement is moderate – the classic example being the removal of silicon nitride in hot phosphoric acid, which, depending on layer thickness, takes an hour or longer and would be uneconomical to perform wafer by wafer.

Spray etching

Spray etching is comparable to spray development in photolithography. Owing to the rotation of the wafer on the chuck, combined with a continuous supply of fresh etch solution, the uniformity is very good. Bubbles cannot form here because of the fast rotation; however, the disadvantage here too is that each wafer has to be processed individually.

As an alternative to sequential processing, spray etching of several batches at once is also possible in a drum, in which the wafers rapidly rotate around a central spray fixture. Immediately afterward, the wafers are dried under rotation in a hot nitrogen atmosphere.

What started out as a disadvantage is today the norm: single-wafer processing has established itself for nearly all critical wet chemical steps. The reason lies in control. Every wafer sees only fresh chemistry, the process time can be set to the second, and any error always affects only a single wafer rather than an entire batch.

A modern single-wafer tool has several pivoting nozzles that apply different media to the rotating wafer one after another – etch solution, rinse water, drying agent – without the wafer ever leaving the process chamber. Consumption per wafer is orders of magnitude lower than that of a bath, which considerably reduces the costs for chemicals and disposal.

This also makes possible something that is fundamentally impossible in a bath: spatially confined treatment of a wafer. A nozzle at the edge can be used to strip only the outermost bevel, while a supply from below can treat only the backside, with the front side protected by a stream of nitrogen.

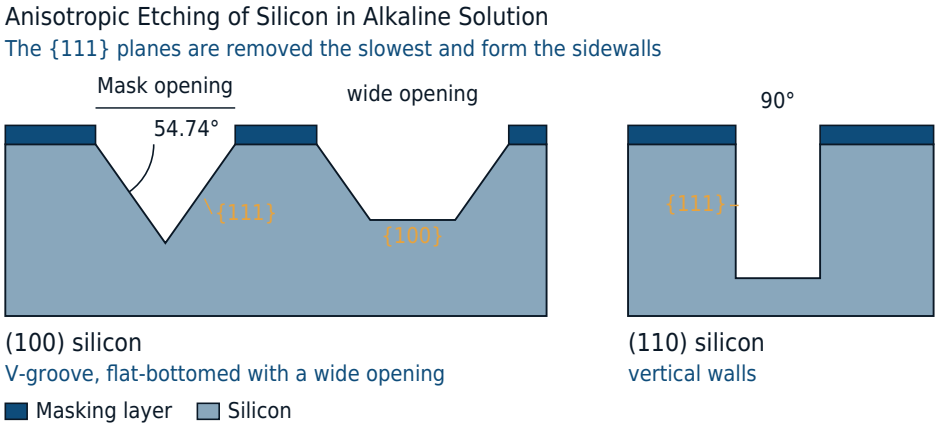
Anisotropic etching of silicon

Although the particles in an etch solution can etch the layer on the wafer in every direction, there are also processes that allow an almost anisotropic etch profile to be obtained during wet etching. These make use of the different etch rates on the various crystal planes.

The cause lies in the number of bonds with which a silicon atom is held in the respective plane of the crystal. In the {111} plane, the density of bonds is highest, and it is correspondingly removed most slowly. The {100} and {110} planes are etched considerably faster – the ratio in potassium hydroxide reaches more than 100:1, depending on concentration and temperature. As a result, the etch proceeds in depth until it reaches {111} planes; these remain standing and

form the sidewalls of the structure. The shape of the result is therefore not determined by the etch time, but by the crystal orientation of the wafer.

Etch profiles depending on crystal orientation



On (100)-oriented wafers, the {111} planes intersect the surface at 54.74°, producing V-shaped trenches and pits with a pyramidal cross-section. If the mask opening is wide or the etch time short, a flat bottom remains and the structure is trapezoidal. On (110)-oriented wafers, the {111} planes stand perpendicular to the surface, so that trenches with vertical walls and a very high depth-to-width ratio can be etched.

Etch solutions

Etching is carried out with potassium, sodium, or lithium hydroxide (KOH, NaOH, LiOH), with tetramethylammonium hydroxide (TMAH), or with an EDP solution (a mixture of water, pyrazine, catechol, and ethylenediamine). In every case, the reaction is driven by the OH^- group (hydroxide group) of these substances:

$$Si + 2OH^- + 2H_2O \rightarrow SiO_2(OH)_2^{2-} + 2H_2$$

The choice of solution is less a question of etch rate than one of compatibility with the rest of the manufacturing process. Potassium hydroxide etches with the strongest anisotropy but introduces potassium ions: alkali ions are mobile in the gate oxide, shift the threshold voltage of transistors, and render a device unusable. In a production line where integrated circuits are also fabricated, potassium hydroxide is therefore ruled out. TMAH contains no metal ions and is compatible with CMOS manufacturing; its anisotropy is lower, but it barely attacks silicon dioxide. EDP is largely avoided today because of its toxicity. TMAH, as a processing solution, is by no means harmless either, being highly toxic through skin contact – in a much more dilute form, namely as a 2.38 %

solution, the same substance is the standard developer used in photolithography.

Limiting the etch depth

Since the etch stops on its own only at {111} planes, the depth has to be defined in some other way if a membrane of a defined thickness is to be produced. Two approaches are common: a layer very heavily doped with boron, which is barely attacked by the lye any longer, or electrochemical control, in which a p-n junction is placed under voltage and the etch comes to a halt at it.

Applications

Anisotropic wet etching plays no role in patterning integrated circuits. Outside of that field, however, it is a standard process:

- Micromechanics: membranes for pressure sensors, proof masses for accelerometers, nozzles for inkjet print heads
- Solar cells: a brief treatment in dilute lye produces a dense array of small pyramids on (100) silicon. This texture causes incident light to strike the surface multiple times and considerably lowers the reflectance.
- Optics and packaging: V-grooves for holding and aligning optical fibers, alignment structures for assembly

Etch solutions for isotropic etching

Different etch solutions are available for the respective materials. In the semiconductor industry, oxide layers are etched with hydrofluoric acid HF:

$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$

The solution is buffered with NH_4F to keep the HF concentration constant. In a mixture of a 40 % NH_4F solution and 49 % hydrofluoric acid (ratio 10:1), the etch rate on thermal oxide is 50 nm/min. TEOS oxides are etched considerably faster, at about 150 nm/min, and PECVD oxides at about 350 nm/min. The selectivity relative to crystalline silicon, silicon nitride, and polysilicon is much greater than 100:1.

The fact that the etch rate depends so strongly on the origin of the oxide is not a side effect but a useful tool: conversely, the etch rate in buffered hydrofluoric acid can be used to assess the density – and thus the quality – of a deposited oxide layer.

A brief treatment in highly diluted hydrofluoric acid, the HF dip, removes the native oxide that forms on any silicon surface in air within a short time. It therefore precedes many processes that require a clean contact to the silicon,

such as epitaxy, gate oxidation, or metal deposition. Afterward, the surface is saturated with hydrogen and thus water-repellent – water visibly beads off it. Since new oxide forms again immediately, the subsequent step must follow promptly.

Silicon nitride is etched with hot phosphoric acid H_3PO_4 at about 160 °C. Here, however, the selectivity to SiO_2 is very low, at 10:1. For polysilicon, the selectivity to nitride is essentially determined by the concentration of the phosphoric acid. To increase the selectivity relative to oxide, dissolved silicon is added to the solution so that it becomes saturated with respect to silicon dioxide and thus barely attacks it any longer.

Crystalline and polycrystalline silicon are first oxidized with nitric acid (HNO_3), after which the silicon dioxide is etched with hydrofluoric acid:

1. $3Si + 4HNO_3 \rightarrow 3SiO_2 + 4NO + 2H_2O$
2. $SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$

Aluminum is etched at about 50 °C with a mixture of phosphoric, nitric, and acetic acid. The nitric acid oxidizes the aluminum, the phosphoric acid dissolves the resulting oxide, and the acetic acid lowers the surface tension so that the solution fully wets the structure and the hydrogen generated does not remain adhered as bubbles. Titanium is etched with a solution of ammonia water NH_4OH, hydrogen peroxide H_2O_2, and water (ratio 1:3:5). Since this solution also attacks silicon once the peroxide is consumed, its bath lifetime is short. The same mixture, in a more dilute form, serves as a cleaning solution for wafer cleaning.

Handling hydrofluoric acid

Among process chemicals, hydrofluoric acid occupies a special position and deserves an explicit warning. It is only a weak acid and initially causes little pain on the skin, but penetrates deep into the tissue. There, the fluoride binds the body's calcium, which can lead to chemical burns reaching down to the bone and to disturbances of the heart rhythm. Symptoms often appear only hours after contact, by which time the damage has already occurred. Handling it therefore requires appropriate protective equipment, a readily available calcium gluconate gel, and proper training – in manufacturing, hydrofluoric acid is handled exclusively in closed systems.

Assessment

In general, wet chemical etching is well suited for removing entire layers on a wafer. The selectivity between the layer to be etched and the one beneath it is usually very good, so there is little risk of removing the wrong layer. In addition, the removal rate per unit time is very high, and in dip etching many wafers can

be etched simultaneously. For small structures, however, wet etching cannot be used, since its isotropic etch profile is unsuitable for this purpose. In this case, layers are removed anisotropically using dry etch processes.

For very fine structures, a second reason comes into play that has nothing to do with the etch profile anymore: at the end, the liquid has to be removed from the wafer again, and it is precisely during this step that the exposed structures can be destroyed.

Drying the wafers

At the end of every wet chemical step comes rinsing with ultrapure water, followed by drying. What sounds like a minor step is, for fine structures, the most critical part of the entire process.

Why drying is a problem

As long as liquid remains between two neighboring fins or lines, its surface tension pulls them toward each other. The force grows the more closely spaced and the taller the structures are. Once two lines touch, they adhere to each other through bonds between their surfaces and do not spring back apart. This structural collapse – known as *stiction*, from *static friction* – is the most common cause of failure for slender lines at the end of a wet process. Affected above all are free-standing elements in micromechanics and tall, narrow resist lines in photolithography.

Drying by simple spin-off or evaporation makes the problem worse, because the receding liquid front then runs directly through the structure. All of the following methods therefore aim either to defuse the transition from liquid to dry, or to avoid it altogether.

Methods

Spin drying
: The wafer rotates rapidly, the liquid is flung outward, and a stream of nitrogen finishes the drying. Simple and fast, but unsuitable for fine structures and prone to leaving behind dry spots.

Isopropanol drying
: The rinse water is displaced by isopropanol, whose surface tension is only about one-third that of water. The capillary forces are correspondingly lower.

Marangoni drying
: The wafer is slowly withdrawn from the water while isopropanol vapor is deliberately supplied at the water surface. The resulting difference in surface tension along the interface pulls the water film away from the wafer, so that it emerges dry from the bath and no liquid has to evaporate

on it.

Supercritical carbon dioxide drying
: The liquid is replaced by carbon dioxide, which is then brought into the supercritical state through pressure and temperature. In this state, there is no longer an interface between liquid and gas, and thus no surface tension either; the carbon dioxide can be released without leaving any residue. This is the most elaborate but also the gentlest method – it is used wherever all the others reach their limit.

The same reasoning underlies the development of dry alternatives to individual wet steps: wherever a layer can be removed with a gas instead of a liquid, the problem is avoided from the outset.