4.2.2 Chemical Etching of Silicon

Isotropic Etching of Silicon

Module is unfinished

- If we neglect exotic mixtures of chemicals, the universal isotropic **Si** etchant is a mixture of **HNO_3 + HF + CH_3COOH** .
  - In other words: Mix nitric acid, hydrofluoric acid and acidic acid (**= HAc**)! The resultant mixture is known as ***CP*x**; the **x** being **1 ...4**, depending on the exact composition - and this abbreviation was chosen for good reasons!
  - The etching characteristics you obtain depend very much on the exact composition and the temperature, possibly on the doping of the **Si**, and to some extent on some small amounts of other chemicals that might be added to the mixture.
  - Some data for two typical mixtures are presented below.

Composition HF : HNO3 : HAc	Temp. °C	Etch rate µm/min	Anisotropy <100> : <111>	Masks for selective etching	Remarks
1 : 3 : 8	20	3	1 : 1	none	Etch rate strongly reduced for doping n: $<3 \cdot 10^{17}$, p: $<3 \cdot 10^{15}$
1 : 2 : 1	20	40	1 : 1	none	

- **CP** etches attack about everything - don't store them in a glass bottle, it will dissolve too!
  - Only some polymers, most notably ***PVC*** and Teflon, are **CP** prove
- They generally work by oxidizing the **Si** (thats what the is doing) and dissolving the oxide (the job of the **HF**).
  - **HAc** is mostly just for diluting the mixture
  - However, **HAc** is also....
- A big problem with the **CP** etches is that they also dissolve all possible masks - usually **SiO_2** or **Si_3N_4** layers - so they cannot be used for **selective etching**
  - At best, **Si_3N_4** may last for some time - if you hurry up selective etching becomes possible in a confined way.
- For a strong imbalance between **HNO_3** and **HF**, the etchant may change its character:
  - Most notably (and not very suprisingly), the etch rate comes way down
  - More surprisingly (but not really, if you think about it): it may now be a **defect etch**, i.e. it attacks **Si** much faster at the place of defects.
- While only **HF** dissolves **SiO_2** , all strong oxidizing agents can oxidize **Si**. It thus is possible to replace the **HNO_3** by some other oxidant. Essentially, two oxidizers are used:
- First, **H_2SO_4** can be used instead of **HNO_3**, typically in a ratio **HF : H_2SO_4 : HAc = 1 : 1: 5**
  - While inferior in over-all "quality" to the **CP** etches, it does not attack **Si_3N_4** masks very strongly and thus can be used for selective (isoptopic) etching.
  - Etch rates are around **(2...5) µm/min**, again depending on someother factors too.
- Second, **CrO_3** is used, a relatively weak oxidizer for **Si**. It only works on "soft spots", i.e. at surface areas were the bonds are weakened because of defects.
  - **Hf + CrO_3 + HAc +** many other chemicals (with no clear role) is the base of most defect etchants - a very important techique in semiconductor development