Whitepaper about the NF processes and chemicals

The NanoFrazor is a versatile tool which allows an unlimited flexibility in terms of processes (patterning, etching, chemicals). In this whitepaper some of the most important data and hints are listed to gain an overview and to find information for an easy access to the stuff going on around the NanoFrazor.

Contents

1 Processes which involve etching

A broad range of applications need very specific processes to optimally match their requirements. Detailed information about the processes can be found in the NanoFrazor manual.

1. High resolution etch (HRE) used to etch silicon, metals, ceramics: sub-20 nm resolution, freedom of design, elevated etching,
2. High resolution lift-off (HRLO) used for deposition of silicon, metals, ceramics: sub-20 nm resolution, freedom of design, elevated etching
3. Simple lift-off (SLO), especially used for deposition of metal contacts: quick process, wet development, design restricted,
4. 3D patterning in resist (3DP), e.g. used as a template for NIL (nanoimprint lithography): profiles up to 100 nm tall
5. 3D transfer (3DT) in silicon or metals: profiles up to 4 µm tall

2 Resists for patterning

2.1 Standard pattern

A standard pattern has a specific size. The unit of standard pattern can be used for sales and for the cost evaluation of cantilevers. The goal is to say how much polymer (PPA) is removed in a normal (average/standard) pattern. It is **1.25 µm³ per pattern**.

$$area * depth_{maximal} * ff_{lateral} * ff_{vertical}$$

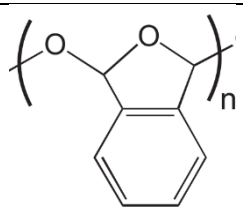
The area is 10x10 µm², the maximum depth is 50 nm, the fictional lateral fill-factor is 0.5, the vertical fill-factor 0.5 as well. This means half of the field is patterned at an average depth of 25 µm.

In conclusion: A normal tip lasts for a removal of about **25 µm³** (experience SBI). This means a tip can write 20 standard patterns.

2.2 Types of most common resists

The most common resist for thermal Scanning Probe Lithography (tSPL) is polyphthalaldehyde (PPA). The best performance (10.7.2017) is obtained with the commercially available linear PPA (anionic) from Sigma-Aldrich. Compared to former PPAs (IBM B34, IDM TN 65/67, JR TSM 5) It contaminates fewest of all, spins very cleanly and has slightly better etch properties.

There are few other resists like molecular glass or modifications of the PPA (eg. Enriched with silicon, cyclic PPA = cationic) which were exploratory but did not show reasonable results.

- PPA-SAl (Sigma-Aldrich linear, 900029) 2016, anionic, commercially available, best performance so far (10.7.2017) - PPA-TMS (JR-MOG-002), cationic, silicon rich for better etch stability (2x in O_2 RIE than TN65/67), but difficult to achieve resolutions better than 20 nm hp. - Molecular glass (Bayreuth), strong contamination and reflow of resist	 *Figure 1: PPA chain*

2.3 Preparation of resist solution

All types of PPA come in solid powder form. It has to be dissolved to make the required concentration in solution. Few general guidelines for a proper solution:

- Solution has to be shaken well, at least one hour.
- After filtering (≤ 0.2 µm) or shaking the solution should stand still for one hour or more. This allows the air bubbles to rise to the surface.
- **Linear PPA** (Sigma-Aldrich) **solutions** should **not be used after 2 months**. The mechanism is that the polymer decomposes and the thicknesses of the solutions decrease. Also the etch resistivity might be reduced. (make only small amounts of solution, not to waste too much)

- Spin **coated layers of linear PPA** (Sigma-Aldrich) should be patterned and processed **within one week**. Otherwise the contamination rate increases and patterning quality is reduced.
- Cyclic polymers (cationic) are generally more stable than linear (anionic) ones.
- Anisole has proved to be the solvent where the PPAs are stable for the longest time.

3 Supporting Resists

For the processes above, a series of different resists can be used.

- PMMA 950k (e.g. Allresist AR-P 672.02), poly(methyl methacrylate): used for the HRE, HRLO, 3DP, 3DT
- HM8006 (JSR): used for the HRE (no longer available)
- PMGI SFG-2S (Microchem), polymethylglutarimide: used for the SLO, stable up to 300°C
- Omnicoat/LOR (Microchem): variations of PMGI, can be used for the SLO
- SOG (spin-on-glass, Honeywell A-314, solvent: 2-Methoxy-1-Methylethuylacetat (MMEA)): tested for HRE and HRLO to replace the SiOx, but SOG is very sticky and contaminates the tip strongly (even with a 2 nm PMMA underlayer)
- x-PS (Azembly EXP NLD-128, Merck Performance Materials), crosslinked polystyrene: used as a brush (stopping layer) for SIS or block co-polymer

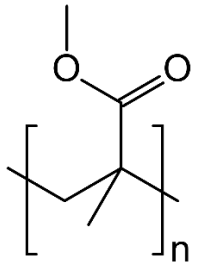
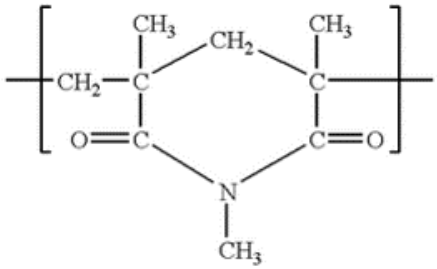
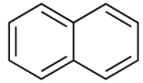
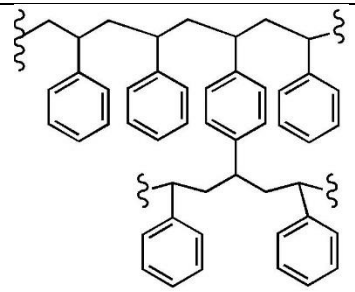
PMMA:	**PMGI:** Tg: 180-190°C	**HM8006:**	**x-PS**
		Not published, but known that it is an aromatic copolymer which contains naphthalene.  Naphthalene	

Table 1: structure of some of the supporting resists

4 Solvents for PPA and other resist

Solvents are used to make a solution out of the PPA powders. Other solvents are used to dilute existing resist solutions to adjust concentration, which eventually determines the layer thickness. Solvents might also have an effect on the wetting effect on existing patterns or blank surfaces

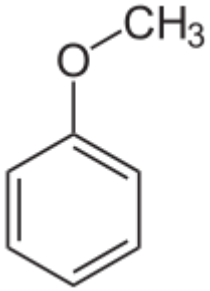
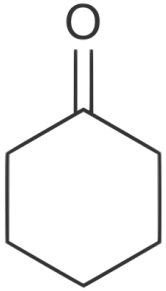
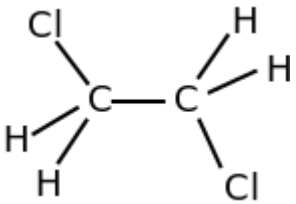
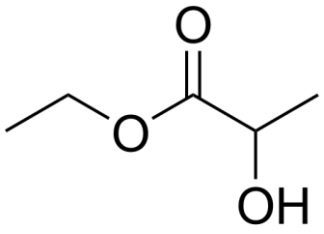
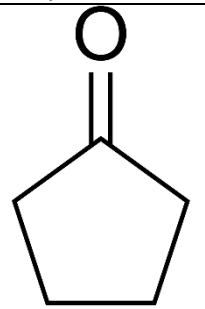
Anisole:	**Cyclohexanone:**	**Dichloroethane:**	**Ethyllactate:**	**G-Thinner (Cyclopentanone, PMGE*):**
$CH_3OC_6H_5$, 0.995 g/mL bp: 154 °C	$C_6H_{10}O$, 0.9478 g/mL bp: 155.6 °C	$C_2H_4Cl_2$, 1.253 g/mL bp: 84°C	$C_5H_{10}O_3$, 1.03 g/mL bp: 151-155°C	Mixture, C_5H_8O, 0.95 g/mL bp: 130.6°C
				
All PPA (stable > 1 month), PMMA (AR-P 672.02)	All PPA (stable < 1 month)	All PPA (allows better coverage over structures)	HM8006	PMGI SFG

*Table 2: Solvents and what they are used for. *Note that the G-Thinner contains small amounts of PMGE (1-methoxy-2-propanol) which is necessary not to precipitate the PMGI solutions. G-Thinner is used for all PMGI SFG, LOR and Omnicoat. There is a T-thinner on offer which is also cyclopentanone with some THFA (tetrahydrofurfuryl alcohol) which is used for PMGI SF products.*

5 Resist deposition, spinning

Spinning is best done at speeds of 2000-6000 rpm. Lower speeds are prone to leave very pronounced edge beads (especially for small rectangular samples, < 1 cm^2). Higher speeds may lead to comets. A lid is not used. The resulting thicknesses are estimations and they might vary depending on the solution, the preparation and the spinner.

- PPA is baked at 90°C (194°F) for 3 min
- Thicker layers should be patterned within one week after spin coating.
- PMMA layers are stable when anisole is spun on them (even 3 nm layers).
- (x-PS conditions: 4000 rpm, 250°C, 5 min results in 4.5 nm, does not wet on SiOx)
- Pretreatment is a gentle oxygen plasma (if allowed on sample). Use HMDS for PMGI for SLO.

- Underlayer for HR: The stack of HM/PMMA, SiOx and PPA can be improved if a small layer of 3 nm PMMA is added. This layer is spun on top of the SiOx and acts as an isolation and soft stop layer under the PPA. It prevents the tip from intensive wear and acts as a heat barrier allowing higher temperatures and higher resolution.

	[rpm]	0.5 %	0.85 %	1.3 %	2 %	3 %	5 %
PPA in anisole on silicon, of linear type (e.g. **SAL PPA)** 90°C, 3 min	**2000**		11		30		95
	3000	8					78
	4000						70
	5000						
	6000		6		20		60

Table 3: Thickness; Aniodic PPA has a smaller viscosity, therefor it produces thinner layers than the cationic ones

	[rpm]	1:19 (v-%)	1:9 (v-%)	1:1 (v-%)	2:1 (v-%)	Pure
PMMA on silicon (e.g. AR-P 672.02) (2w%PMMA solution 672.02 : Anisol) 180°C, 90 sec	**2000**	2.0	4.5			80
	3000			20	33	67
	4000		3.5			60
	5000				28	55

Table 4: Thickness; PMMA is used for HRE/HRLO with 1:19 dilution, for 3DP/3DT the 1:9 solution and for HRLO with thicknesses of 20 up to 300 nm

	[rpm]	1:3 (v-%)	1:2 (v-%)	1:1 (v-%)	Pure
PMGI SFG-2S on silicon (PMGI:G-Thinner), 200°C, 60 sec	**3000**	10	15	20	50

Table 5: Thickness; PMGI is used for the SLO, several layers can be added to make thicker layer of > 50 nm

	[rpm]	1:2 (v-%)	1:1 (v-%)	2:1 (v-%)	Pure
HM8006 on silicon (HM:EL) 225°C, 90 sec	**4000**	20	30	40	50

Table 6: Thickness; HM8006 is used for HRE, the thickness depends on the resolution and the etch conditions

6 Silicon oxide (SiOx)

Silicon oxide is used for the HRE/HRLO, where it serves as a mask to etch the polymer hardmask. Usually 2.5 - 4 nm are evaporated in a Pfeiffer PLS500. An alternative is to sputter the SiOx, where usually layers of 4 nm and more are achieved. Also some tests with atomic layer deposited AlOx to replace the SiOx were made, with the difficulty of less selectivity to PPA.

7 Etch tools, rates and processes

Several tools are used by NanoFrazor users. This chapter serves as an overview and as a guideline to develop own processes. Every lab and every tool have different conditions; therefore, these recipes and statements can be used only as a starting point.

- Support wafer covered with AZ6612 photoresist does not affect the etch properties at very short etch times (< 10 sec, RIE).
- General in RIE, lower power means higher selectivity (i.e. more chemical, less physical etching). Usually at the cost of lower anisotropy.

7.1 RIE (Plasmalab 80plus, Oxford Instruments): thin PPA/PMMA layers, thin ceramic, standard polymer etch

The etching of 10 nm polymer layers is very delicate. The ignition of the plasma has a strong etch impact, especially since the etching times are short, typically around 5-20 seconds. Therefore, it doesn't make sense to discuss the etching rates. Also, the etch stabilities of different PPAs are not that important, since the etch times are so small.

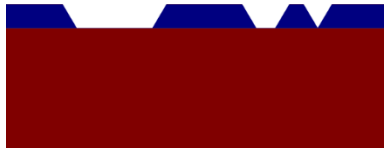
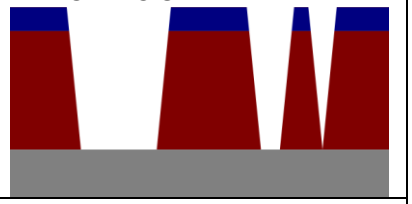
	HR pattern etch	**SiOx etch**	**HM/PMMA etch**	**Silicon etch**
Parameters	- 4/16 sccm O_2/N_2 - 10 W - 15 mTorr, Strike 60 mTorr - Bias 60 V	- 20 sccm CHF_3 - 100 W - 15 mTorr, Strike 60 mTorr - Bias 330 V	- 20 sccm O_2 - 20 W - 15 mTorr, Strike 60 mTorr - Bias 110 V	- 50/15 sccm CHF_3/SF_6 - 200 W - 15 mTorr, Strike 60 mTorr - Bias 500 V
Target	Etch residuals of PPA and PMMA/PMGI underlayer	Open SiOx mask	Structure HM/PMMA for HRE or HRLO	Etch of silicon
Typical stack	- 2 nm PMMA/PMGI - 6-10 nm PPA - **Pattern depth 5-9 nm** - Residual 1-2 nm PPA + - 	- 2.5 nm SiOx (evaporated) - 2 nm PMMA/PMGI (patterned) - 2-6 nm PPA (patterned) - 	- 10 – 50 nm HM *or* - 10 – 300 nm PMMA - 2.5 nm SiOx (up to 5 nm) - 	- Silicon - 20 nm HM - 2.5 nm SiOx 
Etch procedure	**5 seconds**, excluding ignition, etches about 4 nm of PPA and removes all the residuals	**12 seconds**, excluding ignition, etches about 5 nm of SiOx, leaves about 3-7 nm of polymer	Adjust etch time according to thickness	10 seconds, excluding ignition (M. Cooke, Oxford inst.)
Comments	Ignition dominates, 2-10 seconds lead to the same results ➔ robust etch.	CHF3 etch is known to produce pinholes. Also small white spots appear (redeposition)	SiOx is very stable, 3 nm last for about 7 min before the polymers are etched. After etch a HRLO can be made.	
Speed (Rates)	PMGI:PMMA:PPA ➔ **1 : 1.5 : 3** A test of 60 s etch: - 6 nm PMGI - 9 nm PMMA - 20 nm PPA	Rough estimates: - 15 nm/min SiOx - 5 nm/min PPA - 3 nm/min PMMA/PMGI	Rates: - 35 nm/min PMMA - 20 nm/min HM	Etched in 10 seconds: - 7 nm HM - 10 nm Si

Table 7: different recipes on the RIE

7.2 3D transfer with DRIE: amplification of 3D patterns from PPA into silicon or SiOx (or any other material)

Transfer of 3D pattern is in principle easy. But to get a good control over the height, amplifications and roughnesses is challenging. Rates are depending on the tool (history, conditions) and on the sample and pattern itself (fill factor, aspect ratios). Therefor it might be required to calibrate the tool every time before it is used. Nevertheless, the following data should help as a starting point. Ignition is an issue (about 10 sec) for the very short etch times used. This means etch times are more important than etch rates.

- The approach for 3D Transfers follows this order:
  - What z-dimensions of the structure are targeted in silicon (or SiOx)?
  - How big is the amplification factor? It depends on the tool, conditions, etch time and the pattern itself. To find it might require an iterative approach. Etch time of about 30-50 seconds allow
  - This defines the z-dimension of the pattern in the resist.
  - Add the recess (preferably big, e.g. 20-30 nm) and the residual (preferably small) to the z-dimension to get the desired layer thickness.
  - Find the correct etch time which allows to stop in the recess layer
  - Transfer the pattern
  - Remove the rest of the recess layer with solvents or oxygen plasma
- General etch behavior
  - SF6 increases the isotropy
  - Support wafer influences the etch rates on small samples. Support same material as mask ➔ higher amplification, support same as substrate ➔ lower amplification
- The optimal stack should look as the follow:

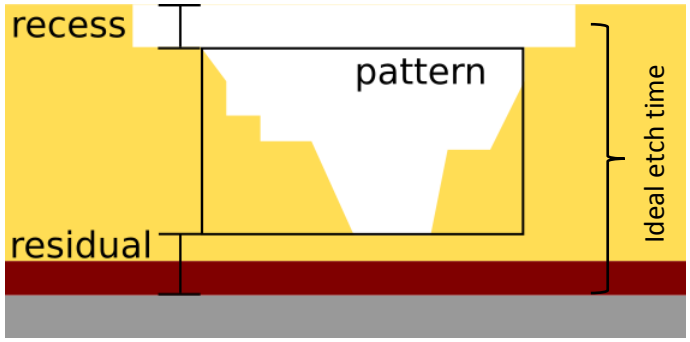


Table 8: 3D pattern schematic

- Thin PMMA layer (~3 nm) for thermal isolation and wear protection ➔ generally better pattern
- For good linear transfer the full pattern should be recessed into the thick layer of PPA, and a residual PPA layer of about 5 nm should be left
- Optimal pattern quality regarding resolution can be achieved with a PPA of ~100 nm thick and a pattern depth of about 65 nm, recess 25
- The residual layers are etched during the undefined ignition time. After few seconds the process stabilizes and the pattern can be transferred linearly into silicon or SiOx.
- The etch should stop in the recess layer. In this way the pattern is fully transferred, but still the PPA of the recess area protects the sample around the pattern.

	PPA into silicon	**PPA into SiOx or TaOx**	**SiOx into silicon**	**PPA into silicon**
Target	Transfer 3D pattern smoothly, linear and anisotropic in silicon	Transfer in oxide	Achieve higher amplification from SiOx into silicon	Use of another tool for the transfer
Tool	AMS200 Alcatel (@ BRNC, IBM)	AMS200 Alcatel (@ BRNC, IBM)	AMS200 Alcatel (@ CMI,EPFL)	SPTS APS (@ CMI,EPFL)
Parameters	- 40/60 sccm SF6/C4F8 - 1500/15 W Source/Chuck - $1.5e^{-2}$ mbar	- 40/60 sccm SF6/C4F8 - 1500/15 W Source/Chuck - $1.5e^{-2}$ mbar	- 40/55 sccm SF_6/C_4F_8 - 1500/30 W Source/Chuck - 3 mTorr - Substrate 20°C	- 10/30/175 sccm C_4F_8/H_2/He - 1200/300 W Source/Chuck - 4 mTorr - Substrate 10°C
Typical stack	- 3 nm of PMMA - 65 nm of PPA - **Pattern depth 50-60 nm**	- 3 nm of PMMA - 65 nm of PPA - **Pattern depth 50-60 nm**	- SiOx	- PPA - Silicon
Etch procedure	30 seconds	30 seconds		
Comments	Selectivity changes with etch time, pattern design and tool condition		Support wafer is important - SiOx (like mask) - Si (like substrate)	
Selectivities: $(\frac{substrate}{mask})$	4 – 10	- 0.7 SiOx (40/60 sccm) - 0.85 SiOx (30/70 sccm) - 0.5 TaOx	- 40, using SiOx substrate - 20, using Si substrate	
Speed (rough estimates)	Etch of 50 sec: - 100 nm PPA - 400 nm Si		35 nm/min for SiOx	

Table 9: different recipes for the 3D transfer

General notes:
- Higher SF_6 concentration results in a better selectivity to PPA for Si
- Lower SF_6 concentration results in a better selectivity to PPA for SiOx
- Oxydation and HF can be used to clean/polish the samples after etching
- Hydrogen in F/C etchants reduces fluorine conc. By forming HF. Lower F/C ratio, reduced rate of Si and SiOx
- Oxygen in F/C etchants increases fluorine concentration by forming CO/CO2, reduces oxide etch rate and prevents C_xF_y forming

7.3 IBE (ion beam etching, Ionfab 300, Oxford Instruments): thin metals, thin ceramics

IBE is especially used if there is no suitable dry etch gas available, which is often the case for noble metals (Au, Ag, Pt). The disadvantage is the non-selective etch properties. Although generally, the metals etch a bit faster, than the polymers (PMMA, PMGI, HM8006). PPA on the other hand has a very low stability.

	Gold etch	**Si etch**
Parameters	- Beam: 250 mA, 600 V, 390 V accl., 10 sccm Ar - Neutralizer: 550 mA, 5 sccm Ar - Platen: 5°C - RF Power: 1000 W - Tilt: 6°	- Beam 300 mA, 600V, 390 V accl., 10 sccm Ar - Neuralizer: 550 mA, 5 sccm Ar - Platen: 5°C - RF Power 1000 W - Tilt: 7°
Typical stack	- 20 – 50 nm HM8006 - 2.5 nm SiOx (patterned by HRE)	
Stripping	Oxygen Barrel Asher / Piranha	Oxygen Barrel Asher / Piranha
Rates	- 1 nm/sec gold - 1-3 nm/sec HM	- 9 nm/min Si

Table 10: IBE recipe

7.4 ICP, inductively coupled plasma, (100, Oxford Instruments)

Tests on an ICP where conducted to etch the PPA and the PMMA.

	PPA/PMMA etch	**Si etch**
Parameters	- 45/5 sccm H2/Ar, 20 mbar - ICP 400 W - RF 20 W, Bias 120 V	- 30 sccm HBr, 5 mbar - ICP 200 W - RF 20 W,
Typical stack	- 2 nm PMMA/PMGI - 6-10 nm PPA - **Pattern depth 5-9 nm** - Residual 1-2 nm PPA +	
Rates	- 42 nm/min PPA - 9 nm/min PMMA	- 5.6 nm/30 sec Si - < 1 nm/30 sec HM

Table 11: ICP recipe

7.5 SIS – Sequential Infiltration Synthesis (Al2O3 infiltration)

The SIS is a method to infiltrate AlOx into a patterned PPA film. The goal is to harden the PPA for better etch selectivities. First results show that the infiltrated PPA (type IDM TN76) etches about 4x slower in the RIE using the "HR pattern etch" (also 4x slower in H_2/N_2 plasma @ IMEC). The x-PS could not be etched with the same recipe. Further experiments must be conducted.

Tool	Picosun R-series
Recipe	- Alteration of TMA (Trimethylaluminium) and H_20 - 6 cycles - 80°C
Effects	- PPA might swell (IMEC observation) - PPA might also shrink or be etched (IBM observation)

Table 12: SIS data

7.6 Various materials (Mos2, Graphene, …)

	Graphene	**MoS_2**
Tool	RIE Plasmalab, Oxford Instruments	RIE Plasmalab, Oxford Instruments
Parameters	- 20 sccm O_2 - 20 W - 15 mTorr, Strike 60 mTorr - Bias 110 V - Time 20-60 sec/Layer	- 20 sccm O_2 - 20 W - 15 mTorr, Strike 60 mTorr - Bias 110V
Typical stack	- 20 – 50 nm PPA - 2.5 nm SiOx (patterned by HR etch)	- 20 – 50 nm PPA - 2.5 nm SiOx (patterned by HR etch)
Stripping	- short dip in HF - rinsing in Aceton/IPA - heating in N_2/Ar atmosphere recommended to fully remove PPA (˜500°C)	- MoS_2 forms MoOx which is soluble in water (short dip), rinsing in IPA - short CHF_3 etch - stripping in Aceton/IPA - heating in N_2/Ar atmosphere recommended to fully remove PPA (˜500°C)

Table 13: Etch of various materials

7.7 Various tools

	Barrel asher using oxygen	**Barrel asher using hydrogen**	**Ozone and UV**	**RIE BRNC**
Tool	PVA-TEPLA Gigabatch	Tepla	Samco UV-2 Stripper/Cleaner	Plasma NPG80, Oxford Inst.
Target	- Clean substrate from any organic residuals - Improve adhesion of PPA to substrate	Remove residual, etch PPA and PMMA underlayer	Etch PPA, PMMA, PMGI	Etch PPA/PMMA
Parameters	200 W, 500 sccm O_2, 0.8 mbar, 1 min	- 5% H2, 95% Ar - 100 W - 1 mbar	- 60°C - Support wafer with AZ1505 resist	- 4/36 sccm O2/N2 - 80 mTorr, 10°C - 15 W, 75 V Bias
Rate	About 1 nm/sec for PPA/PMMA	- 4 nm in 6 sec PPA - PMMA similar	- PPA etches about 0.5 nm/min in ozone - PPA in Ozone and UV about 1 nm/min - PMGI/PMMA < 0.1 nm/min	12 nm for 15 sec
Comments	For harsh removal of any organics: 600 W, 500 sccm O_2, 0.8 mbar, 1-10 min		Rough surfaces	Too harsh for the very thin layers

Table 14: Various tools

7.8 Wet development

For the simple lift-off a short dry etch in combination with the wet development allows a resist profile for subsequent evaporation. After patterning, a short barrel ash of the PPA residuals should be performed (see barrel asher, but 5 sec of the gentle recipe are enough {200 W, 400 sccm}). The wet developer is a mixture of TMAH (Tetramethylammonium hydroxide), e.g. diluted AZ326 MIF (e.g. Microchemicals DE) or AR300-47 (Microresist). These developers dissolve the PMGI, but don't etch the PPA.

Developer: AZ326 MIF has **2.38%** of TMAH in H20, which is 0.265 mol/L
AR300-47 has **0.2 mol/L** TMAH in H20, which is 1.80%
AZ300 MIF has **0.261 mol/L** TMAH in H2O, which is 2.35%

Dilution: Use 10 mL of the AZ326 MIF and 5.6 mL H20 to get a 0.17 mol/L dilution.
Use 17 mL of the AR300-47 and 3 mL H2O to get a 0.17 mol/L dilution
Use 17 mL of the AZ300 MIF and 9 mL H2O to get a 0.17 mol/L dilution

Rate: 0.17 mol/L develops with about 1 nm/sec
0.15 mol/L develops with about 0.3 nm/sec

Comments: more diluted solutions (0.1, 0.12 mol/L) did not develop, rate < 1 nm/min

Adhesion: PMGI itself is an adhesion promoter. But for this specific wet development it is suggested to use HMDS. It prevents the delamination of the PMGI/PPA stack.

15.3.2017, spi

Rinsing: dip sample in pure water for few seconds, then IPA and dry it with nitrogen

Others: KOH (1:4) (AZ400) etches also the PPA about 100 nm/min, cannot be used for a lift-off

8 Wet etchants

Piranha solution: Cleaning of any organic residuals, might etch metals. Solution is: concentrated H_2SO_4 three parts and one part peroxide H_2O_2 (30%). Attention, solution gets very hot

BHF/HF: Hydrogen fluoride, buffered or pure. Very dangerous! Use only by trained users! Removes silicon oxides and nitrides. Resists are generally more stable in BHF than in pure HF

9 Dry etchants, some notes

CO Carbon monoxide is used today in many dielectric etch recipes because CO provides higher selectivity and greater profile control than fluorocarbon and oxygen-based etch processes. (Ricci (PALL Microelec.) Preventing Contamination in Dielectric Plasma Etch Processes, https://microelectronics.pall.com/content/dam/pall/microelectronics/literature-library/non-gated/ABG-101-1104.pdf)

NH3 Ammonia could be used for etching Copper (?)