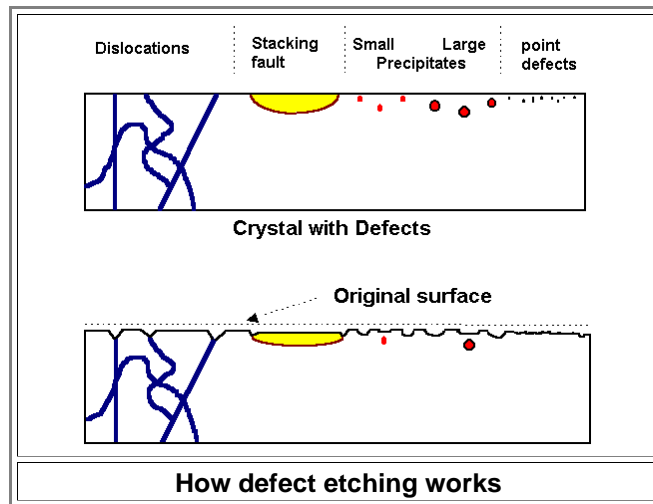


# Defect Etching in Silicon

## Basics of Defect Etching

Defect etching is based on *preferentially* etching (= dissolving) a material in places where you find defects. The basic idea behind this **preferential etching** is to mark defects intersecting the surface by a small pit or groove, so they become visible in a microscope. It is easy in principle,

- Start with a well polished surface that does not show any structures in a **light microscope** (including high magnifications and sensitive modes, e.g. phase or interference contrast). Find an etching solution that dissolves your material much more quickly around defects than in perfect regions (that is the tricky part). Expose (= etch) your sample in this solution for an appropriate amount of time. What happens (if everything goes right) will be something like this:



- The figure shows a model crystal with several kinds of defects intersecting the (polished) surface, and the surface structure after preferential etching of defects.

After preferential etching you obtain well developed **etch pits** (actually something looking more like pointed etch cones) at the intersection points of **dislocations** (including partial dislocations) and the surface and **etch grooves** at the intersection line of **grain boundaries** and **stacking faults** with the surface. **Precipitates** will be shown as shallow pits with varying size, depending on the size of the precipitate and its location in the removed surface layer. Areas with high densities of very small precipitates may just appear rough. Two-dimensional defects like grain boundaries and stacking faults may be delineated as grooves.

- There is a certain problem with grain boundaries, however: They may also be *delineated*, i.e. rendered visible, with chemicals that do *not* preferentially etch defects, but simply dissolve the material with a dissolution velocity that depends on the grain orientation (this is the rule and not the exception for most chemicals). In this case grain boundaries show up as *steps* and not as *grooves*. Small steps and grooves, however, look very similar in a light microscope and may easily be mixed up. You might think: So what! - in any case I see the grain boundary. Well, almost right, but not quite. There are problems. Grain boundaries separating two grains with similar orientation with respect to the surface would not be revealed. The delineation of grain boundaries obtained under uncertain etching conditions suggests that you delineated *all defects* - but in fact you did not. Delineation of grain boundaries thus must not be taken as an indication that the etching procedure works and there are no defects, because you don't see any!

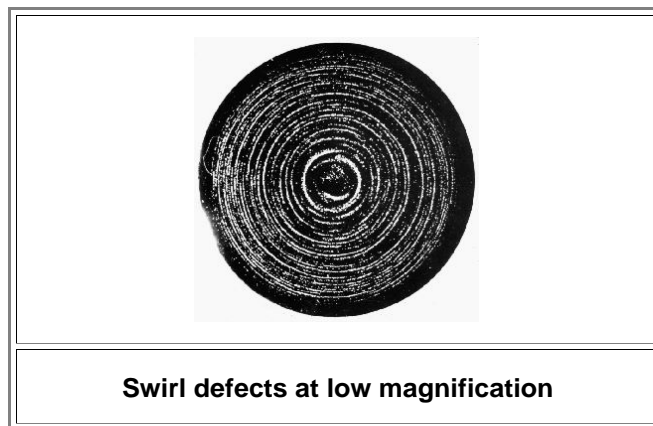
Before we look at examples and case studies, two important points must be made:

1. Defect etching for many scientists is a paradigm for **"black art"** in science. There are good reasons for this view. Nobody knows how to mix a preferential etching solution for some material from theoretical concepts. Of course you must look for chemicals or mixtures of chemicals that react with your material, but not too strongly. But after this bit of scientific advice you are on your own in trying to find a suitable preferential etch for your material. Well-established preferential etching solutions usually have unknown and poorly understood properties. They sometimes work only on specific crystallographic orientations; their detection limits for small precipitates are usually unknown; they may also depend on other parameters like the doping level in semiconductors; and so on.
2. Defect etching *in practice* is more *art* than science. Beginners, even under close supervision by a master of the art, will invariably produce etched samples with rich structures that have nothing to do with defects - they produced so-called **etch artifacts**. It takes some practice to produce reliable results.

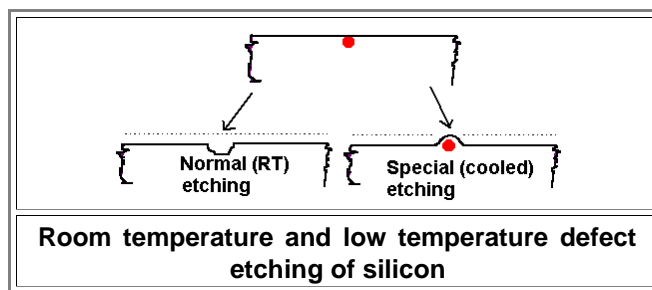
- **But:** Defect etching still is by far the most important and often most sensitive technique for observing and detecting defects!  
There are many routine procedures for delineating the defects structure of *metals* by etching. Here we will focus on defects etching in Silicon, which is still the major technique for defect investigations in **Si** technology. In what follows we look at the power and possible mechanisms of preferential etching in the context of examples from recent research.

### Defect Etching Applied to Swirl Defects in Silicon

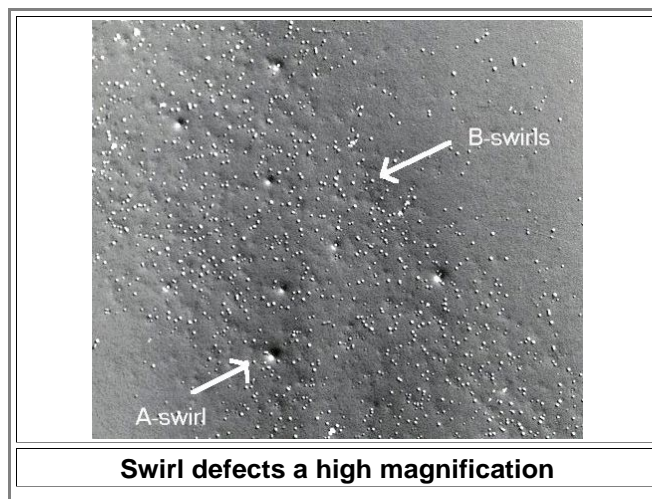
- ▶ The name "Swirl defects" was used for grown-in defects in [large Si crystals](#) obtained by the float-zone technique in the seventies.
- Swirl defects are a subspecies of what now is known as "**bulk micro defects**" (**BMD**); they are nothing but agglomerates of the point defects present in thermal equilibrium near the melting point, with possible influences of supersaturated impurities still present in ultra clean **Si** (only oxygen and on occasion carbon). Whereas the relatively large swirl defects are no longer present in [state-of-the-art Si crystals](#), point defect agglomerates and oxygen precipitates still are - there is no way to eliminate the equilibrium defects! **BMDs** are a major concern in the **Si** industry because they cause malfunctions of integrated circuits. The link leads to a [recent paper](#) on growing large silicon crystals.
- ▶ Most of the examples relating to **Si** are taken from the work of **B.O. Kolbesen** (formerly at Siemens; now retired, after being a professor at the University of Frankfurt).



- The name "swirl" comes from the spiral "swirl-like" pattern observed in many cases by *preferential etching* as shown on the right. The picture shows what you see on a whole 100 mm wafer. Close inspection at high magnifications revealed two types of etch features which must have been caused by different kinds of defects; see below. Lacking any information about the precise nature of the defects (which etching can not give), they were termed "**A**" and "**B**-swirl defects".
- ▶ Understanding the precise nature of swirl defects was deemed to be very important for developing crystal growth techniques that could avoid these detrimental defects.
- But etching alone can not give structural data. Other techniques, in particular [transmission electron microscopy](#), could not be applied directly because the density of swirl defects was too small. The likelihood of having a defect in a typical **TEM** sample was practically zero. A combination of a special etching technique and **TEM**, however, could give the desired results.  
The power and the "black art" component of defect etching is nicely demonstrated by the following development: A "special etch" which was simply the old solution, but cooled to about freezing temperatures, did not produce etch pits (and thus removed the defect) for A-swirls, but hillocks *still containing the defect*.
- ▶ What could one use to defect-etch silicon? One needs some potion that is not able to dissolve perfect silicon but can attack the silicon atoms in a "weakened" state around some defect. Knowing that silicon is always covered with a thin layer of silicon dioxide or quartz ( $\text{SiO}_2$ ), the trick is to use hydrofluoric (HF) acid to dissolve the oxide, and an oxidizer to oxidize the "weak" silicon parts.
- Use a strong oxidizer like nitric acid ( $\text{HNO}_3$ ) and you dissolve all of the silicon. Use a weak oxidizer like  $\text{H}_2\text{O}_2$  and nothing happens. The oxidizer of choice is chromium oxide ( $\text{CrO}_3$ ). Dissolve it in water, add HF plus a few other ingredients that make the result nicer without anybody knowing why, and you are in business. You also have a concoction of some of the most dangerous chemicals known man.  
The ratios of the constituents matter very much. One particular recipe (known as "Sirtl etch") works only on {111} surfaces, another one (known as Seiter etch) is best on {100} surfaces, while the "Secco etch" works on all crystallographic planes. Why? Nobody knows for sure.
- Temperature, too, is important. Use a Sirtl etch for swirl defects at room temperature or around  $5^\circ\text{C}$  ( $40^\circ\text{F}$ ), and the results are breathtakingly different:



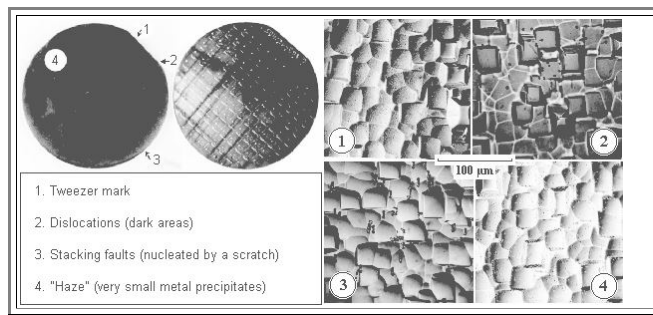
- At room temperature the usual etch pits are found, meaning that the defect that caused it had been removed. But at low temperature there is a hillock instead of a pit for the bigger kind of swirl defect! That means the defect causing differential etching is still there! Here is what this looks like in a (very advanced) light microscope:



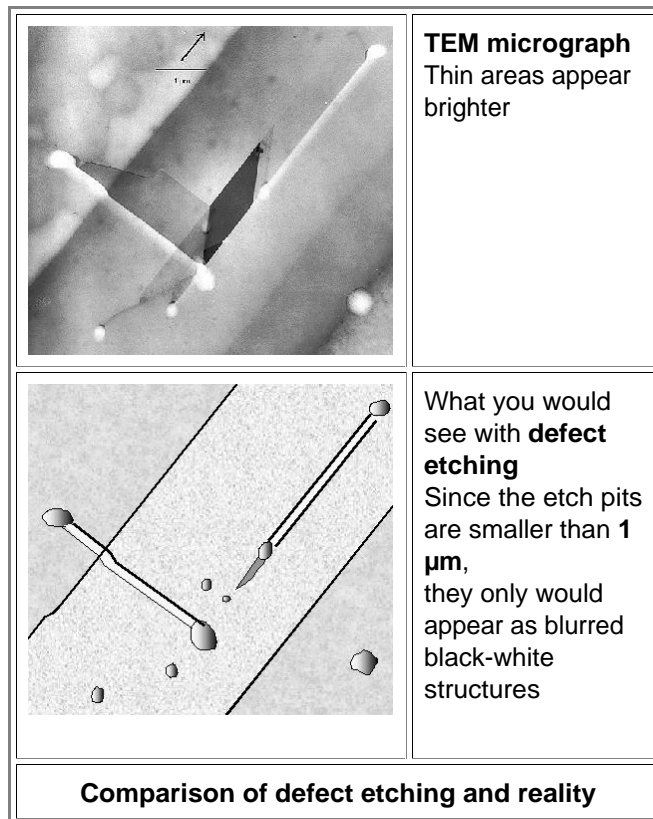
- Not that pits and hillocks appear as a black-white dots. For hillocks the white side is towards the left, for pits towards the right, however.
- Now there was a break! The hillocks identified the precise location of the **A-swirl** defects and the defects were still there! A special preparation technique rendered the areas containing hillocks transparent for **TEM** investigations, and the structure of **A-swirls** defects could be identified. They consisted of dislocation loop arrangements that were generated by the agglomeration of interstitials. This gave the first direct evidence that [self-interstitials are important in Si](#).
- B-swirl** defects could not be identified with this technique - their nature is still not all that clear.

### Process Control by Etching Defects during the Manufacture of Integrated Circuits

- The manufacture of **integrated circuits (IC)** involves many processes prone to introduce defects in the more or less perfect starting crystal.
  - For example, all high temperature processes induce [temperature gradients](#) which lead to stress and thus to a driving force for plastic deformation. Since the starting material is dislocation free, the decisive process is the nucleation of the first dislocations which is much easier if small precipitates or dislocation loops are already present. Thermal oxidation introduces **Si** interstitials with a strong tendency to agglomerate into stacking fault loops, so-called **oxidation induced stacking faults (OSF)**. Ion implantation destroys the lattice to a large degree up to complete amorphization. Even upon careful annealing some defects may be left over. And all processes tend to induce trace amount of metals which will diffuse into the **Si** and eventually precipitate.
- As a general rule, all defects in the electronically active part of an **IC** (roughly the the first **5 μm - 10 μm** of the wafer) are deadly for the device. They have to be avoided and that means that they have to be monitored first. The method of choice is *preferential etching*. Lets look at an example. The pictures show a **Si** wafer with several defect types introduced during very early stages of processing. Defect etching made possible to identify the causes as shown.



- One more example serves to illustrate the "*what you see must be interpreted*" point. Shown is a complex defect composed of stacking faults, dislocations and possibly a microtwin in full splendor in a **TEM** micrograph (top), and a schematic outline of what the preferential etching would look like in an optical microscope (bottom).



- The planar defects are inclined in a thin foil; what one sees is the projection. One surface was preferentially etched; at the intersection of the defect with this surface the etch features can be seen as bright areas (the sample thickness is smaller at etched parts). The stacking fault lines will be clearly visible in an etch picture, but the various dislocations involved are etched with different strengths. It will not be possible to conclude from the etch pattern alone on the complexity of the actual defect.

▶ We are now able to compare weaknesses and strength of preferential etching for defect detection.

Strength	Weaknesses
<ul style="list-style-type: none"> <li>• Simple and cheap</li> <li>• Rather sensitive</li> <li>• Applicable to large areas</li> <li>• Needs no special knowledge (as e.g. <b>TEM</b>)</li> </ul>	<ul style="list-style-type: none"> <li>• Black art</li> <li>• Detection limit unclear</li> <li>• What you see must be interpreted</li> <li>• Problems with artifacts</li> <li>• Mechanism not clear</li> <li>• No systematic developments of etches</li> </ul>