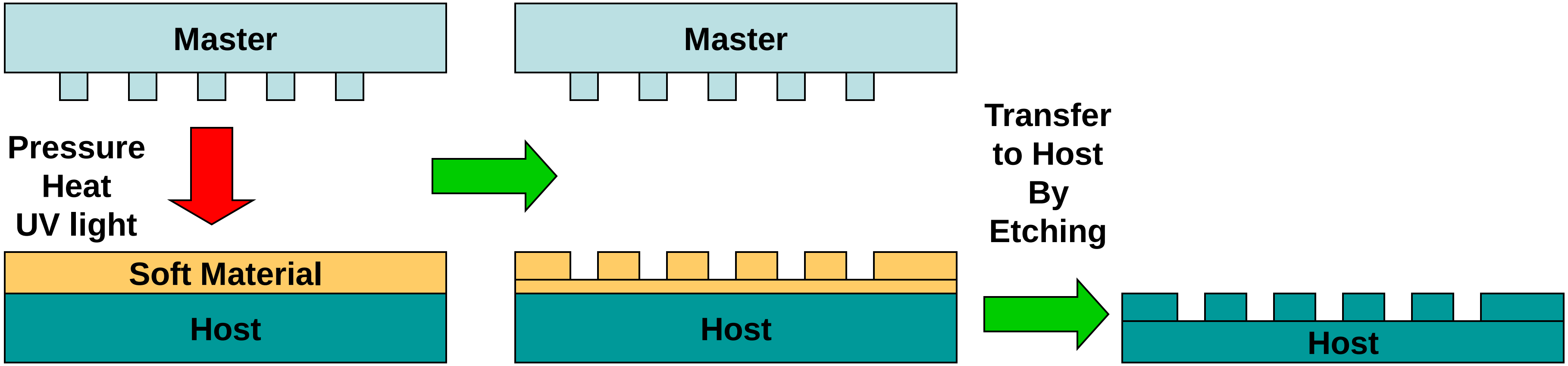
Thermal Nanoimprinting Basics

Nanoimprinting is a way to replicate nanoscale features on one surface into another, like stamping

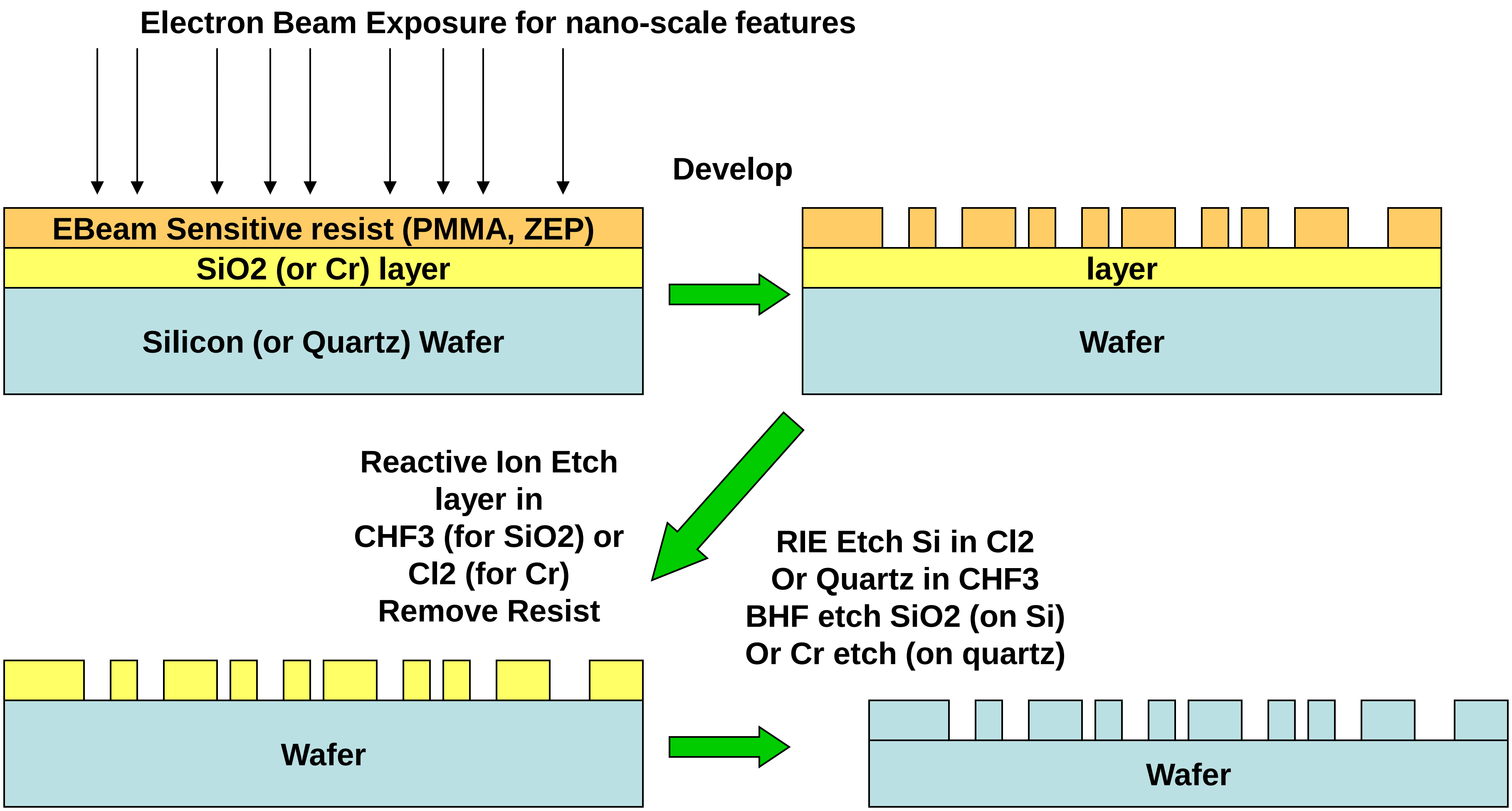
Master copies are made by traditional fabrication techniques (optical/ebeam lith) and can be re-used many times.

For Nanoscale features, traditional techniques can be expensive and time consuming.

Nanoimoprinting allows us to replicate these features over and over again, reducing overall cost for the researcher. Only one expensive master copy needs to be made.



Making a Master with Nanoscale Features



With our JEOL E-beam writer, we can make features as small as 10 nm.
This basically mimics current photomask production techniques

Non-Stick Coating

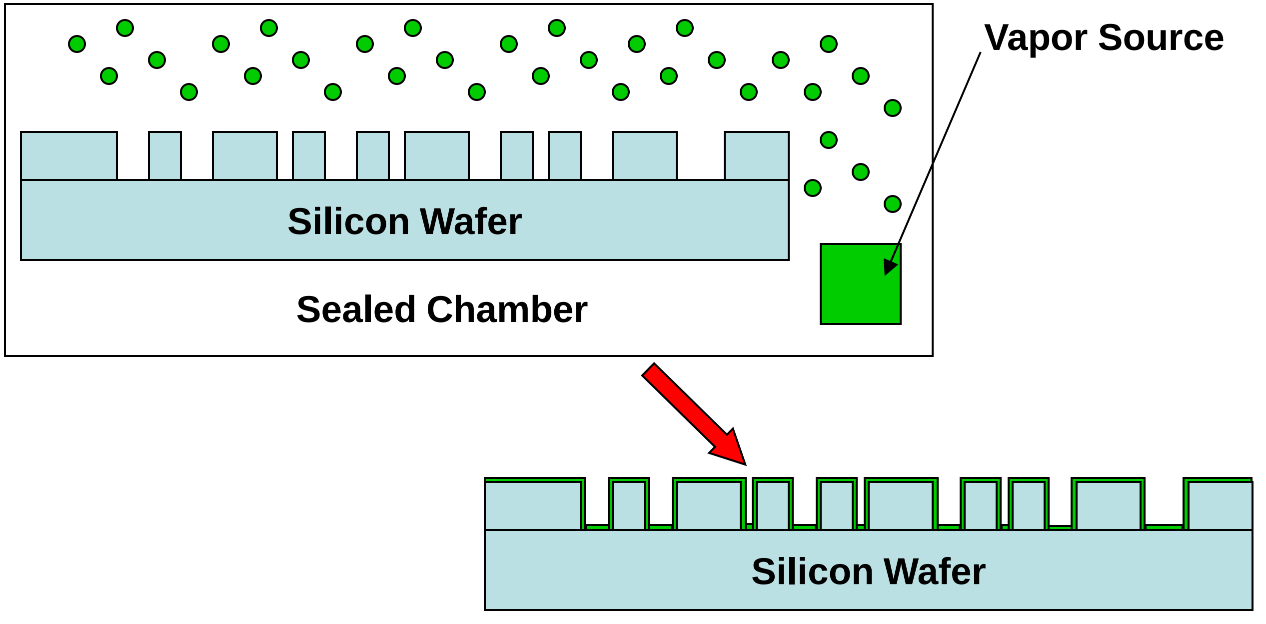
After master formation, the master is often prepared with a non-stick layer to facilitate master removal from the polymer after imprinting.

The non-stick layer is a self-assembled monolayer of fluorocarbon monomers.

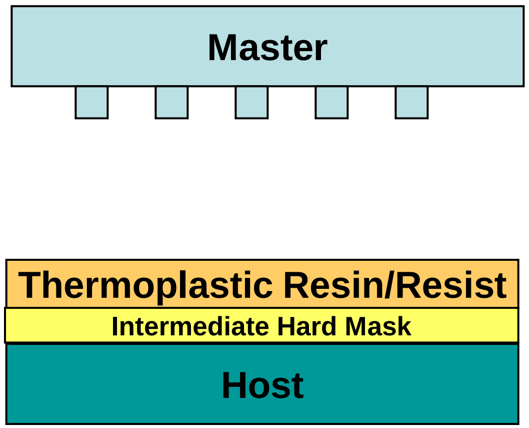
The particular fluorocarbon we use is perfluorodecylytrichlorosilane (FDTS).

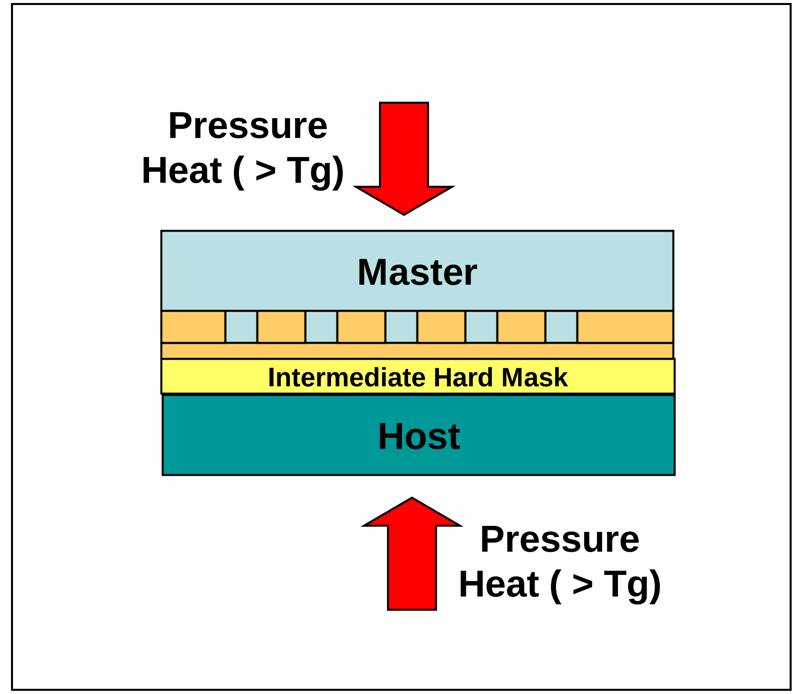
We use vapor coating in a clean-dry environment process as follows:

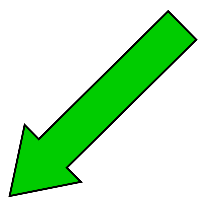
1. **Use Technics PEII etcher for 2 minutes at 300mT/100W first to "activate" the silicon surface for reaction with the FDTS.**
2. **Use Standard FDTS program on the MVD tool for this.**
3. **Hot plate bake at ~100C for 2 minutes following deposition.**
4. **H2O Contact Angle ~ 110 Degrees.**

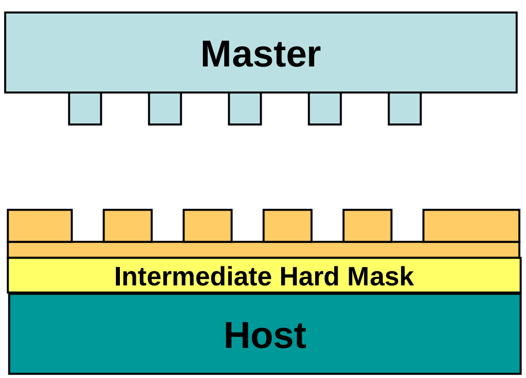


Process Flows (Thermal Imprinting)









Master should be smaller or of same size as substrate

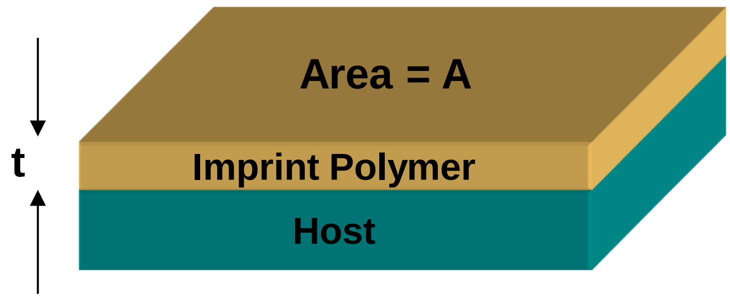
Remove from Chamber And Separate.

Use razor blade at edge.

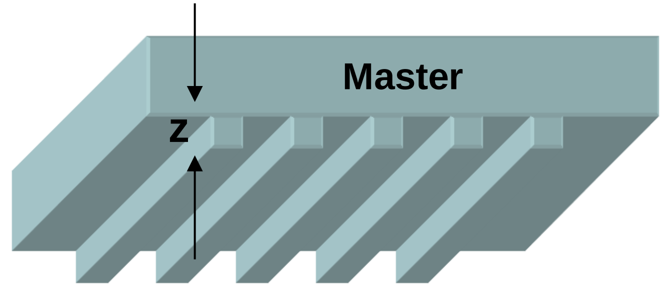
This is a polymer flow or displacement problem
Residual Layer Left: Cannot “squeeze” out everything

Case 1: Uniformly Distributed Patterns on Master

How much polymer do I need to deposit and how much residual layer is left?
This is a volume conservation problem (1st Order)



Volume of Polymer $V_{poly} = t \times A$



Surface Area Etched = F x A (F = Fill factor)

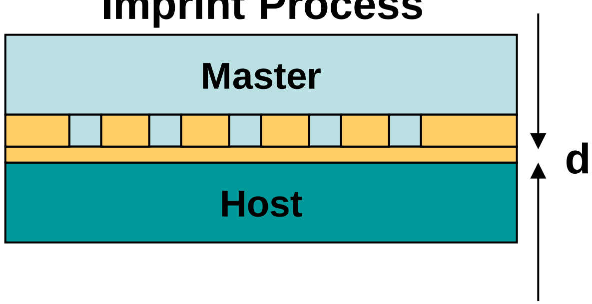
Volume Etched $V_{etched} = z \times F \times A$

$$(d \times A) + V_{etched} = V_{poly}$$
$$d = t - F \times z$$
$$t = d + F \times z$$

Choose polymer thickness so that $20\text{nm} < d < z/4$

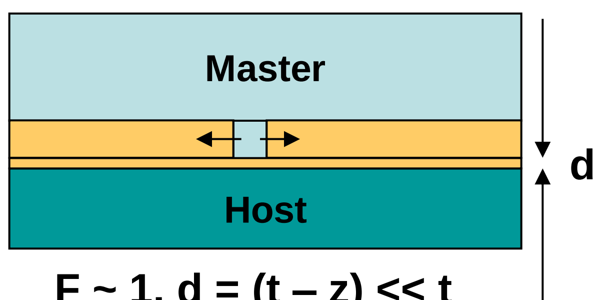
$$(20\text{nm} + F \times z) < t < (z \times (F + 0.25))$$

Imprint Process

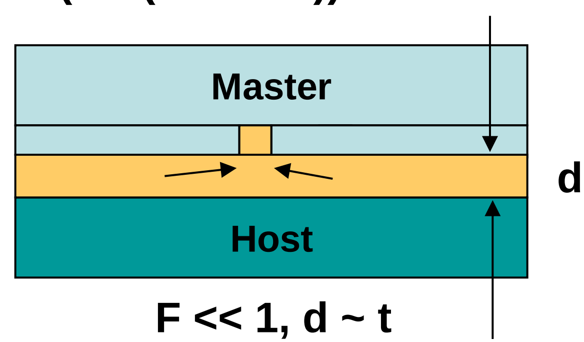


After imprint, residual layer of thickness d is left

In general, having d< 20nm is not recommended

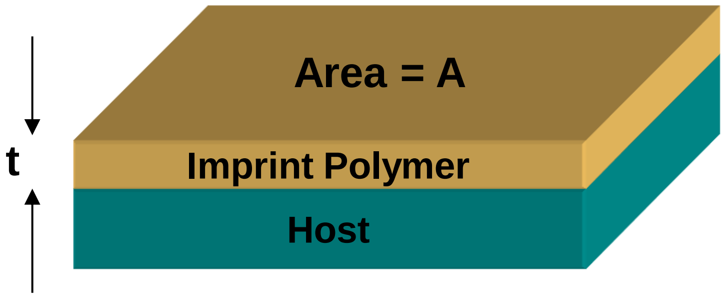


$F \sim 1$, $d = (t - z) << t$
Pushing away polymer

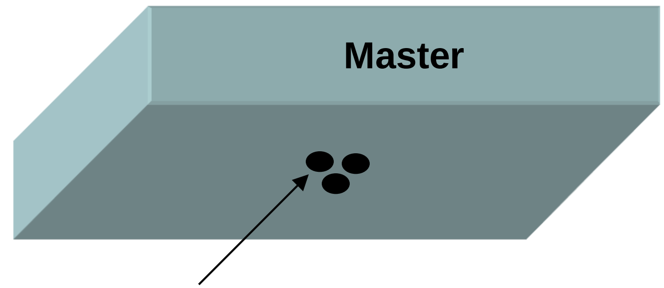


$F << 1$, $d \sim t$
Polymer fills in hole

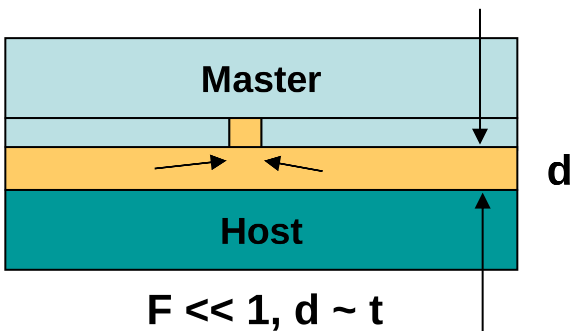
Case 2: Non-Uniformly Distributed Patterns on Master: Etched Master Area << Imprint Area



Volume of Polymer V_{poly} = t x A



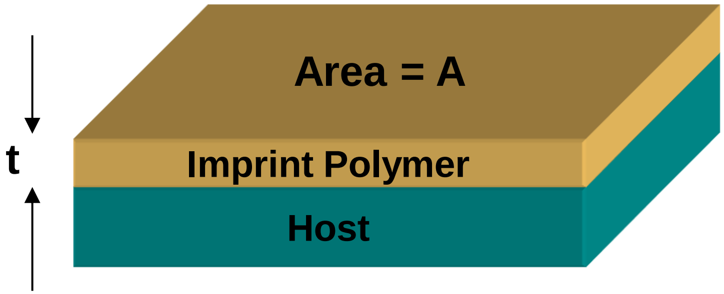
Etched Structures, Fill Volume Small
Etched Depth = z



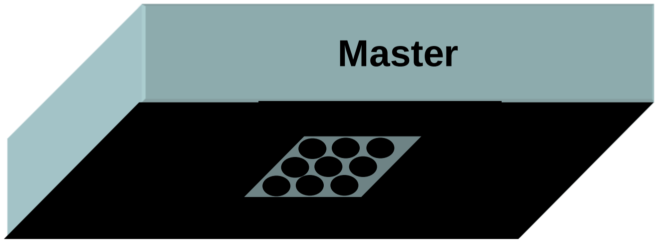
F << 1, d ~ t
Polymer fills in Etched structures

d ~ t, independent of Z
Choose polymer thickness 20nm < t < z/4

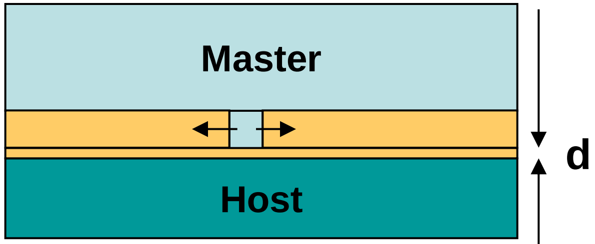
Case 3: Non-Uniformly Distributed Patterns on Master: Etched Master Area ~ Imprint Area



Volume of Polymer V_{poly} = t x A



Etched Area(Black), Fill Volume Large
Etched Depth = z



F ~ 1, d = (t – z) << t
Pushing away polymer

20nm < d ~ t – z
Choose polymer thickness for 20nm < d ~ z/4
t ~ 1.25 x z

Case 4: Mixed Cases

For mixed cases of features, the total volume argument only holds if the polymer is given enough time to flow long distances. This is the most difficult case since Cases 2 and 3 result in very different residual thicknesses. Very low viscosity is required to equilibrate the thickness over large areas. It is better to avoid this condition if possible. UV-cured resists are more suited to the extremely mixed cases. See Scheer, et. al. Microelectronic Engineering 56 (2001) 311–332, 2001 for a thorough description of this

Process Flows (Thermal Imprinting)

What material and process parameters affect flow ?

WLF Equation: $\log(t/t_o) = \log(\eta/\eta_o) = -C1(T-T_g)/(C2 + T-T_g)$, T_g = glass transition temp

Time response depends on viscosity, glass transition temp.

At $T-T_g$, viscosity ~ 1e12 Pa s for all polymers
At $T = 100\text{ K} + T_g$, decrease by factor of 1e11 !!

What about actual rate of filling.

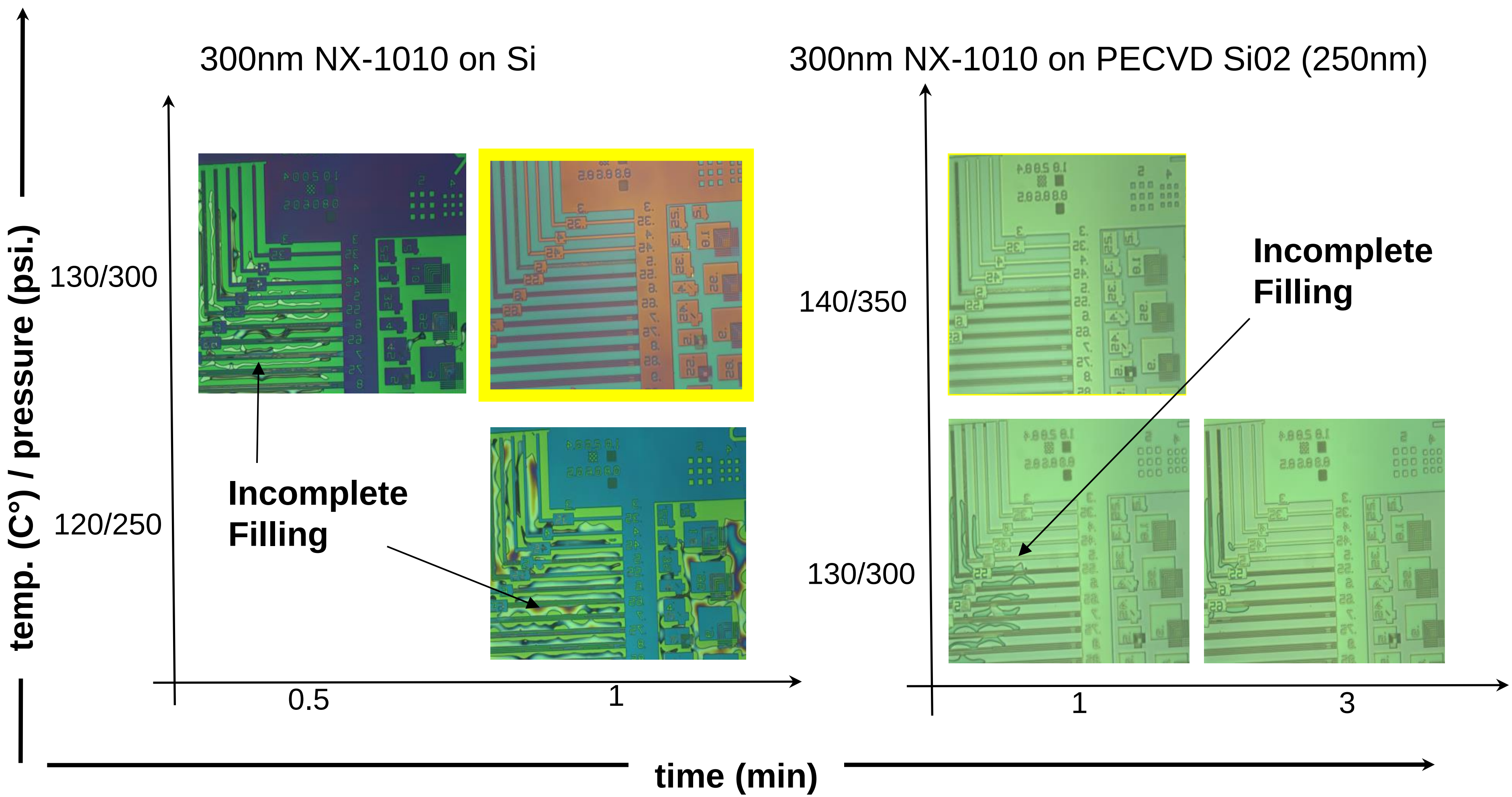
$V(t) \sim p_{eff}\, h(t)^3/(hR_{eff}^2)$, v = vertical imprint velocity, h=actual polymer height
R_{eff} = effective stamp dimension, p_{eff} = effective pressure

P_{eff} depends on local contact area and applied force
R_{eff} depends on how large the effective contact area is

R_{eff} is quadratic dependence, h is cubic, p_{eff} is linear

All after Ref. 1, Scheer, et. al. Microelectronic Engineering 56 (2001) 311–332, 2001

Process Flows (Thermal Imprinting)



For complete filling of large and small features, need to increase pressure*time*Temp

Underlying materials make some difference (flow properties change – surface tension)

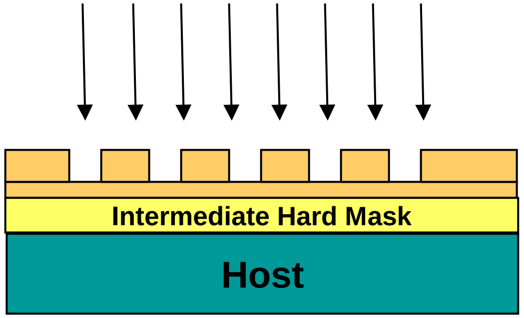
Process Flows (Thermal Imprinting)

Residual Layer Removal:

1. RIE#5, O2, 20sccm, 10mT, 100W : Rate is ~110nm/min.

2. Panasonic2, O2, 50sccm, 2 Pa, 50W ICP, 25W Sample : Rate is ~100nm/min

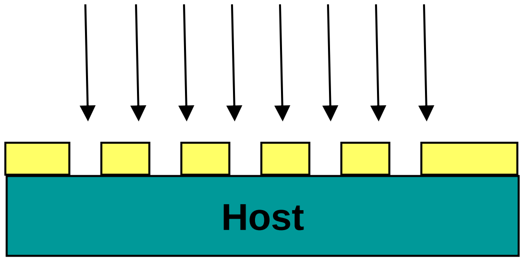
O2 RIE for Residual Layer Removal
CHF3, CF4, SF6, or Cl2 for Hard mask etch



$ER_{\text{Hard Mask}} > ER_{\text{Polymer}}$

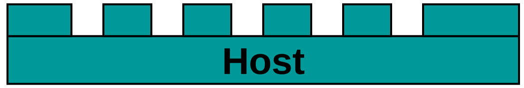
Remove Polymer w/Solvent Or O2 plasma

Cl2 or F-based RIE into Host



$ER_{\text{Host}} > ER_{\text{Hardmask}}$

Chemically Strip Hard Mask



Now have Inverse Duplicate of Master

Some Materials Considerations

Imprint Resist:

PMMA very inexpensive. Tg high. Processes often need 180-200C, 600psi
Separation of master/substrate more difficult.
Nanonex resists. Tg lower. Designed for imprint. 140C, 300psi to start.
mrI-2000 series. Process similar to Nanonex, 150C, 350psi to start.

Master Material:

Silicon: cheap, good for thermal imprinting and for soft-lithography

Substrate material Coefficient of Thermal Expansion (CTE):

If Substrate and Master have large CTE difference,
can have issues with separation.

Hard-mask intermediate layers:

SiO_2 : SiO_2 to polymer etch ratio 1.5:1 for CHF_3 based etch.
Si: SiO_2 etch ratio in Cl_2 etching 10:1. Cl_2 based etch

Cr: polymer to Cr etch ratio only 0.5:1, maybe as high as 1:1 Cl_2/O_2 etch
Cr:SiO_2 etch ratio > 10:1 for fluorine-based etch.

Imprinting Process for Nanonex System

Spin coat polymer or other imprint material onto wafer.

Bake polymer or material to drive out solvents.

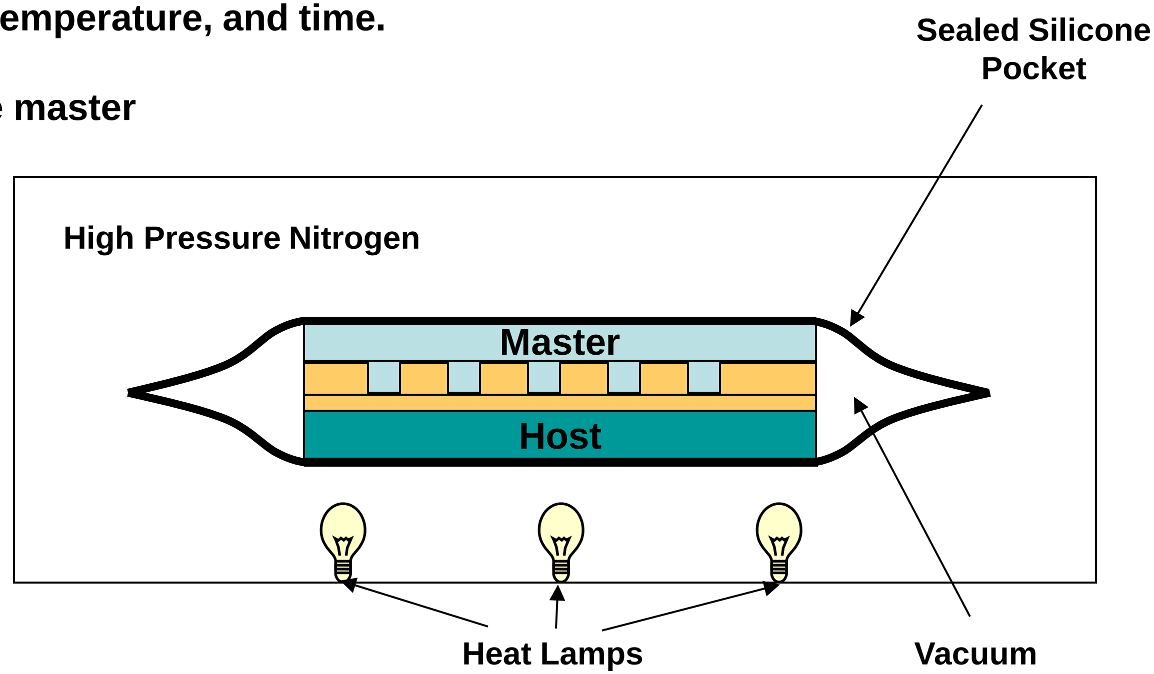
Place the treated mold onto the polymer coated wafer.

Place in machine. Machine schematic and picture is below. See tool page for tool operating procedures

Run process for a set pressure, temperature, and time.

Remove samples and release the master

Nanonex NX-2000



Using Air Pressure Guarantees Pressure Uniformity

Some Pictures of Results