

Loosing Large Amounts of Money with Wet Chemistry

Illustration

- Usually, the big disasters in chip production are kept quite confidential - you don't want to admit that you have problems, and you don't want to help your competitors to avoid these problems.
 - However, as time goes by, confidentiality is no longer necessary. But people have other problems now, so still nothing is published.
 - Well, here is the exception: The short story of a major disaster in the early production of the **1 Mbit DRAM** in the new Siemens factory in Regensburg, as it happened back in about **1985**.
- Managerial wisdom had decided not to trust the research and development team with the development of the **1 Mbit DRAM** (Siemens (and Phillips) then were about **1** year behind the leading Japanese and had started a race to catch up), but to take a license from Toshiba, the top memory producer then.
 - Not that we liked it. But the new factory was dutifully converted to the Toshiba process - all the equipment, all materials, everything whatsoever, was identical to what Toshiba had and did - with good yields of functioning devices.
 - But the German factory produced exclusively junk - the memory chips didn't work. Nobody, including the Toshiba engineers, had the faintest idea why.
 - This went on for almost **6** months - at losses of about **5 - 10** million marks a month. Then the problem was found and solved. First empirically, then by understanding what happened.
- Since it was evident that something *we* did must be different from what *Toshiba* did, the search focussed on the few differences that were unavoidable for some reason or other.
 - The culprit that was finally identified, was an extremely simple chemical: **H₂O₂**; used in the mixtures for cleaning the wafers.
 - In contrast to practically all other chemicals, the **H₂O₂** was not bought in Japan from the source Toshiba used, but from a German company because it simply would not have survived months of traveling aboard a ship. **H₂O₂** always decays into water and **O₂** in the course of weeks, and since it is a slightly dangerous chemical, the airlines refused to transport it.
 - So there was no choice but to buy it in Germany - and of course the German **H₂O₂** was carefully checked for cleanliness (it was actually cleaner than the Japanese stuff).
- Somebody finally convinced an airline (Alitalia) to fly in a barrel of the Japanese stuff - and a miracle happened and good chips were produced using it.
- What has happened? Nobody knew, but who cares if it works? Well the research oriented guys do care, and in due course the mystery was unraveled.
 - As it turned out, **H₂O₂** always contains some *stabilizer*, and this is neither displayed on the label nor do the producers tell you what it is. The stabilizer is needed to keep the remaining traces of metal ions, that are still present - even in ultrapure **H₂O₂** - complexed (i.e. surrounded by the stabilizer molecules); in particular **Fe⁺⁺**.
 - And this complexation is necessary because "naked" metal ions would catalyze the decay of **H₂O₂** into water and oxygen - the "shelf life" of your chemical would be very short without a stabilizer.
 - Now Siemens, as most other western producers, used some variant of the classical "**RCA**" cleaning procedure which is always acidic, i.e. it works at **pH** values **<< 7**.
 - The Japanese, however, had invented a new alkaline cleaning procedure, relying heavily on "Choline", a simple organic leach, i.e. they worked at **pH** values **>> 7**.
- As it turned out, the stabilizer in the Japanese **H₂O₂** worked in an alkaline environment, while the German stabilizer did not.
 - This was purely accidental, neither the Japanese, nor the Germans, nor anybody else, had ever to worry (or even knew) about the stability of **H₂O₂** stabilizers.
- As a consequence, whenever an alkaline cleaning was carried out with the German **H₂O₂**, Fe was no longer complexed and some of it was deposited on the **Si** substrates.
 - This must be expected to happen, because **Si** is less noble than **Fe** with respect to its electrochemical potential. We are talking tiny amounts of deposited **Fe** here, far less of what is still contained in ultra-hyperpure chemicals.
 - The iron deposited in this way would diffuse into the **Si** as soon as it was heated. This did not do much damage, and that was why every measurable parameter always looked quite good during processing - only at the end the chips started to deteriorate.
 - The reason for this was that at every heating cycle, **Fe** was diffusing around a bit more, until eventually small precipitates formed (needle-like FeSi₂)
- And these precipitates killed some gate and capacitor oxides - and since it needs only *one* dead transistor (out of about **1,5** million) to kill a chip, the yield was practically non-existent.

- There is just no way you can anticipate that. And the detective work in this case was complicated because the effect (dead transistor) was not traceable to the reason (incorporation of iron), because first measurable deviations from expected behavior occurred many process steps *after* the original cause.
- Many process lines could tell similar stories. From what one hears or suspects, one rule that might be good to know evolves: The really big disasters in chip manufacture are more likely to have their roots in humble wet chemistry than in the sophisticated processes everyone talks about.