Defect Etching in Silicon

Advanced

- The big **Si** wafers are prime material for defect etching because they combine a really large area (**300 mm** wafers are now (**2001**) appearing in production) with a (hopefully) very small defect density, and sometimes very small defects (precipitates and point defect agglomerates).
  - In consequence, the main advantages that defect etching has to offer - large areas and high sensitivity - is exactly what you need.
- It is therefore not surprising that defect etching was and is the method of choice for getting an overview for what is going on in your sample. Main areas of interest are
- "*Native*" defects in **Si** crystals and unprocessed (or just pre-processed) wafers. Essentially, researchers hunt for:
  - The unavoidable *agglomerates of the point defects* that were present at thermal equilibrium at high temperatures. There are all kinds, and their classification is not too clear - in the seventies, people considered "swirl defects" (subdivided into **A**- and **B**-defects), then came **C**-defects, and more recently **D**-defects. The practitioners in the production lines prefer abbreviations like "***COP***" ("Crystal originated particles or pits") or "***LPD***" (for "light point defects", which does not mean light-weight point defects but "point defects detected by scattering light") that simply includes everything that some very expensive equipment detects on the surface (including etch pits).
  - The actual defects behind "**LPDs**", e.g., might be vacancy agglomerates ("**D**-defects") in the form of voids (which are, after all, small pits if cut by the surface of a wafer), particles that are stuck to the wafer surface, "precipitates" of organic molecules which will form on wafers kept a long time in a plastic container, or .... - just anything that scatters light.
  - Defects related to *oxygen* (i.e. oxygen precipitates or stacking faults caused by oxygen precipitation). This includes also oxygen precipitation intentionally introduced in the bulk of a wafer - and only in the bulk - by some special heat treatment for reasons of "**intrinsic gettering**".
- *Process induced defects*; meaning everything generated during the processing of an integrated circuit or other Si devices.
  - There are many defects that may occur: *Dislocations* produced by plastic deformation due to large temperature gradients, oxidation induced *stacking faults*, metal *precipitates* - the Hyperscipt is full of examples (check the matrix of modules)
  - Specialities include large power devices, where just *one* defect in a wafer can kill the whole device (in integrated circuit manufacture it would just kill one out of some **200** chips).
- Defects in *solar **Si***, i.e. "cheap" **Si**, mostly multicrystalline and full of defects of all kinds.
  - *Grain boundaries* abound, but more important are often the dislocations and precipitates of impurities. Optimized chemical etching together with plenty of experience allows to distinguish the different types.
- There are many defect etches for **Si**, They all rely on the basic chemistry of forming and dissolving an oxide. Since SiO_2 dissolution always requires **HF**, all defect etches contain hydrofluoric acid and thus are very dangerous chemicals.
  - The "trick" is to make the dissolution process difficult in general, so that it may become enhanced at defects. Why it should be enhanced is obvious on the one side - the bonds around defects are weakened after all - and rather tricky on the other side - electronic properties certainly may play a role, too.
  - The common defect etchants (or "etches") therefore restrict one of the crucial reactions, and that is usually the oxidation (after all, it is the Si that contains the defect, and not the SiO_2).
  - One of the first defect etches developed, the so-called **Dash** etch, therefore simply took the standard Si dissolution chemistry (always HNO_3 + **HF** + **HAc** (**HAc** = acetic acid)) but with far less HNO_3 than the standard solution. While it worked, it was not optimal in terms of selectivity and sensitivity and in producing etch features that allow to distinguish between certain types of defects. And, most disadvantageous, it needed etch times of **4 - 16 hrs**.
- The next approach then replaced HNO_3 by an oxidant that is still sufficiently strong to oxidize **Si**, but just barely so - CrO_3 (dissolved in water). Several etches were developed and are used, but we will see that there is still a "black art" component.
  - The first CrO_3 based etchant is called "**Sirtl etch**" after its inventor (Ms. **Adler**, who was a co-author (and probably did the work), has been forgotten by now). It employs **HF** + CrO_3 + H_2O in a ratio of **HF**(H_2O free) : H_2O : CrO_3 ≈ **1 : 0,4 : 0,2**.
  - The Sirtl etch works well, *however only on {111} surfaces*.
  - A less well known etch is called **Seiter etch**, employing (**HF** + CrO_3 + H_2O in a ratio of **HF** : H_2O ≈ **1 : 9** with **120 g** of CrO_3 dissolved in **100 ml** of the H_2O. Its peculiar behavior is that it etches defects very well, but (as far as is known) *only on {100} surfaces*.
  - A great etch used by many researchers is the **Wright etch**. It mixes **HF(conc)** + CrO_3 + H_2O in a ratio of **1 : 0,5 : 1** and throws in **0,5** HNO_3**(conc)**, some $Cu(NO)_3$ (**2** grans for **60 ml** H_2O) and **1** unit **HAc**.

- What the **Cu**-nitrate does is (relatively) unclear.
- The **Secco etch**, finally, using (**HF + $K_2Cr_2O_7$ + H_2O** in a ratio of **HF : H_2O = 2 : 1** with **44 g $K_2Cr_2O_7$** dissolved in **1 l** of the of **H_2O**. *It etches defect on all surfaces*.

There are lots of more etches - most notably, perhaps, the "**Schimmel**" etch (a kind of improved Secco etch); and a literature search will easily find upwards of **50** papers dealing with defect etching in **Si**. No really good explanation has been offered for the strong dependence of the etch anisotropy on the composition.

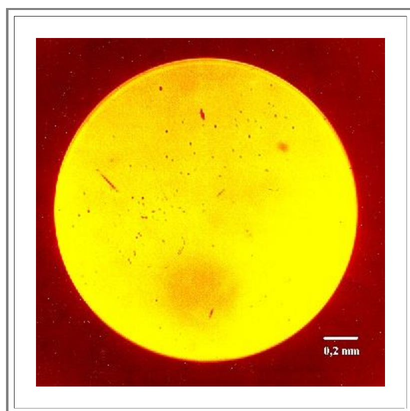
Seiter gives a short comparison of the major etches that is reproduced below.

Etch	Composition (Mol %)			Results on {100}	
	Solvent [1]	HF	Oxidizer [2]	line defects	"point" defects
Secco	67,6	32,2	0,17	pits	shallow pits or hillocks
Sirtl	71,2	26,3	2,5	pits or mound	-
Wright	78,5	16,1	5,4	pits	shallow pits
Seiter	78,5	5,9	15,6	mounds	mounds
[1] H_2O + CH_3COOH (HAc); [2] CrO_3 + HNO_3					

- You see that the oxidizing part is the limiting factor indeed, and that on occasion you get mounds or hillocks and not pits, i.e. the dissolution is slower at the defect site and not faster.
- Try to make sense of this, and you will be a scientific hero.

But their are more puzzles:

- While a regular Sirtl etch used at room temperature etches defects always faster than bulk Si, it reverses its behavior to some extent at lower temperatures, say **10 ^{o}C**. Than a *hillock* may form instead of an etch *pit*. While the defect now is just as visible as with an etch pit, we have the dramatic difference that the defect is *still there*! This technique, together with a rather tricky specimen preparation for a subsequent **TEM** investigation was pioneered by **Kolbesen** et al.
- This was the key to finding the swirl defects shown in the link. Their density is so low that just blindly searching with the **TEM** would make it very unlikely of ever finding one. This becomes clear when looking at a typical **TEM** specimen:



- This is a **TEM** specimen where the whole area is transparent to the electron beam. It is so thin, that it is also transparent to regular light - what you see is a light optical micrograph.
- The small dark dots are the hillocks produced by defect - etching the front side. Under the hillocks are the dislocation loop defects shown in the link.
- The hillocks are visible in the **TEM** at very low magnifications (say around **5.000x**) and thus allow to find the defects.
- Without this guidance, you have quite a job of finding the defects: The magnification necessary to see the dislocation loops is about **50.000x**; i.e. the screen shows about **5 µm^2** of the sample. The area you have to scan is about **5 mm^2** - you must find the **20 - 50** defects by looking at about **1.000.000** screen pictures, i.e. your chances of hitting one "blind" are about **1 : 20.000.**

The original papers:

W.C. Dash, J. Appl. Phys., **27** (1956) 1193

E. Sirtl and Annemarie Adler, Z. Metallkunde **52** (1961) 529

H. Seiter, in "Semiconductor Silicon 1977", ed. H. Huff, E. Sirtl; Electrochem. Soc. Proc. Series, p. 187

F. Secco d'Aragona, J. Electrochem. Soc. **119** (1972) 948

Margarete Wright Jenkins, J. Electrochem. Soc. **124** (1977) 757

B.O. Kolbesen, K.R. Mayer and G.E. Schuh, J. Phys. E, **8** (1975) 197

A Warning

Working with **HF** without taking proper precautions may well severely injure or even kill you. Make sure you know what you are doing! Also make sure that you can identify **HF**, even in small droplets that might have been spilled somehow.

There is a little HF tester or in the market that you should always have in reach. Here is the address: Dr. V. Lehmann; FAX ++49 89 56826696; e-mail: vl@hf-acid-sensors.de; Bau & Vertrieb elektronischer Messgeräte; Geyerspergerstr. 53; D-80689 München