# 1 Wet chemistry

## 1.1 Wet etching

## 1.1.1 Principle

The principle of wet etching processes is the conversion of solid materials into liquid compounds using chemical solutions. The selectivity is very high since the used chemicals can be adapted very precisely to the individual films. For most solutions the selectivity is greater than 100:1.

## 1.1.2 Requirements

The following requirements have to be fulfilled by liquid chemistry:

- the mask layer must not be attacked
- the selectivity has to be high
- the etch process has to be able to be stopped by dilution with water
- reaction products must not be gaseous because they could shadow other regions
- constant etch rates all along the process
- the reaction products must be solubly to avoid particles
- environmental safety and ease of disposal are necessary

#### 1.1.3 Batch etching

In batch etching multiple wafers can be etched simultaneously, filters and circulating pumps prevent particles from reaching the wafers. Since the concentration of the chem-

istry is decreased with each processed wafer it has to be renewed often.

The etch rate, in other words the abrasion per time, has to be well known to ensure a reproducible process. A precise tempering is essential since etch rates increase with increasing temperature.

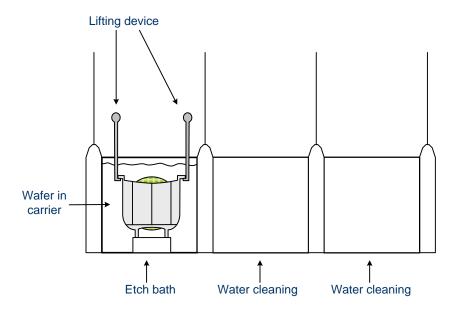


Fig. 1.1: Batch etching

A lever can transfer the wafers in horizontal and vetical direction. After the wafers have been etched, the etch process is stopped by purging with water in seperate baths. Subsequent the moisture is removed in spin-dryers.

The advantage of the batch etching is the high throughput and the simple construction of the etch tools. However, the uniformity is low.

## 1.1.4 Spray etching

The spray etching is comparable to the spray development in lithography. Due to the rotation of the wafer simultaneously to steadily renewed etch chemistry the uniformity is very good. Bubbles can't emerge because of the fast rotation, however, each wafer has to be processed separately.

As an alternative to the single wafer process the spray etch can be done on multiply wafers at a time. In a spin etcher the wafers are placed around spray nozzles and revolve concentrically. Afterwards the wafers are dryed in a hot nitrogen atmosphere.

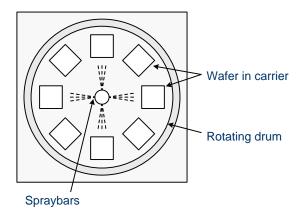


Fig. 1.2: Spray etching

### 1.1.5 Anisotropic etching of silicon

Although the molecules in liquids can move in every direction there are wet etch processes to create an almost anisotropic etch profile. For this approach the unequal etch rates on different crystal orientations are utilized. (100) and (110) oriented crystal faces can be etched much faster than (111) oriented. Thus 'V' shaped trenches (100 silicon) or trenches with perpendicular sidewalls can be fabricated. The etching is either done with potassium, soda or lithium lye (KOH, NaOH, LiOH) or with an EDP dilution (a mixture of water, pyrazine, catechol, and ethylenediamine). Responsible for the reaction is in either case the OH<sup>-</sup> ion (hydroxyl):

$$\mathrm{Si} + 2\,\mathrm{H}_2 + 2\,\mathrm{OH}^- \longrightarrow \mathrm{SiO}_2(\mathrm{OH})_2^{2-} + 2\,\mathrm{H}_2$$

However, anisotropic dilutions are not applicable for microelectronic devices but for micromechanics.

#### 1.1.6 Etching solutions for isotropic etching

There are individual dilutions for all the different materials. For example silicon dioxide is etched by hydrofluoric acid (HF):

$$SiO_2 + 6 HF \longrightarrow H_2 SiF_6 + 2 H_2 O$$

The dilution is buffered with  $NH_4F$  to maintain the concentration of HF (so-called buffered HF, BHF). In a mixture of 40 percent  $NH_4F$  and 49 percent HF (ratio 10:1) the etch rate on thermal oxide is 50 nm/min. TEOS (CVD) oxides and PECVD oxides are etched much faster (150 nm/min and 350 nm/min, respectively). The selectivity compared to crystalline silicon, silicon nitride and polysilicon is much greater than 100:1.

Silicon nitride is etched by hot phosphoric acid ( $H_3PO_4$ ). The selectivity in contrast to silicon dioxide is low (10:1). In polysilicon the selectivity compared to silicon nitride is primarily defined by the concentration of the phosphoric acid.

Crystalline or polycrystalline silicon are at first oxidized with nitric acid (HNO), afterwards the oxide is etched with HF.

$$\begin{split} 3\operatorname{Si} + 4\operatorname{HNO}_3 &\longrightarrow 3\operatorname{SiO}_2 + 4\operatorname{NO} + 2\operatorname{H}_2\operatorname{O} \\ &\operatorname{SiO}_2 + 6\operatorname{HF} \longrightarrow \operatorname{H}_2\operatorname{SiF}_6 + 2\operatorname{H}_2\operatorname{O} \end{split}$$

Aluminum can be etched at 60 °C with a mixture of nitric and phosphoric acid, titan is etched with a mixture of ammonia water (NH $_4$ OH), hydrogen peroxide (H $_2$ O $_2$ ), and water (ratio 1:3:5). Because this mixture can attack silicon as well its lifetime is low.

In general wet etching is suitable to remove entire layers of the wafer. The selectivity is very high for most materials, and therefore there is no risk to etch the wrong film. In addition the etch rate is very good, in bath etching many wafers can be processed at a time. However, for small structures the wet etching can't be used since its isotropic character causes lateral etching of the masked films. For this approach layers are removed by dry etching with anisotropic etch profiles.