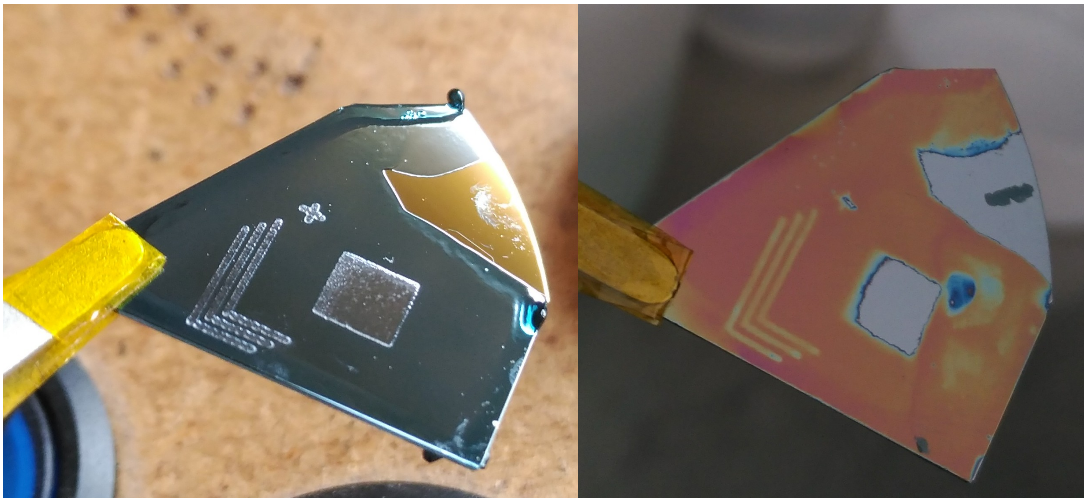
Semiconductors @ Home



Cookbook!

Nixie

This is my adventure ~~rulebook~~ cookbook! Before continuing, make sure you have the latest version, as this particular document will get updated often (as often as I figure out processes, and I'm up to write something).

Unlike the Compendium, this cookbook will attempt to actually hold your hand, and guide you as best as possible in understanding the processes involved, and how to perform them. Also, using the least possible amount of maths. **;)**

I want to write the book I would liked to have found in the first place.

This "book" will contain swearing, puns and fun references, in no particular order or amount. NSFK$_{\text{ids}}$

You have been warned.

Index

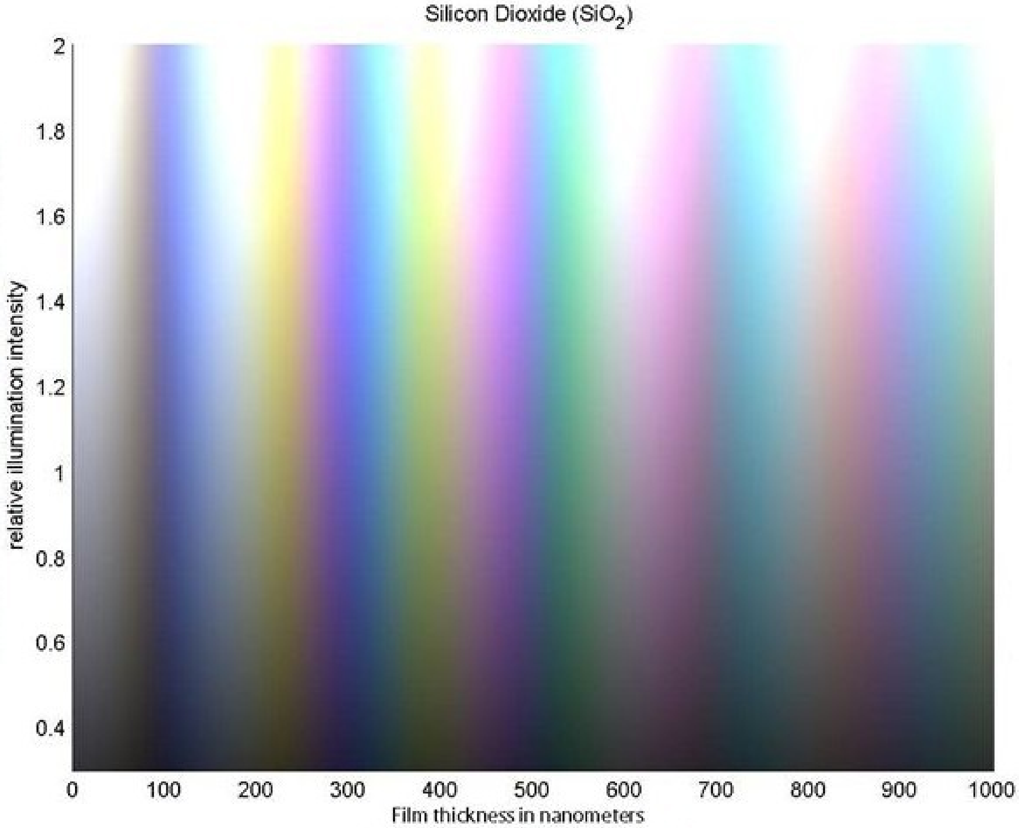
XX is used as this document is constantly being updated.
All link to the apropriate chapter.

Silicon oxide growth.

Throw some silicon in the oven to see what happens.

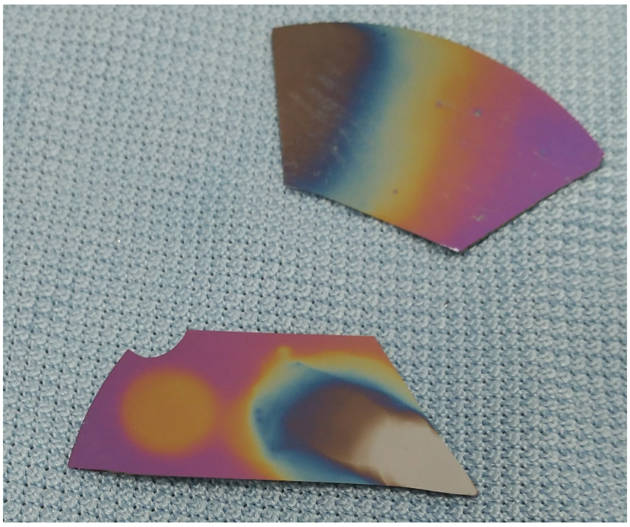
First, remember, the particulars of your oven can vary greatly from mine, so you should do some test runs on small pieces, and check times vs oxide growth, but my findings should give you a ballpark of where to start from.

First, an Oxide thickness chart, so we can have fancy colors for starters:



The first time I put silicon in the oven, I left it about 60 minutes.

After aplying HF under a slight breeze from the fume hood, it was etched in a way that revealed all the colors to easily discern the thickness.



As we can see, it descends from purple (≈300nm) to gold, white, blue, brown and white again. (the leftmost corner is bare silicon at that point, proven by silicon's hydrophobia[1] to HF).

Further characterization pending.

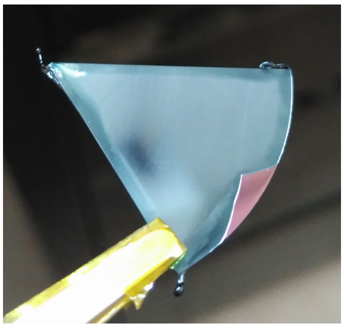
Silicon oxide growth can be performed dry, with pure O2, or wet, with a steam generator.

Since not that many people has O2 readily avaliable, but everyone has a glass of water and a paper napkin, we will assume that any oxidation happens in a wet environment with that method.

To the right you can see the complex setup. A glass of distilled water and a napkin with a stainless frame to hold it just in front of the opening.

The heat will evaporate the water and the capillarity will draw more to the tip. (next to it, a 12V ultrasonic evaporator for a more controllable version of this)

DiY PMMA resist.

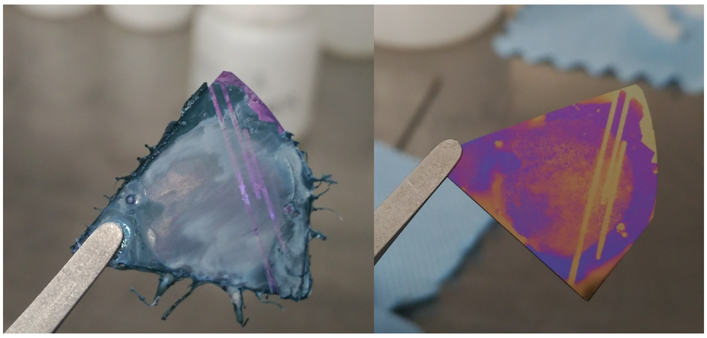


To get fancy thin films like the rightside one, PMMA has to be dissolved in a suitable solvent.

Most used product is Anisole, but it is almost exclusively a lab chemical. I am lucky enough that I have a reliable (and legal) source of Chloroform, altough, in case of necessity, can be made at home with simple products (but requires further distillation, keep that in mind).

Don't be lured into using acetone, because, even if it does dissolve PMMA, evaporates too quickly leaving an unsuitable film, no matter what you do afterwards.

Example of acetone film. Only the thick borders have protected the oxide, and not very well.



For the suitable products, here's my recipe for the laser etching PMMA resist:

1gr of (black) pmma per 10ml of Chloroform.

I have tried other concentrations: 0,5/1,5/2grams/10ml, but the first was too tin for the laser and the last two where too thick to be practical.

This mix should be stored in dark glass containers with PTFE lined lids. In case you don't have those at hand, you can use small jam jars (50ml) and cut a disc of PTFE for the lid, but make sure you store them away from light.

Don't be tempted to make large quantities of the product to achieve excellent repeatability, as it won't work. Each time you open the container, a bit of the solvent will inevitably evaporate, making your mix thicker. Since each thin film uses a very small amount of it, it's better to just mix small batches, like 10ml per bottle. Leave it at least 24h to fully dissolve.

Thin film coating.

Once you have the PMMA resist ready, it's time to apply. Spin coating is an art in itself, and is a skill you will need to hone with your own machine, depending on how fancy you make it.
With mine, there are a few ways to do it

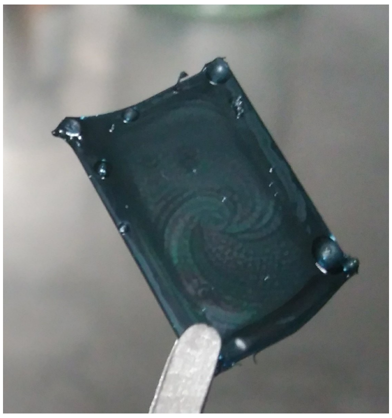
- Apply, no spin.
- Apply, spin.
- Spin, apply, accelerate.

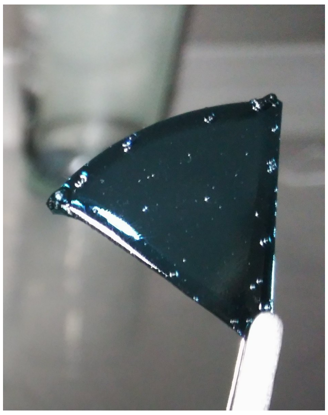
For me, the one that works best is the last. I start the spin @ 1300rpm, and as centered as I can, let go a few drops of the resist until I think that the whole piece is covered. Then I wait about 20 seconds, and accelerate the piece to 2600rpm for 30 or more seconds.
Remember to put a paper strip to catch the leftovers, and then trow them away in an hermetic container. (I use empty soft drink bottles XD)

After that, it's time for the hot plate. My best result recipe is:

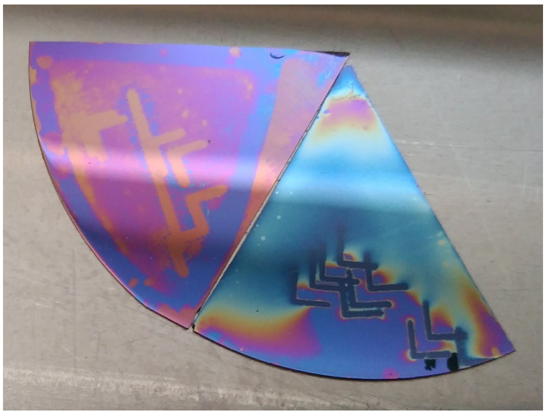
Bake 15 minutes@60ºC + cook @180ºC for 30 minutes.

With that, you will turn a matte film into a shiny surface. Once the layer is cristallized, proceed with photolitography.





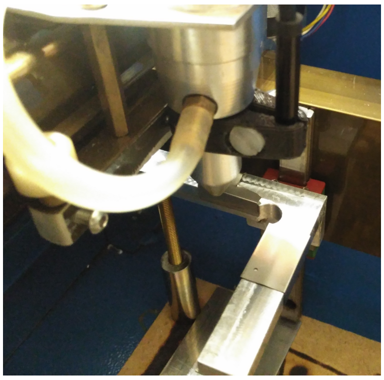
Keep in mind that, if you use the laser in not cristallized PMMA, this will be the result. On the left, the HF sweeped through, and under the lines, on the right, the etching is much more focused. ↓



Photolitography.

Everyone knows that old saying: "Learn to walk before you run", right?

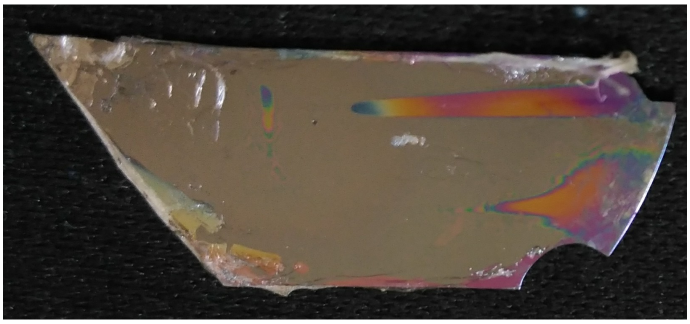
We will talk about laser photolitography until all the processes are nailed down, before trying out some of the other wild ideas (DiY e-beam and UV resin). Laser etching is limited to 150um wide etching unless you spend a fortune in special lenses, and even then, thin PMMA films on silicon do not react that well to laser.



The actual setup has been explained with detail in the compendium, but to resume, it's a glorified focusing tool. With that, one can really nail down the focus point of his installed lens.

Anyways, I will assume you already set it up, so I'll talk about laser power and wafers.

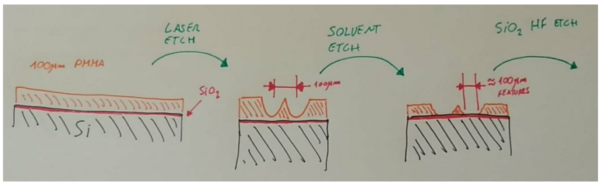
Silicon is very transparent to CO2 laser light, so it has a hard time reflecting or absorbing enough power to help in the cutting process, difficulting the actual etching of the litography.



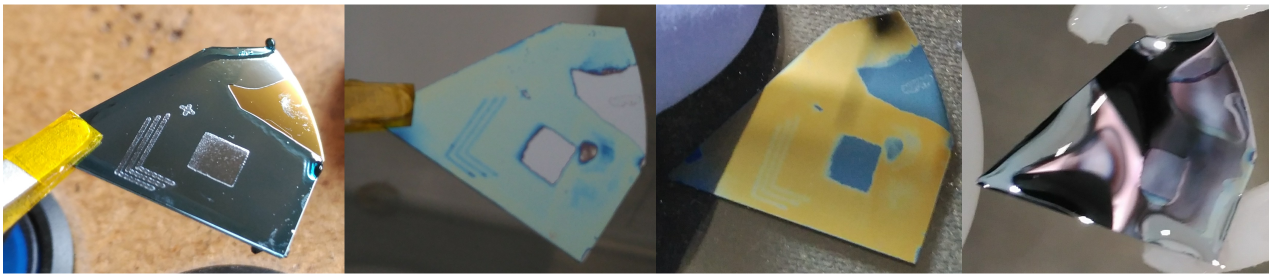
If you dump enough power into it, tough, it will get hot, and probably damaged too. To the left you can see a test piece. A small hairline crack has developed in the long colored track, due to heat. The bottom etch got so hot, it evaporated much of the resist too (in the laser path)

Knowing that, one can deduce that if the process doesn't work at low powers, it won't work. Don't push it, m'kay? My K40 laser with a good brand name lens operates @ 5mA or whereabouts (top power is 18mA).

The process was devised as follows:

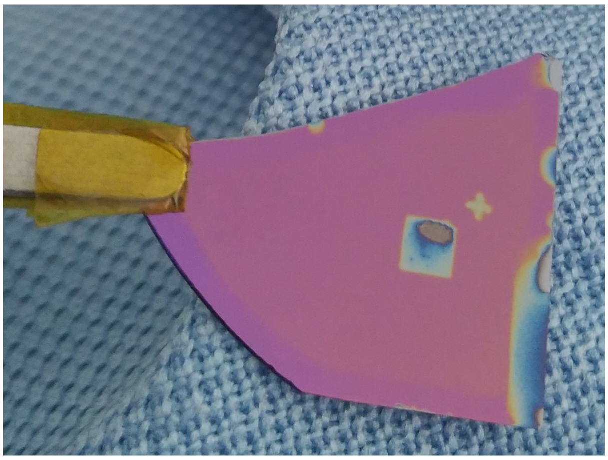


With that, these results where achieved.
(Test pattern, first etch, failed diffusion, second etch)



However, after some testing, I have found that the solvent etch is not actually needed (doesn't work, really). HF will seep through the bottom of the trenches (and the rest of the crystallized PMMA, for that matter, at a slower rate) and still etch.

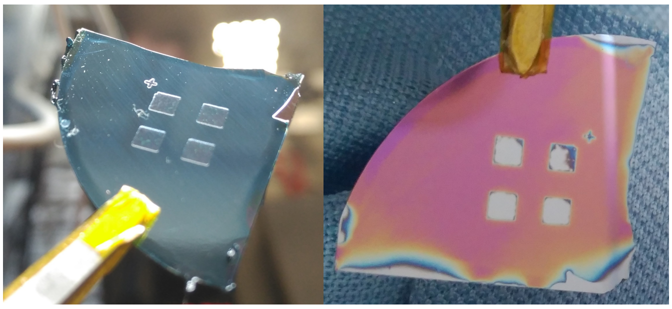
To the right you can see the latest test. The image is much more defined than before. Did not etch all the way through because I removed it from the HF bath too early. ^^U



2sq. Mm test and "+" fiducial.

Next test was performed with a 4 square file and left in a 2% HF bath for 45min.

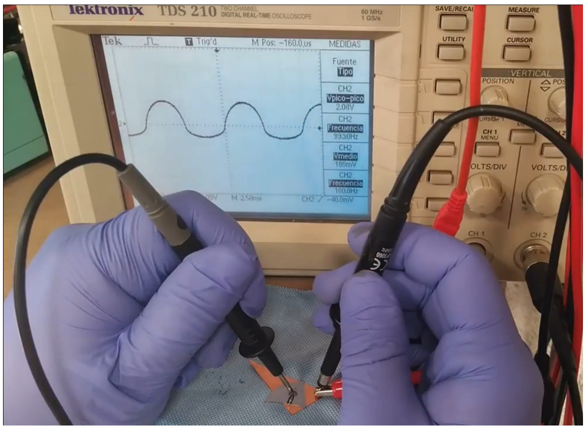
The whole surface etching is heavier than the previous test, but this time it did reach bare silicon. At this moment I am still playing with 300um thick oxide, a bit too thin, but good enough for some tests. The PMMA did had some issues, but I'm not sure if it dettached due to SiO_2 etch or just due to interaction with the HF, more tests will be made.



Diffusion.

First diode-ish behaviour:

(1h @ 900ºC with Boric acid) The heavi atenuation is because I'm crossing all the wafer to close the circuit and is a big resistance. Touching elsewhere also has a slight alteration in voltage because this silicon did not had a protective oxide layer on top, and boron diffused everywhere, starting from the point source.

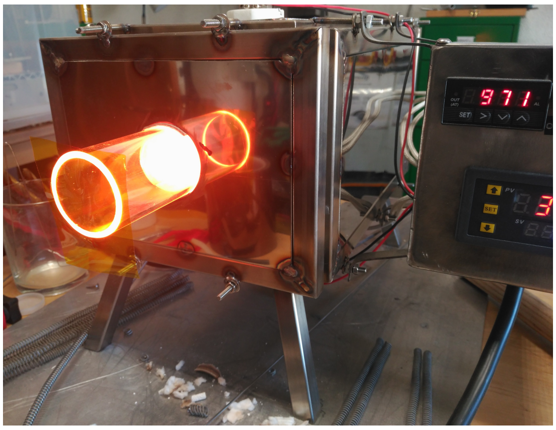


After some unsuccesful trials with Boric acid, I found this paper that explained a bit about the process/behaviour of the boric acid as dopant.

Basically you have to dehydrate the acid, then bake it under inert atmosphere above 300ºC (they used N_2, I used Ar) to transform the H_3BO_3 into $HBO_2+B_2O_3$, wich in turn will transform the $2B_2O_3$ into $4B + 3SiO_2$.

The Boron will diffuse into the silicon above 900ºC, but it will also form a borosilicate glass coating on top, because ~~*Boron is a bastard*~~ not all the boron will be absorbed.

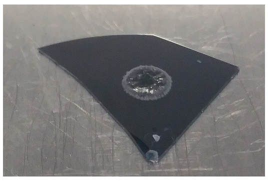
If you don't have the metal endcaps for the tube to hold the inert atmosphere in, Kapton tape will hold onto the ends of the fused Quartz tube at full blast, if the tube is long enough. Using Kapton proves two things:



1: the ends of the tube don't get that hot. (kapton would fall off)

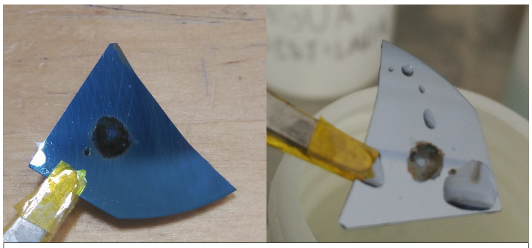
2: I'm a lazy bastard.

Jokes aside, flood the warm tube (400ºC) with Ar and close the ends. Some of it will escape, but since it is heavier than air, and the silicon shard rests at the bottom, it will have enough left for the process.



With that, I saturated 50ml of distilled water with boric acid powder (deionized water is a purer form, but did not have it at hand). They especifically say something about thin films...but I kinda ignored that, ^^U →

Two things happened. First, once the water started to evaporate, boric acid started to pop and crackle. But there was some left so I guessed I would try it anyways, as the oven was already at temp.


Before and after 2h HF bath the glass was still there XD.

Second thing: I used so much of it that the BSG (borosilicate glass) layer was impossible to remove with my current 2%HF solution.

It's my guess that the bluish oxidation in the surface came from the boron acid, as the bottom of the piece hadn't oxidized at all.

In the industrial processes, Boron can diffuse just by having a piece of it in the same furnace, so I would guess that putting some boron oxide on top on an unused part of the silicon would also diffuse into unprotected areas, altough at a much slower speed.

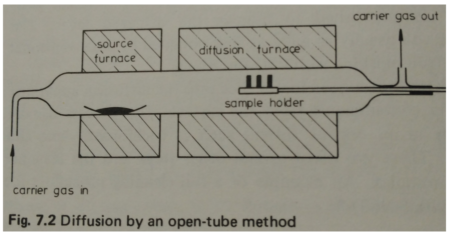


Fig. 7.2 Diffusion by an open-tube method

So, a new test was made to see how "passive diffusion" would work. Theory (p.178 Introduction to diffusion by B. Tuck) says it is a used process, at least with boron. By putting a disc of the material alongside the wafers and raising the temperature to 900/1000ºC, the boron will diffuse in them.

So, my guess is that putting boric acid on top of the silicon oxide, near the etched features, would still dope the silicon. I lost the references so I had to chase the two pink swquares for the diffusion area. It had a less sharp diode effect, but it did do something. This was left for 30 minutes @ 400ºC with Argon for the H_3BO_3 to switch to B_2O_3, then cooked for 2h @ 1000ºC

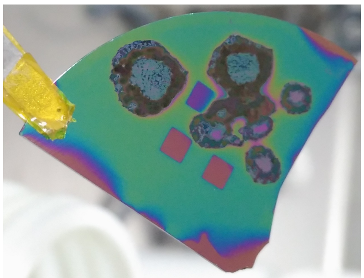


Image links to video. ^^

Sputter deposition.

As said before, to make interconnects and other things, we need to diposit metal over the silicon. The chosen material is Aluminum.
The why's are excellently explained in page 134 of "Introduction to microelectronic fabrication" by Richard C. Jaeger. So I'm going to just skip copypasting that bit, and let you do some work. Besides, you should already have that book if you are reading this (IMO).

To confirm that the machine works, both aluminium and copper have been sputtered succesfully. They are regarded as very difficult to do, so this should prove the point. Below you can see the aluminium and copper targets, and their results.

To hold down the targets I use high temperature double sided tape (until I weld attaching points in the end plate). For thin targets (copper) works well, as the heat transfer to the refrigerated endplate is excellent. The aluminium target is 1.6mm thick and doesn't perform so well (falls off, XD), but I'll get to that in time.

Starting procedure:

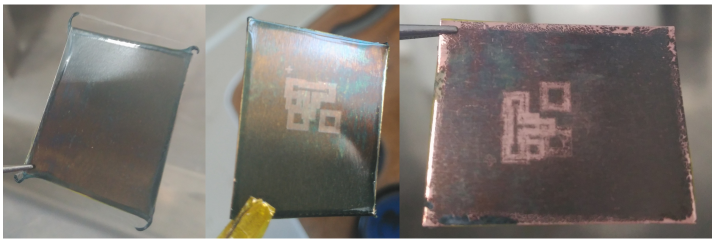
1. Clean everything. Dust goes everywhere, and it will fuck up your pump, if nothing else. I have dogs, I know what I'm talking about.
2. Check that the DC output roughly equals the AC input times√2.
   Use thick gloves, as you are dealing with mains and HV voltages.
3. Start the vacuum pump and let it do it's thing. Depending on the size of your chamber, between 10 and 20 minutes should be enough. This is not a very critical process.
4. If you have an HVAC valve, close it and allow some volume of Argon to the chamber. Open the valve again. You are "cleaning" as well as you can the chamber from oxygen and nitrogen (and other gases) from the residual atmosphere.
5. Slowly increase the voltage while allowing a small bit of Argon in. The plasma should light up, maybe arc a bit. Quickly close the gas valve and continue increasing the voltage to stabilize the plasma.
   Incrasing it too much will arc again and kill the plasma, and not increasing enough will extinguish it too. It's a tricky process but can be mastered.

Notes:

- If the plasma trap extinguishes, no amount of voltage (in relative terms) will restart it. The gas has been evacuated and there is not enough to begin again. Repeat the starting procedure. Control pump oil temp (If you can't touch the casing, it's too hot).
- Chamber values should be around 350V-0,3/0,5A (for mine, with 100mm between A-K). More than that will risk melting the target/endplate or damaging the magnets, if not actively refrigerated.
- The chamber walls will get coated too, at some point you will loose the sight of the objectives, keep that in mind. It can also arc easily if you allow too much deposition in the walls before cleaning.

Metal etching.

It works like SiO_2 etching: Apply resist, bake, pattern, etch, clean resist. To the right, a test in a copper sheet with some aluminium deposited on top (oxidized black).



It was part of the first copper shield of the glass feedthrough. XD

Al thickness was extremely small, hence the pitted look of the etch. Back was protected with kapton, and H_3PO_4 bath was 10 minutes.

Materials list:

1-5ml brown glass vials (NO PTFE)

5-100ml brown glass vial (NO PTFE)

5ml pipettes

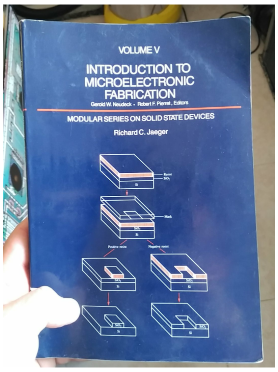
PTFE film, 0,25mm

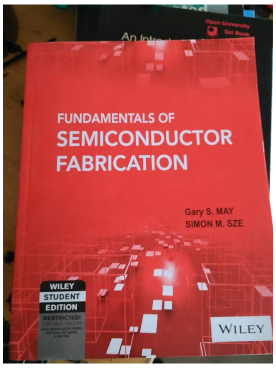
50ml HDPE bottle.

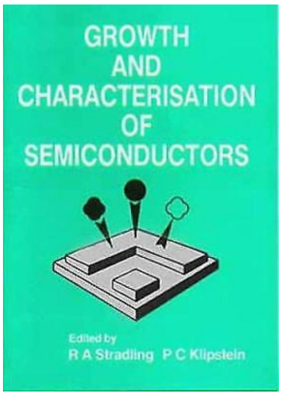
100-1000ul micropipette

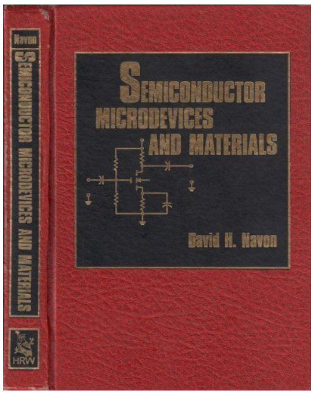
Bibliography.

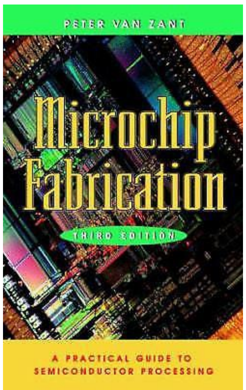
Books I have bought, mostly read or got info from. All where bought secondhand, mainly because some of the knowledge we seek, is hidden in many pre 1980 books, when the industry was new/growing, but everything wasn't as hiden as trade secret as it is now. I also just bought some because why not, it makes for a cool library.

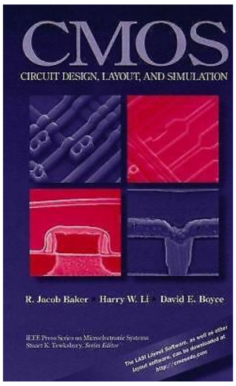


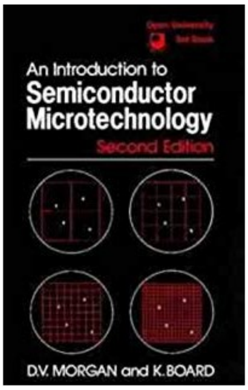


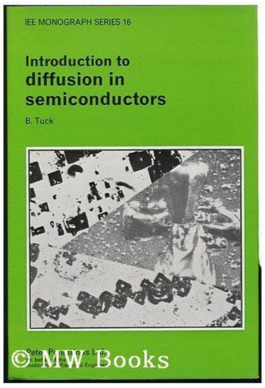












Interesting links:

Cooking with Jeri (obviously): https://www.youtube.com/watch?v=w_znRopGtbE

Indistinguishable from Magic: https://www.youtube.com/watch?v=NGFhc8R_uO4

Robert Baruch-CMOS reverse engineering: https://www.youtube.com/watch?v=FMdYuGpPicw