4.2 Etching of Silicon

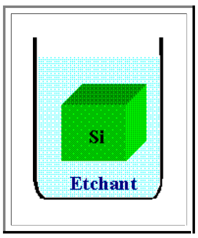
4.2.1 General Remarks

What is Etching?

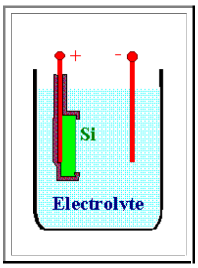
- **Etching** of silicon can mean several things:
  - The **chemical** dissolution of **Si**. In other words, **Si** will dissolve upon simple immersion in certain chemicals.
  - The **electrochemical** dissolution of **Si**. In this case dissolution takes place in certain chemicals called electrolytes - different from the ones for purly chemical etching - if, and *only if*, electrical current is passed through the **Si** - electrolyte junction.
  - The dissolution of Si in a **Plasma**. Dissolution takes place if **Si** is exposed to a suitable Plasma, i.e. a low density "vapor" of electronically excited ionized atoms or molecules and free electrons which often have considerable kinetic energies in addition. Usually plasma etching takes place at low concentrations, i.e. at low pressures. Plasma etching may use chemicals (usually gases) different from those used for chemical or electrochemical etching.
- Etching is not only a key process for any **Si** technology, it is rather poorly understood. In particular, the electrochemical and plasma etching of **Si** is full of surprises, empirical receipes, and counts among the "black arts" compared e.g., to rather well understood if complex processes like ion implantation or diffusion.
  - In typical microelectronic products, chemical etching has been abandoned in favor of plasma etching around **1985**; electrochemical etching so far has never been used.
  - However, for **microsystems** or "***MEMS*** " (= micro electronic and mechanical systems) applications, *chemical* etching is the crucial process par excellence, we will cover that briefly in an own subchapter.
  - Electrochemical etching, though known since the fifties, was seriously investigated only since about **1990**. It produces a (still growing) wealth of new phenomena and has a large potential for new products which is investigated by many research groups. The first large scale product based on **Si** electrochemistry was introduced in **1999**; it is mentioned int he contect of the "Silicon on Insulator" subchapter
  - There are special big conferences dedicated to etching of **Si**, especially to plasma etching and electrochemical etching.
  - We will neithrt treat plasma etching in this script, nor electrochemical etching as an emerging new technique.

Basic Experiments

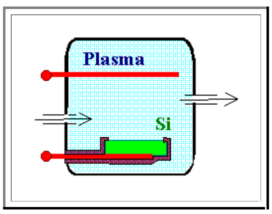
- The simple drawing below illustrates the basic etching experiment for the three etching modes mentioned.



- *Chemical etching*
- Silicon, here in the form of a cube - e.g. a single crystal with **{100}** surfaces - is immersed in an etchant and will dissolve.



- *Electrochemical etching*
- Some parts of the **Si** sample are exposed to the electrolyte. The back side contact and other parts are protected. A voltage between the back side contact and a counterelectrode of some inert material (usually **Pt**) allows to apply a voltage which may cause a current to flow across the interface **Si** - electrolyte.
- Many chemical reactions may occur, some will dissolve the **Si**.

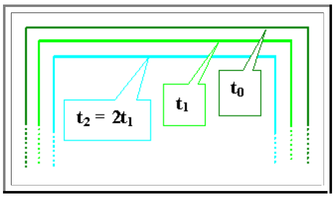


- *Plasma etching*
- In a vacuum vessel, some gas is introduced and excited to a Plasma by, e.g., applying a high-voltage/high-frequency power source between the Si and sone other electrode.
- **Si** may be etched, the products of the reactions and the unused gas are moved out of the system.

- There are many (much more complicated) ways of producing a plasma and having it interacct with the **Si** surface.

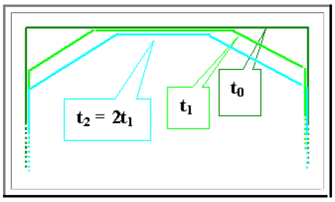
If any etching occurs, it may happen in several, very distinctive ways. They can be discussed most easily if we imagine that the **Si** sample is a single crystal with, e.g., **{100}** surfaces as indicated the first picture.

- The **{100}** cube may dissolve homogeneously. This looks something like this



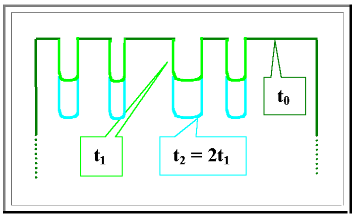
- The cube dissolves homogeneously, i.e. the dissolution rate is constant and independent on any crystallographic or other details. The dissolution is **isotropic** .

- The **{100}** cube may dissolve in a way that changes its shape. This happens whenever the dissolution of some crystallographic planes is faster that some other ones, or, generally speaking, if the dissolution rate depends on the crystallographic orientation.



- Certain crystallographic planes dissolve much faster than others, the dissolution is **anisotropic**.

- The dissolution may proceed by forming a pattern of its own e.g. by etching pores in the crystal. This self-induced patter formation process may have some crystal anisotropy in addition, e.g. the pores are always oriented in certain crystallographic directions. This not only may get extremely complicated in theory, it actually does happens in the (electro)chemical etching of **Si** and it realy is excruciably complicated!



- Patterns emerge; in the example small pores grow into the Si. There are many other patterns obtainable; especially with electrochemical etching.
- While the places where pores start to grow may be totally random, the growth direction of the pores may be in a special crystallographic direction - some crystal anisotropy comes in on a secondary level.

- Other patterns may be tied to defects in the crystal, i.e. a little pore or pit develops wherever a defect, e.g. a dislocation line intersects the surface - we have defect etching. Again, this may work (very) differently on different crystallographic surfaces

By now it becomes clear that etching is very complex and has many facets to it. The situation is becoming even more complex if we consider etching through a mask, i.e. only defined parts of the **Si** surface are exposed to the etching agent.

- This is of course the standard procedure encountered in technology. All the observations made above apply and some new points may come in on their own.
- However, we will not treat this case here, but in the context of the upcoming chapters and subchapters.

Etching of **Si** always can be done in two principially unrelated ways (which often occur in a mixture, causing some of the complication):

- **Direct dissolution**, cursorily expressed by the "chemical" formula
Si + something = Si-compound(dissolved) + something else.
A simple example (and reality is actually not as simple as that) could be

$$\mathrm{Si + 2HF \Rightarrow SiF_2 + H_2}$$

- **Oxidation** in a first step, **followed by oxide dissolution** in a second step, e.g.

$$\mathrm{HF + HNO_3 \Rightarrow SiO_2 + ...}$$

$$\mathrm{SiO_2 + 2HF \Rightarrow SiF_2 + ...}$$

- These simple examples make clear that even the basic chemistry is not so simple; we will come to that later.

- One last general remark:
  - The truncated chemical equations above use hydrofluoric acid (**HF**), and nitric acid (**HNO_3**). This is not accidental, but what you have to use in many cases. Some other chemicals may be useful, too, but there is an important general rule:

Etching Silicon always uses some of the most dangerous chemicals known to mankind! **Beware and be sure you know what you are doing!**

- Hydrofluorous acid is nothing to joke about! The same is true for most of the other chemicals involved.
  - However, taking proper precautions, experiments are possible and routinely done. Huge quantities of the dangerous chemicals are used up every day in semiconductor technology and there have been very few serious accidents.
  - Do not be afraid of using chemical etches! Make sure you know the safety measures and have somebody with experience initiate you. Most accidents happen because people are careless or afraid!