

Technical Disasters in Microelectronics

Illustration

Few human enterprises are so exclusively based on science as the making of semiconductor products. There is no empirical knowledge, no fiddling around in the garage, or just running across some neat discovery by sheer luck. There is *only* Material Science (also called semiconductor physics in this case) to guide your engineering. Nevertheless the unexpected happens. "Recipes" that performed flawlessly for years suddenly don't work anymore.

Here are a few examples that I experienced myself.

The H₂O₂ Incident

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 by talking about it.

However, as time goes by, confidentiality is no longer necessary. But people have other problems now, so still nothing is published.

Well, here is one exception: The short story of a major disaster in the early production of the **1 Mbit DRAM** (1 Megabit memory chip) in the new Siemens factory in Regensburg, as it happened back in about **1985**.

Managerial wisdom had decided not to entrust the research and development team (of which I was a part) with the development of the **1 Mbit DRAM**. The bosses decided to take a license from Toshiba, the top memory producer then. Siemens (and partner Phillips) were about 1 year behind the leading Japanese and had started a race to catch up. We would have won, of course, but it wasn't to be.

Not that we liked it. But the new factory was dutifully converted to the Toshiba process—all the equipment, all materials, everything whatsoever was absolutely identical to what Toshiba had and did. Toshiba had good yields of functioning devices and was making money.

But our German factory produced exclusively junk, the proven recipe did not work in Regensburg. Nobody, including the Toshiba engineers, had the faintest idea why. This went on for almost **6 months** - at losses of about **5 - 10 million Dollars** 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 in the production process that were unavoidable for some reason or other.

The culprit that was finally identified was an extremely simple chemical: hydrogen hydroxide (**H₂O₂**); used in the "detergents" 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** decays into water and **O₂** in the course of weeks, and since it is a slightly dangerous chemical, the airlines refused to transport it.

There was no choice but to buy it in Germany. 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. With it a miracle happened: good chips were produced.

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 traces of a secret *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.

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 base, 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 worried (or even knew) about the stability of **H₂O₂** stabilizers.

As a consequence, whenever an alkaline cleaning was carried out with the German **H₂O₂**, iron ions were no longer complexed, and some of them ended up on the silicon **Si** surface.

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, just a small part 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 iron silicide; **FeSi₂**)

- These precipitates killed some gate and capacitor oxides and thus a transistor. 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 if not all process lines could tell similar stories. From what one hears or suspects, one rule evolves that might be good to know: 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.

Know your Carbon (and Oxygen)

- In the very early days of microchip production around 1975, several factories all over the world started to produce non-functioning chips seemingly from one day to the next. The proven recipe suddenly didn't work anymore. This caused a lot of confusion and frantic research, of course.
- What had happened, as we and others found out, was that the major producers of silicon crystals had changed its recipe for growing silicon crystals just a little bit. The resulting product was exactly identical to what had been made before—as far as the measured properties were concerned. But you just could not make good chips with those crystals. Logic dictated that something must be different—but what?
 - It turned out to be the carbon still incorporated in the silicon crystals in tiny amounts, far below of what chemist would call "high purity". It was rather difficult just to measure it, so nobody usually did. With the new process the carbon concentration was just a little bit higher than before.The higher carbon concentration by itself would not have made a difference to the transistors made in the silicon. It made a difference to other impurities still contained in the silicon at even lower levels, however. It sort of catalyzed the precipitation of some of those impurities, i.e. the formation of tiny clusters of these things. Too small to be visible in a microscope but large enough to kill a transistor.
- Knowing what happened allowed to take counter measures and chip production resumed.

Provide the Right Dirt

- Around 1995 a factory that made so-called electrolyte capacitors (something found in nearly every piece of electronic hardware) called me, asking for help.
 - In their production process they run large sheets of high-purity aluminium foil through a chemical bath with some voltage applied. The proper recipe then produced zillions of small holes in the Al sheet; making it porous in other words. That was absolutely necessary for the product, and the recipe had worked for many years without a problem.Then from one day to the next it didn't work anymore. No holes in the Aluminium sheet.
- Obviously, something in the aluminium must have changed. To make a long story short, this time it was not too much of some impurity but too little,
 - The aluminum foil producer had changed the process a little and more or less accidentally made its aluminum a bit purer. What we learned then is that the process of pore etching in aluminium actually needs a certain impurity. It needs just a tiny little bit of that (secret) stuff - but that you must provide.
 - I was not really much involved in this problem so I don't even know of the colleagues who dealt with that problem ever found out *why* this particular element was needed.