Developing Etching Process for Nanostructures on InGaP and AlInP Using OX-35 Etcher

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EE412 Final Presentaion, Spring 2014

6/6/2014

Accomplishments

Systematic etching calibration on 4 materials with 2 series of recipes

First time in SNF on Ox-35

InGaP and AlInP nanostructures achieved

First time in SNF with RIE?

Process insights that will help future users

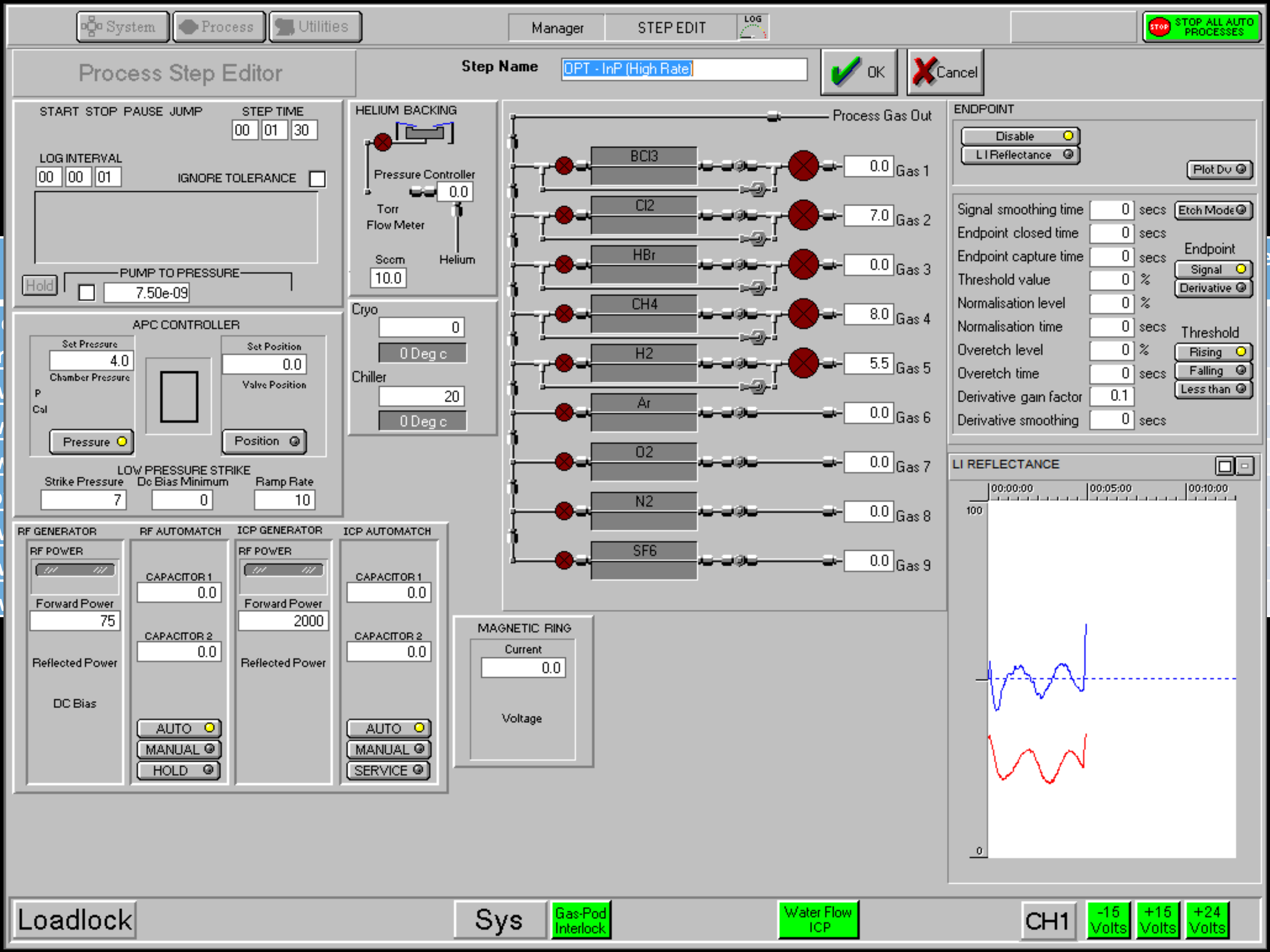
Ox-35

Materials


25W 2mT 1min
InP InGaP AlInP LBInGaP LBAlInP LBSi
1:45
25W 8mT 1min
1:45
InGaP
AlInP

Recipes

Chamb pressur	20
DC pow	70
ICP pov	2000
Cl2 flov	0
CH4 flo	0
H2 flow	0
SF6 flov	20
O2 flow	100



Step Name OPT - InP (High Rate)

STEP TIME 00 01 30

LOG INTERVAL 00 00 01

PUMP TO PRESSURE 7.50e-09

Set Pressure 4.0

Set Position 0.0

Strike Pressure 7

Dc Bias Minimum 0

Ramp Rate 10

Pressure Controller 0.0 Torr

Flow Meter 10.0 Sccm

Cryo 0 — 0 Deg c

Chiller 20 — 0 Deg c

RF POWER Forward Power 75

RF AUTOMATCH CAPACITOR 1 0.0

RF AUTOMATCH CAPACITOR 2 0.0

ICP RF POWER Forward Power 2000

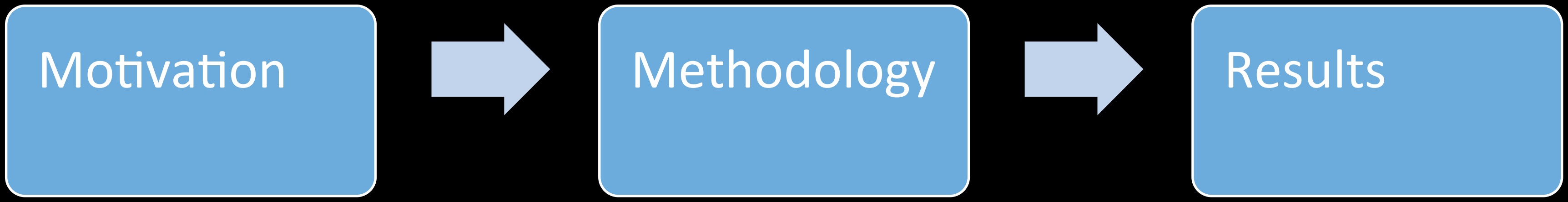
ICP AUTOMATCH CAPACITOR 1 0.0

ICP AUTOMATCH CAPACITOR 2 0.0

MAGNETIC RING Current 0.0

BCl3	0.0	Gas 1
Cl2	7.0	Gas 2
HBr	0.0	Gas 3
CH4	8.0	Gas 4
H2	5.5	Gas 5
Ar	0.0	Gas 6
O2	0.0	Gas 7
N2	0.0	Gas 8
SF6	0.0	Gas 9

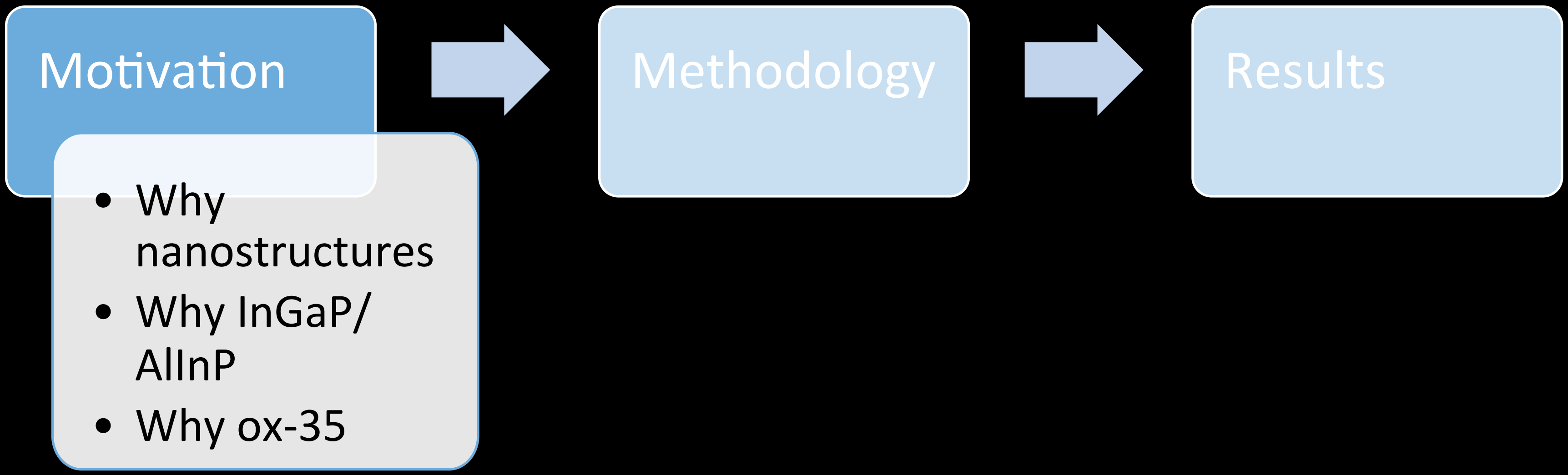
Signal smoothing time	0	secs
Endpoint closed time	0	secs
Endpoint capture time	0	secs
Threshold value	0	%
Normalisation level	0	%
Normalisation time	0	secs
Overetch level	0	%
Overetch time	0	secs
Derivative gain factor	0.1	
Derivative smoothing	0	secs



Motivation

Methodology

Results



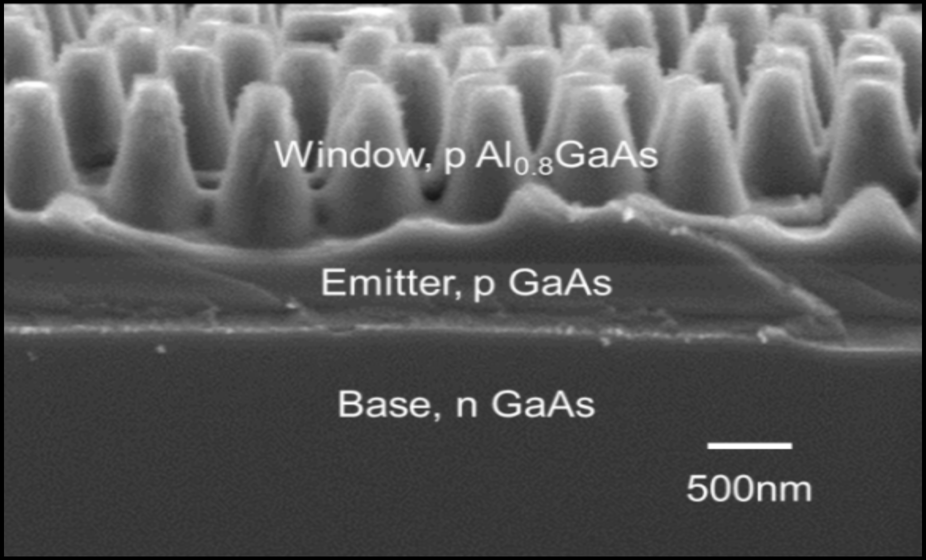
Motivation

- Why nanostructures
- Why InGaP/ AlInP
- Why ox-35

Methodology

Results

Nanostructures on III-V: PROS



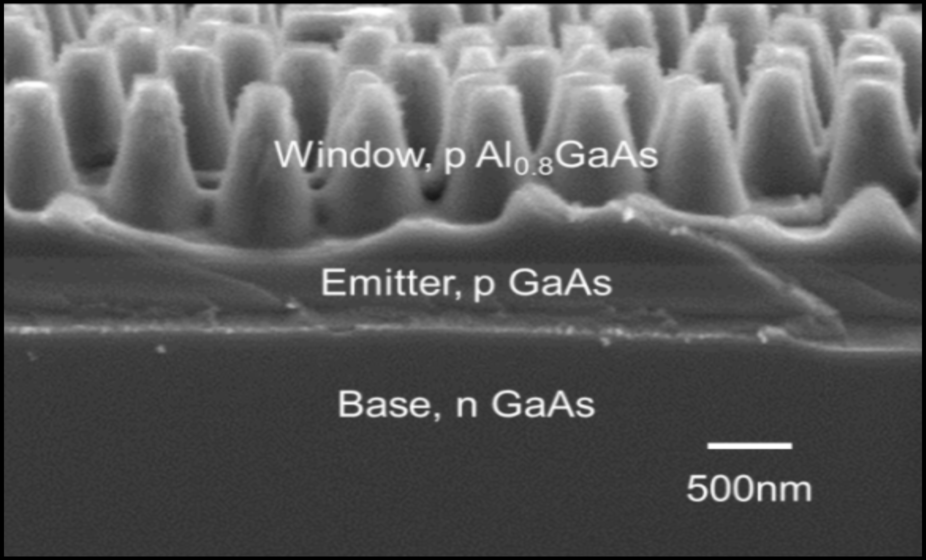
Anti-reflection

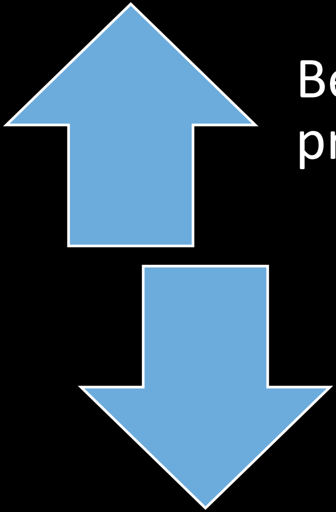
Better light management

Better light extraction

D. Liang, et al. *Nano Letters* **2013**, *13* (10)

Nanostructures on III-V: CONS





Better optical properties

Larger surface recombination loss

Solution: do it on materials with smaller surface recombination!

D. Liang, et al. *Nano Letters* **2013**, *13* (10)

Why on InGaP and AlInP

InGaP

- Smaller surface recombination rate
- Common top junction material for multi-juntion solar cells

AlInP

- Large bandgap
- Common window layer material for PV and LED

Bonus materials: why InP and SiO2

InP

- Simpler material to etch, good starting material

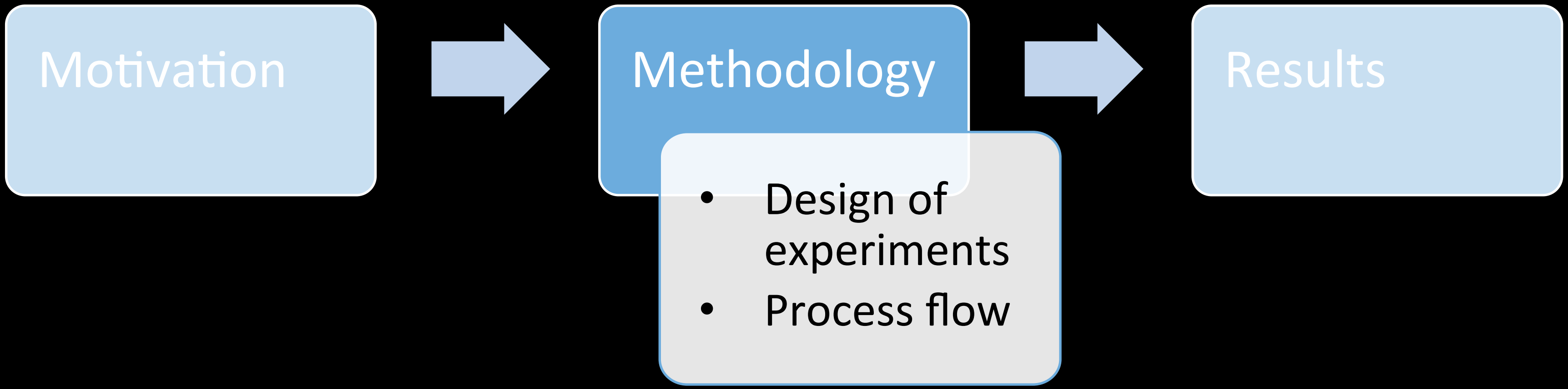
SiO2

- Mask for nanostructure etching

Why Reactive-ion Etching (RIE)

Comparing to Inductive Coupled Plasma (ICP) and Electron Cyclotron Resonance (ECR) Etching

- Low temperature (allows photoresist mask)
- Higher etching rate
- Better selectivity
- More controllable and repeatable



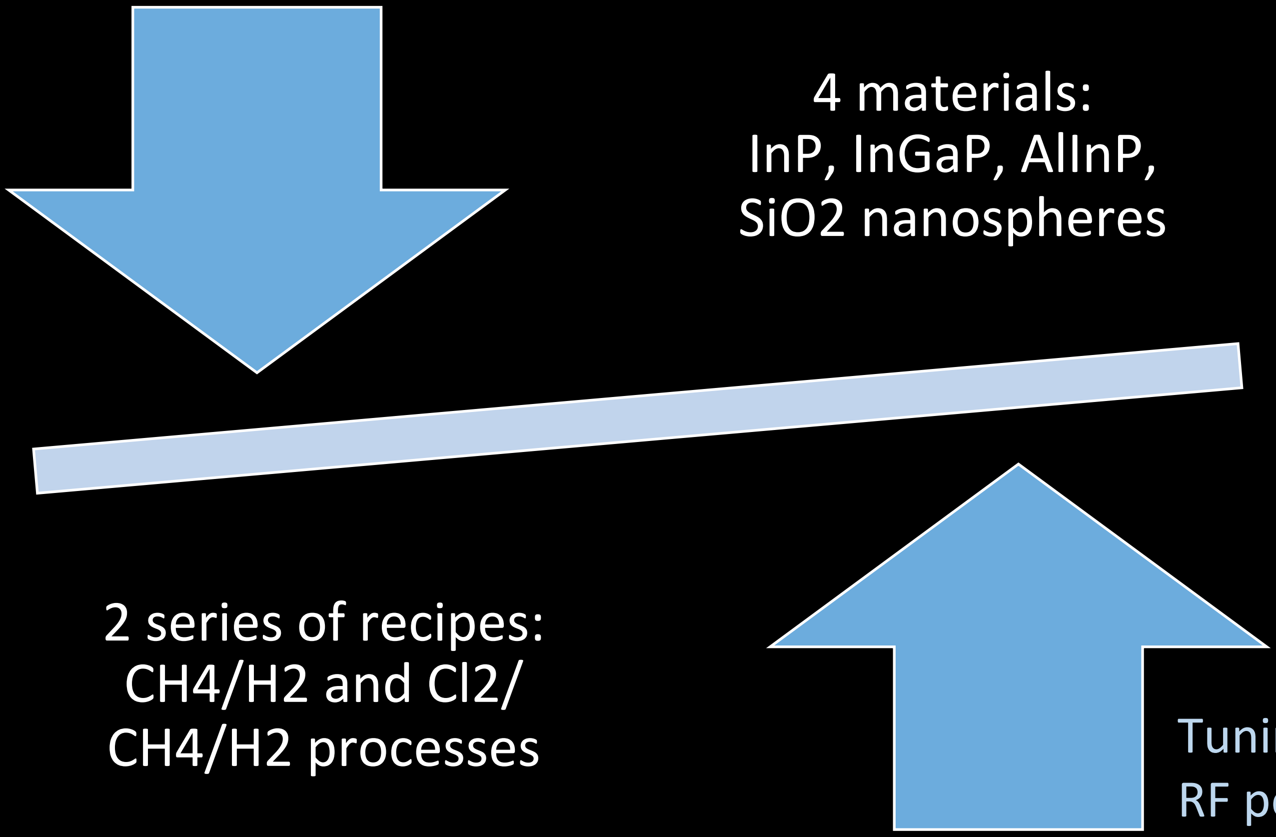
Motivation

Methodology

- Design of experiments
- Process flow

Results

Design of Experiments



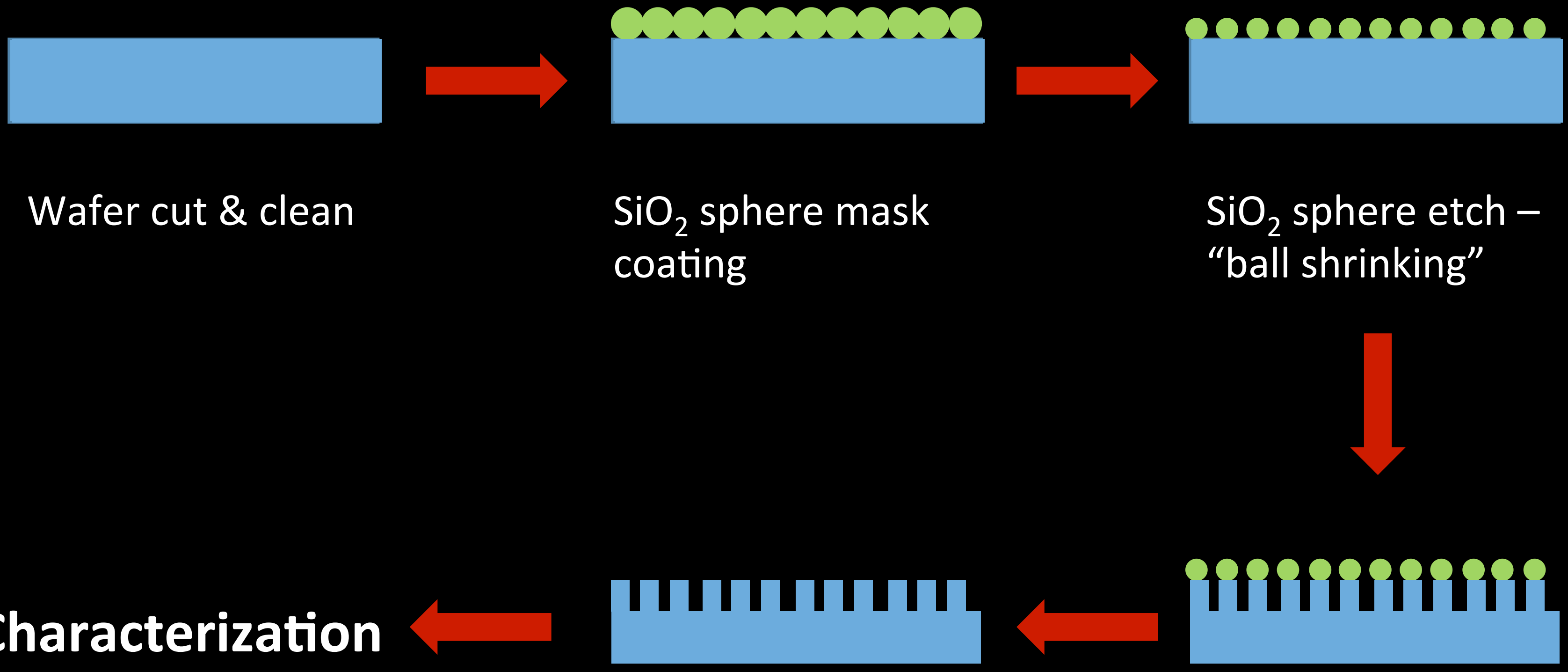
4 materials:
InP, InGaP, AlInP,
SiO_2 nanospheres

Etching rate,
conformity, mask
condition, etc.

2 series of recipes:
CH_4/H_2 and $Cl_2/$
CH_4/H_2 processes

Tuning:
RF power, pressure,
chemical composition
(imcomplete)

Process Flow:
Nanostructure Formation



Wafer cut & clean

SiO_2 sphere mask coating

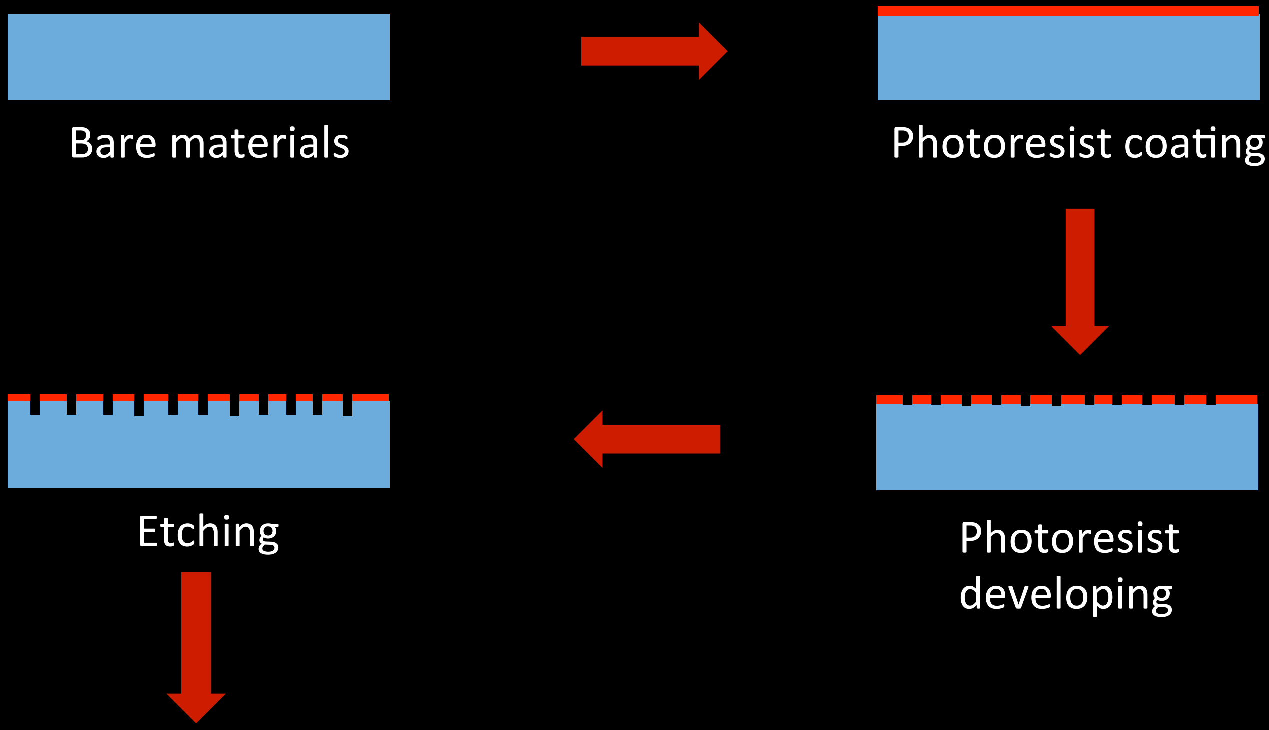
SiO_2 sphere etch – “ball shrinking”

Sample dry etch

Sample wet etch

Characterization

Process Flow:
Process Calibration



Bare materials

Photoresist coating

Photoresist developing

Etching

Characterization

Tools

Ox-35 Etcher

Wet benches

Headway

Karlsuss

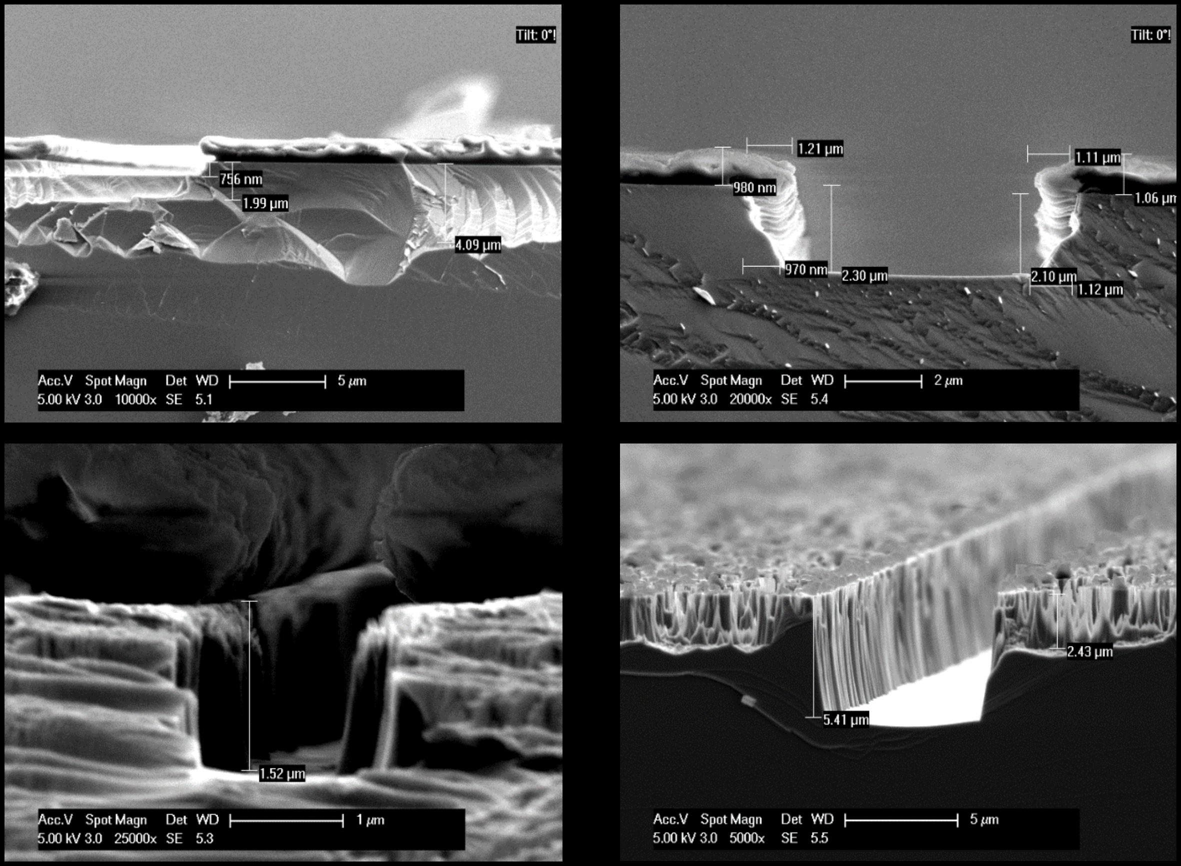
Motivation → Methodology → Results

- Etching calibration
- Nanostructures

Results Overview

Material	Recipe	Etch Rate (vertical/horizontal) (nm/min)	Undercut (nm/min)	Sidewall Angle (dec)	Smoothness (bottom/sidewall)	Photoresist Condition	Comments
InP	Low ER	154	81	67.3	Smooth/rough	Polymer observed	Significant polymer formation
	High ER, 75W 4mT	750	NA	>86	Smooth/zigzag	Degraded, porous	
	High ER, 25W 4mT	404	1500	51	Rough/rough	Degraded	
	High ER, 25W 2mT	NA	NA	NA	NA	NA	Etching failed
	High ER, 25W 8mT	269	<0	13.3	Rough/rough	Wavy, locally peeled	
InGaP	Low ER	70	8	84	Smooth/smooth	Polymer observed	Significant polymer formation
	High ER, 75W 4mT	>300	<0	>80	Smooth/zigzag	Degraded	Epi etched through
	High ER, 25W 4mT	240	<0	78	Rough/mild zigzag	Degraded	
	High ER, 25W 2mT	192	NA	75.3	Smooth/smooth	NA	SiO2 mask
	High ER, 25W 8mT	178	300	39	Very rough/very rough	Wavy	
AlInP	Low ER	<5	NA	NA	NA	NA	No etching observed
	High ER, 75W 4mT	>300	NA	NA	Smooth/zigzag	Porous	Epi etched through
	High ER, 25W 4mT	428	1140	varying	Smooth/rough	Porous	
	High ER, 25W 2mT	365	NA	82	Smooth/smooth	NA	SiO2 mask
	High ER, 25W 8mT	90	1340	7.1	Very rough/very rough	Wavy	
SiO2	Low ER	<5	NA	NA	NA	NA	No etching observed
	High ER, 75W 4mT	70/2	NA	NA	NA	NA	
	High ER, 25W 4mT	<50/<50	NA	NA	NA	NA	
	High ER, 25W 2mT	<50/<50	NA	NA	NA	NA	
	High ER, 25W 8mT	<50/<50	NA	NA	NA	NA	
	Chamber Clean	400/300	NA	NA	NA	NA	

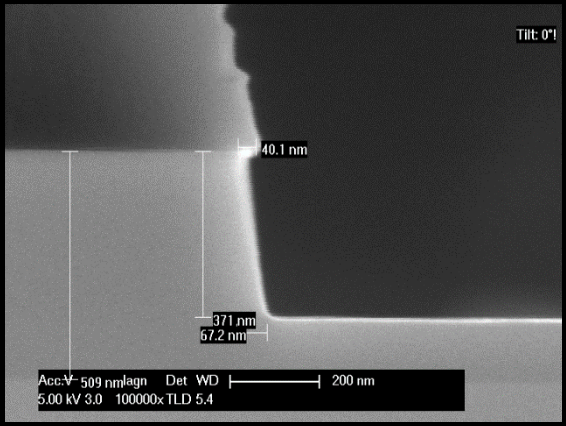
InP

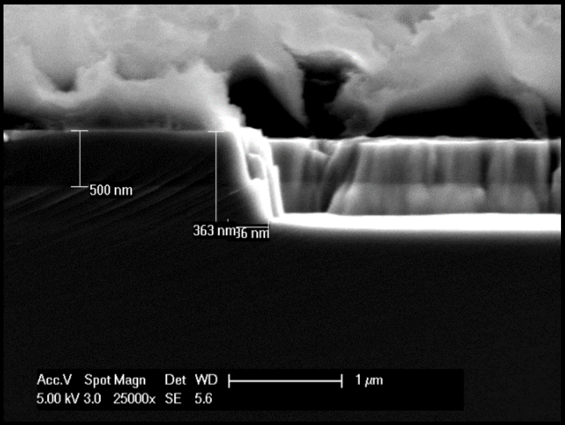


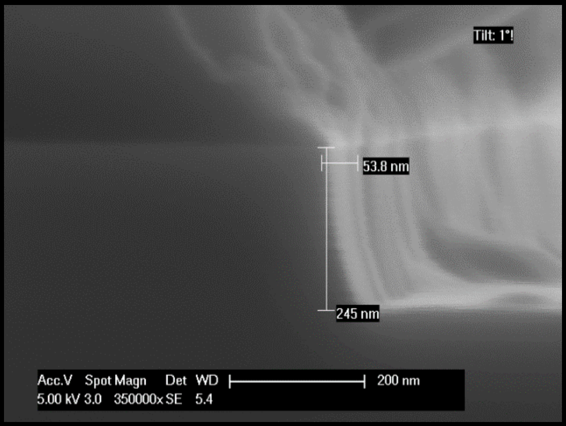
✓ CH4/H2 recipe:
ER=154.4nm/min
SW angle=67.3˚
Significant polymer formation

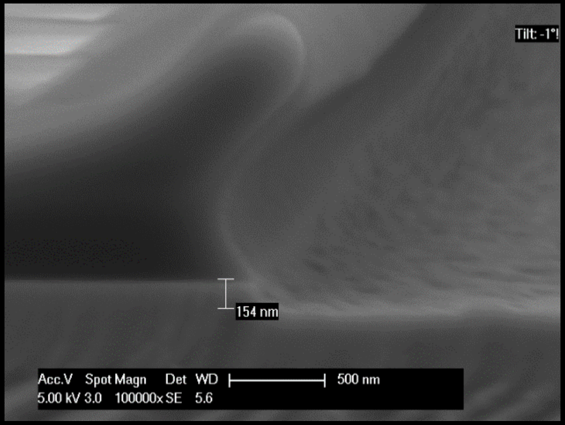
✓ Cl2/CH4/H2 recipe:
ER=750nm/min
PR mask was etched porous

InGaP





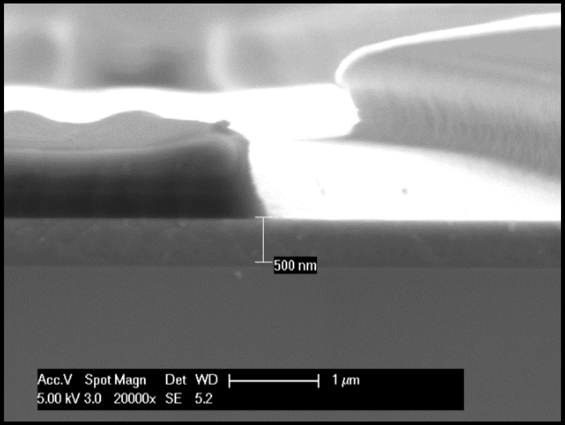


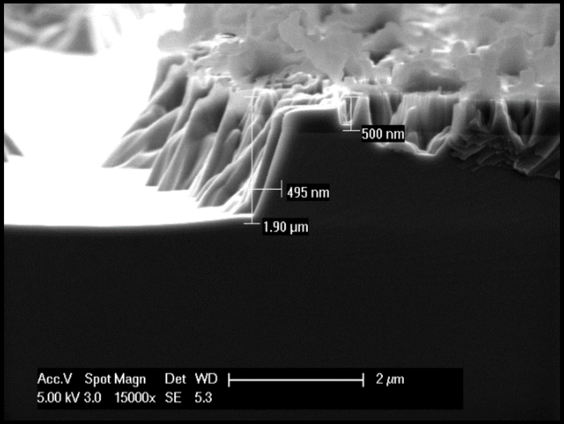


- ✓ CH_4/H_2 recipe:
  ER=70nm/min
  SW angle~90˚
  Very smooth sidewalls and bottom
  "Capping" effect

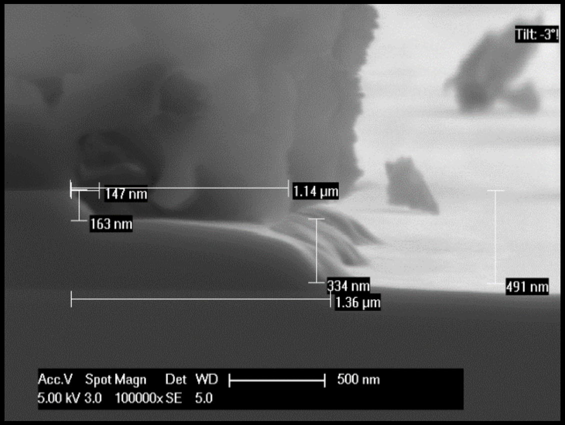
- ✓ $Cl_2/CH_4/H_2$ 25W, 8mT recipe:
  ER=178nm/min
  Undercut=300nm/min
  SW angle~39˚
  Good conformity for nanostructure etching

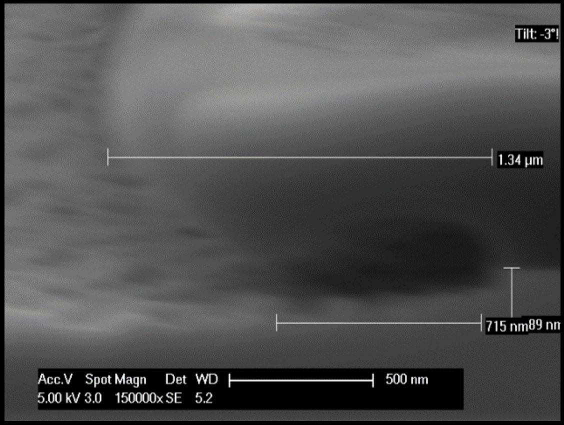
AlInP





- ✓ CH4/H2 recipe:
Doesn't etch at all!

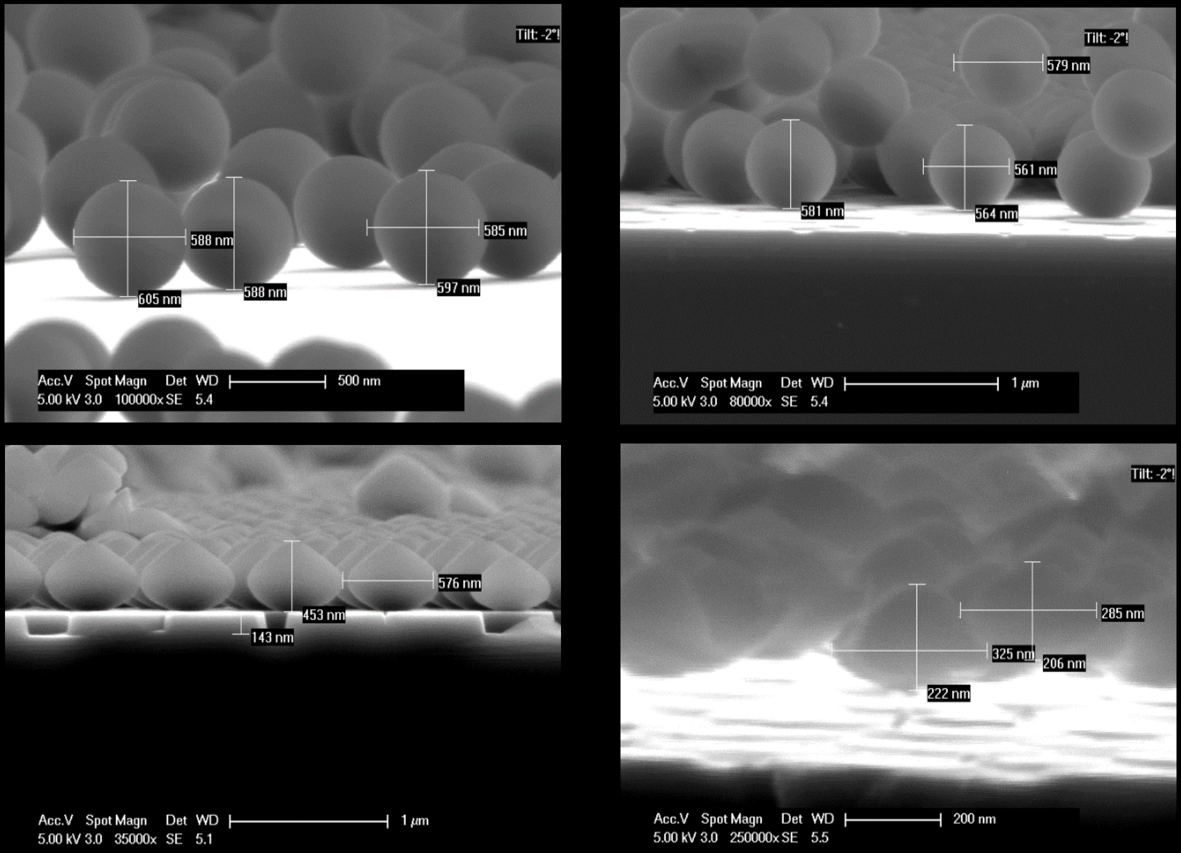




- ✓ Cl2/CH4/H2 75W, 8mT recipe:

ER=90nm/min
Undercut=1340nm/min
SW angle~7.1˚
More chemical than physical

SiO2 Nanospheres



✓ CH4/H2 and Cl2/CH4/H2 recipes:

Negligible etching rate

= good selectivity

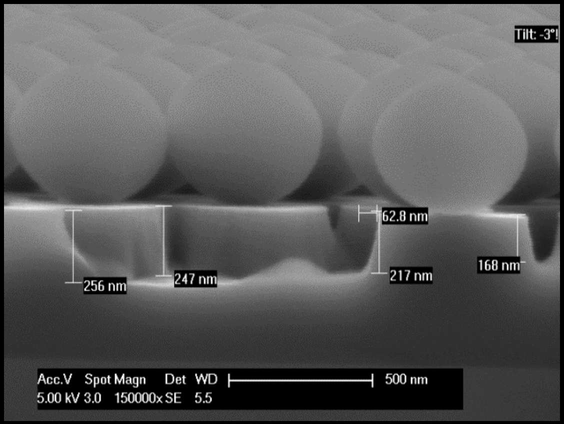
✓ O2/SF6 chamber clean recipe:

L. ER=400nm/min

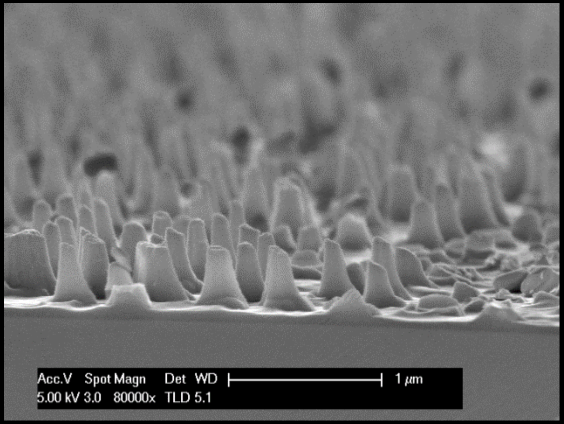
V. ER=300nm/min

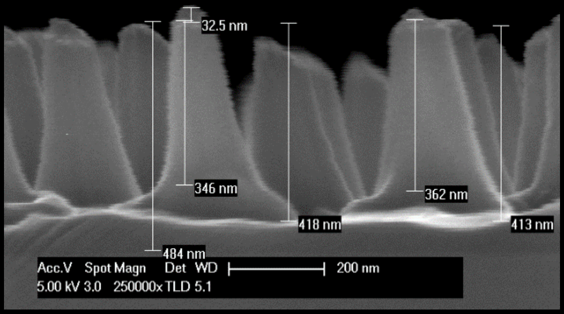
Ideal for ball shrinking!

InGaP Nanostructures



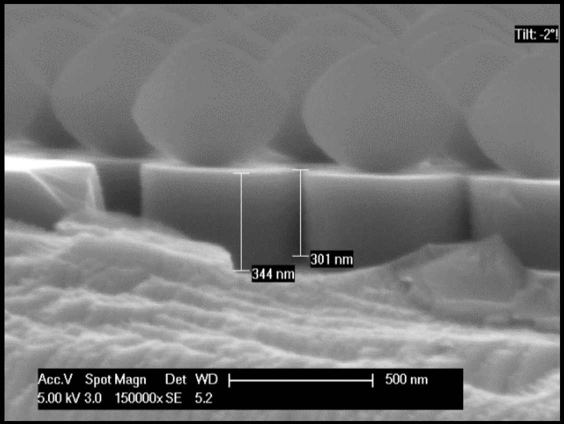
$\mathrm{Cl_2/CH_4/H_2}$ 25W 4mT, 1min



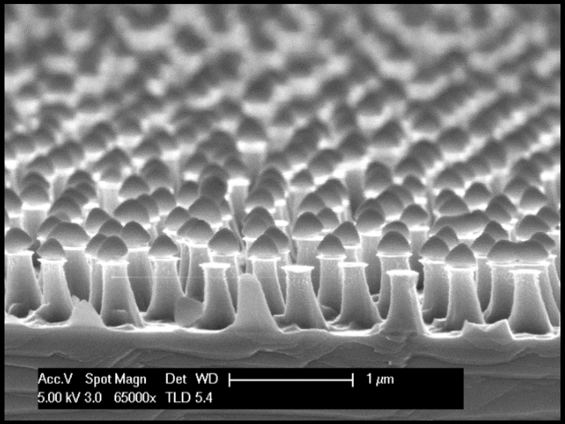


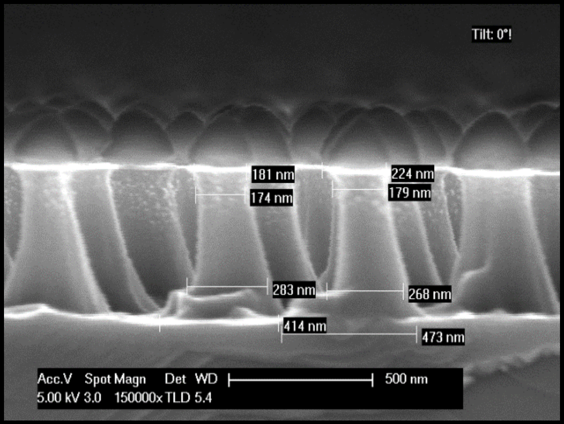
$\mathrm{O_2/SF_6}$ 70W 20mT, 1min
+
$\mathrm{Cl_2/CH_4/H_2}$ 25W 8mT, 2min

AlInP Nanostructures



Cl2/CH4/H2 25W 4mT, 1min





O2/SF6 70W 20mT, 1min
+
Cl2/CH4/H2 25W 8mT, 2min

Conclusion on Experimental Results

InP

- Both Cl2/CH4/H2 and CH4/H2 recipes etch well
- Cl2 recipe is faster but rougher

InGaP

- CH4/H2: slow, smooth and straight
- Cl2/CH4/H2: ideal for nanostructure etching

Conclusion on Experimental Results

AlInP

- CH_4/H_2: doesn't work!
- $Cl_2/CH_4/H_2$: very sensitive to Cl_2, resulting in large undercut

SiO_2 nanospheres

- Survives both $Cl_2/CH_4/H_2$ and CH_4/H_2 processes
- O_2/SF_6 chamber clean recipe is ideal for shrinking!
- Shrink more on InGaP than AlInP

Accomplishments

Systematic etching calibration on 4 materials with 2 series of recipes

InGaP and AlInP nanostructures achieved

Process insights that will help future users

Additional Process Insights

- CH4/H2 recipes generates a lot of polymer
  - Accumulative process time should not exceed 20min before chamber clean
    - (or very bad thing will happen)

- InGaP:
  1min 1:6 dilute HCL dip recommended to remove oxide

- AlInP:
  Almost always comes with GaAs cap, 1min citric acid dip + 1 min HCL dip recommended

Process insights that will help future users

Motivation

- Why nanostructures
- Why ox-35

Methodology

- Design of experiments
- Process flow

Results

- Etching calibration
- Nanostructures