

Mask requirements

Objectives

- Full selectivity: no growth on the mask
- Mechanically & chemically stable throughout the growth cycle
- No impurity release from the mask
- Fully removable after epitaxy

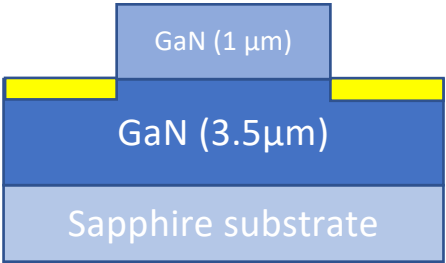
Requirements

- No interaction of adatoms / adatoms with mask material
- Mask openings of controlled morphology
- No contamination during mask fabrication
- No chemical interaction with substrate

SiO₂ vs W mask in SA-MOVPE of GaN

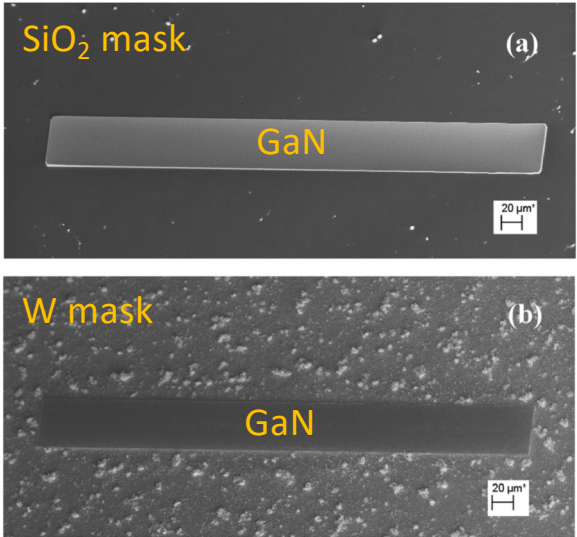
I. Mahaboob *et al.*, Univ. Albany (NY), J. Vac. Sci. Technol. B 36(3), 2018

- LP - MOVPE (13 kPa)
- Sapphire substrate
- T = 1040° C
- TMGa, TMAI, NH₃, SiH₄
- H₂ as carrier gas



- Protects the underlying SiO₂
- SiO₂ / SiN_x : 150nm / 150nm, PECVD
 - W: 60nm, e-beam evap.

SEM top view

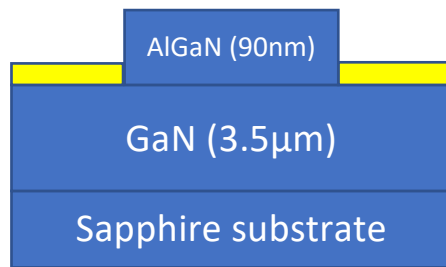


Poor selectivity using W mask

Growth	Mask	Hall		SIMS	
		n (cm ⁻³)	[C] (cm ⁻³)	[O] (cm ⁻³)	[Si] (cm ⁻³)
Planar GaN (3.5μm)		5.8 10 ¹⁶	2 10 ¹⁷	3 10 ¹⁷	-
SAE GaN (1μm)	SiO ₂ /SiN _x	8 10 ¹⁸	3 10 ¹⁷	2 10 ¹⁷	7 10 ¹⁸
SAE GaN (1μm)	W	1.6 10 ¹⁹	3 10 ¹⁷	7 10 ¹⁸	-

Si and O contamination from SiO₂ and W mask

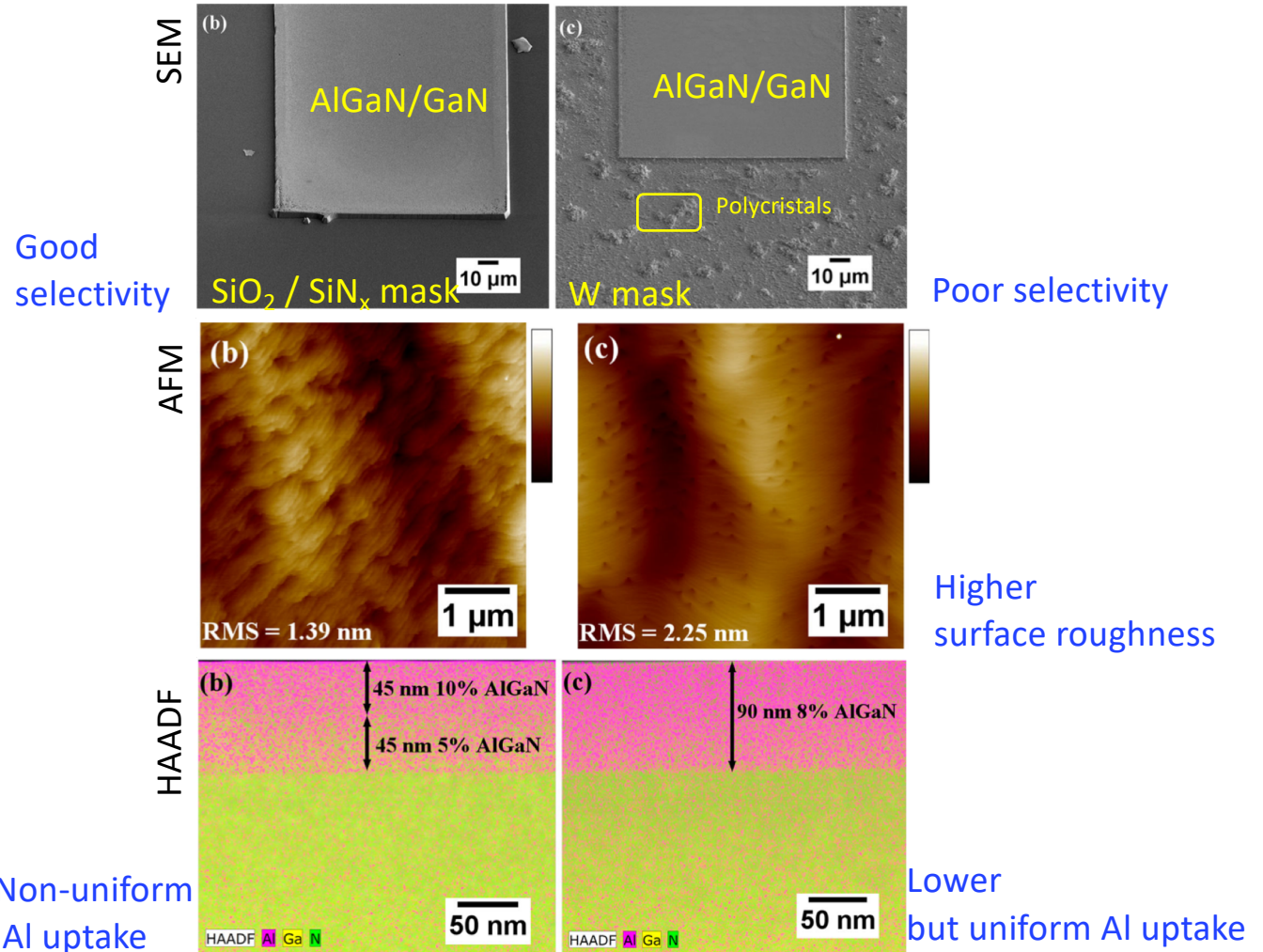
SA-MOVPE OF AlGaN / GaN : SiO₂ vs W masks



- Higher dislocation density with W mask
- Si contamination from SiO₂ mask
- O contamination from W mask
- No 2DEG because of high n-type contamination by mask

I. Mahaboob *et al.*, Univ. Albany (NY), J. Electron. Mat. Vol.47, N° 11, 2018

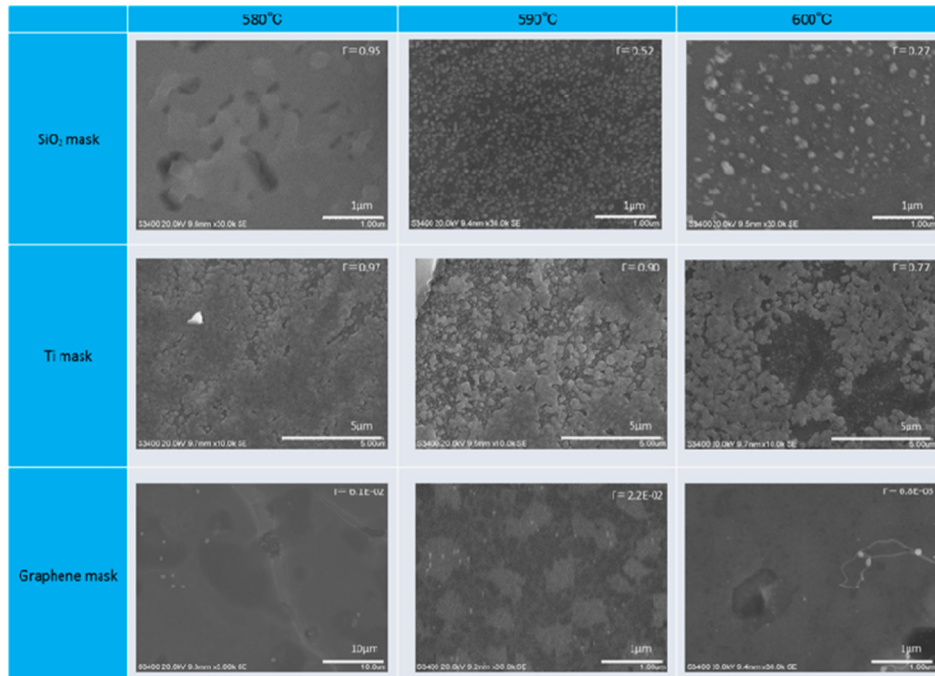
Introduction to MOVPE of III-V semiconductors
PHYS-747 Doctoral course in Physics (2022)



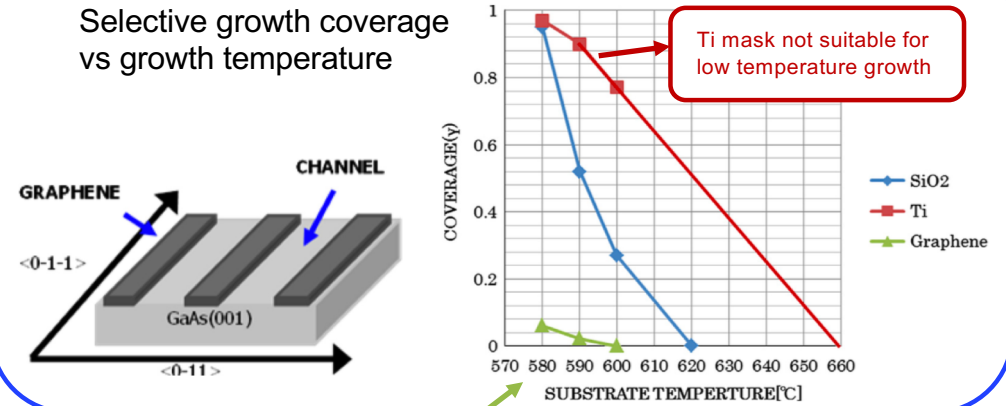
GaAs homoepitaxy using graphene, Ti and SiO₂ masks

- SiO₂ mask (by spin coating of organic solution)
- Ti mask 40nm (by electron beam deposition)
- Graphene mask (by CVD)
- MBE (T: 580° -620° C)

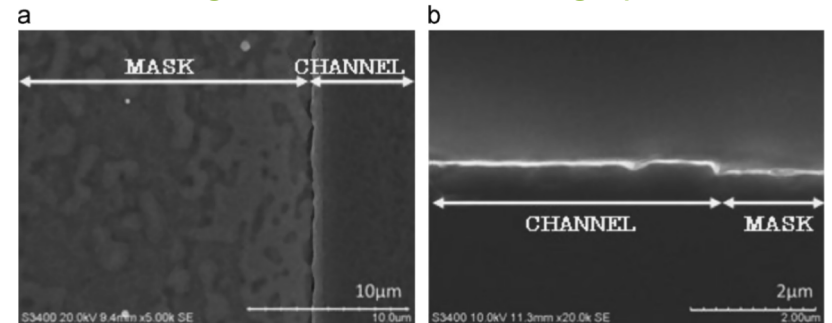
Polycrystals on mask surface after GaAs growth



Y. Hirota *et al.*, Meijo Univ., J. Crystal Growth 401 (2014) 563



Selective growth at 600° C with graphene mask



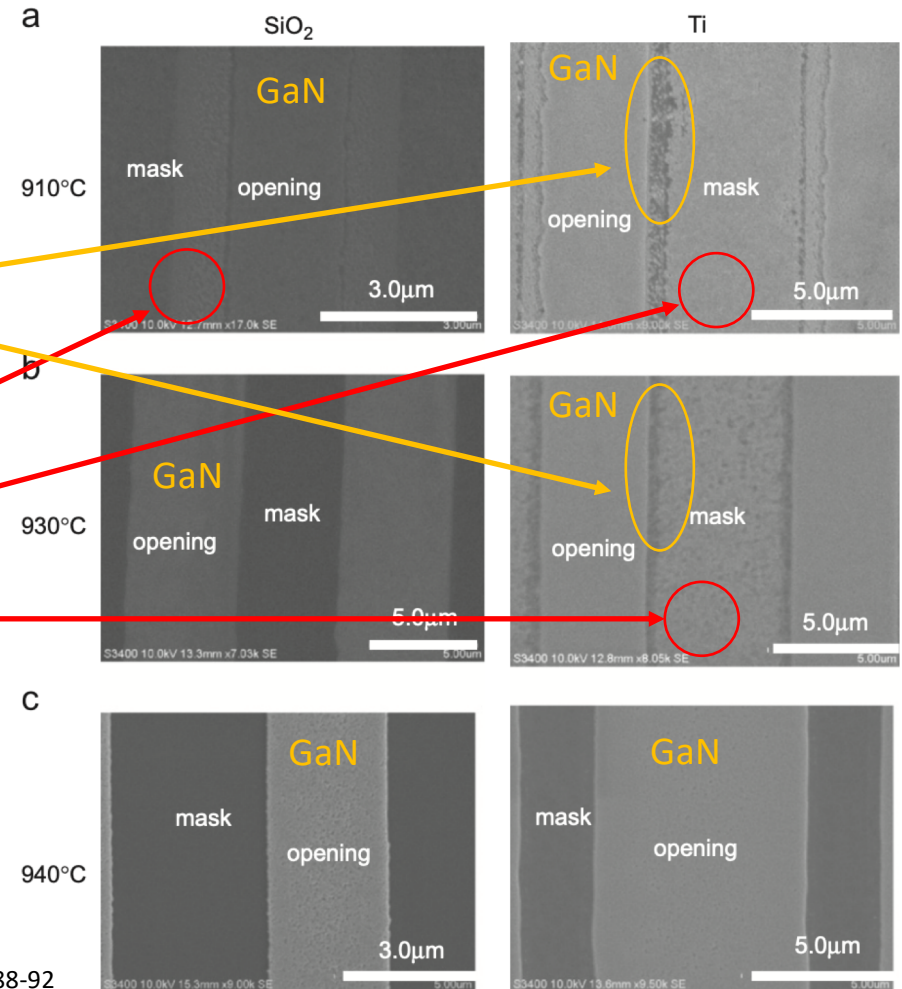
SAE: mask issues

Si & Ti mask in GaN SA-MBE

- 2.5 μm GaN/Al₂O₃ (0001)
- Ga cell: 820, 849° C
- RF N source
- GR: 0.065, 0.1 $\mu\text{m}/\text{h}$
- T_{sub}: 910, 940° C
- Ti 5nm (e-beam evap.)
- SiO₂ (organic solution)

Polycrystals are visible:
< 930° C on SiO₂ mask
< 940° C on Ti mask

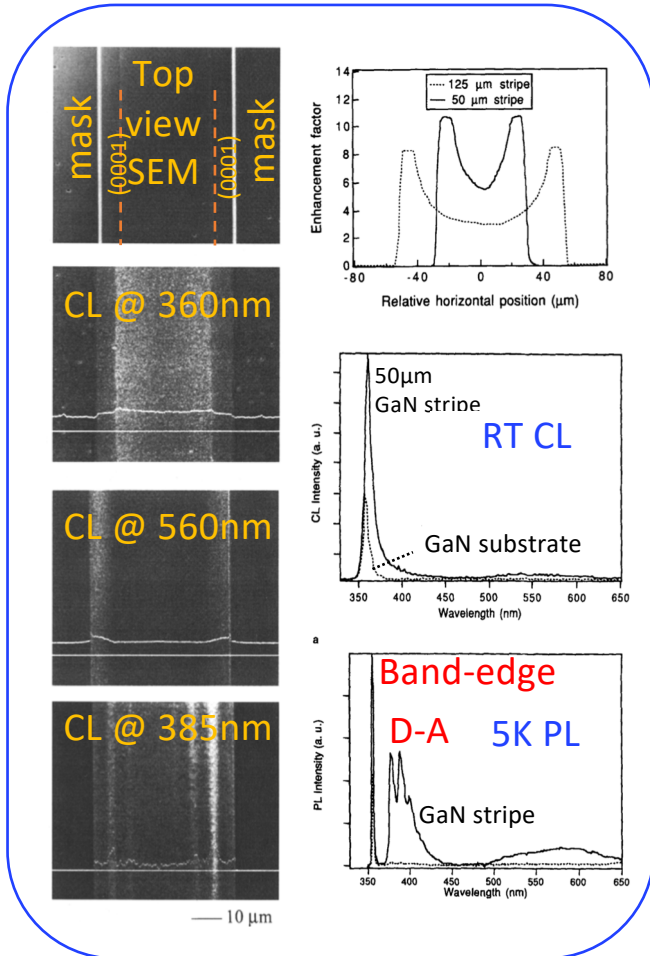
Reduced deposits
near mask edge



SiO₂ mask: **evaporation** dominates

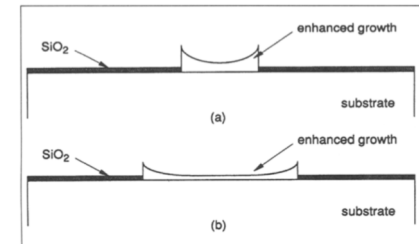
Ti mask: significant **migration** on the mask surface

SA-MOVPE of GaN: cathodoluminescence evidence of impurity incorporation



X. Li *et al.*, Univ. Illinois, J. Electronic Mat., Vol. 26, N° 3, 1997

- AP-MOVPE
- 1-3 μm GaN epi on Sapphire
- H₂ as carrier gas
- TMGa, TMAI, NH₃
- T = 1020° C
- 60nm SiO₂ PECVD



- Edge morphology affected by NH₃ flow: lower effective V/III ratio
- Lateral gas phase diffusion above mask + surface migration on epi
- Stronger band-edge emission at RT CL and 5K PL
- More impurity-related transitions near the mask edges

Selective and non-planar epitaxy

APPLIED PHYSICS LETTERS **97**, 243102 (2010)

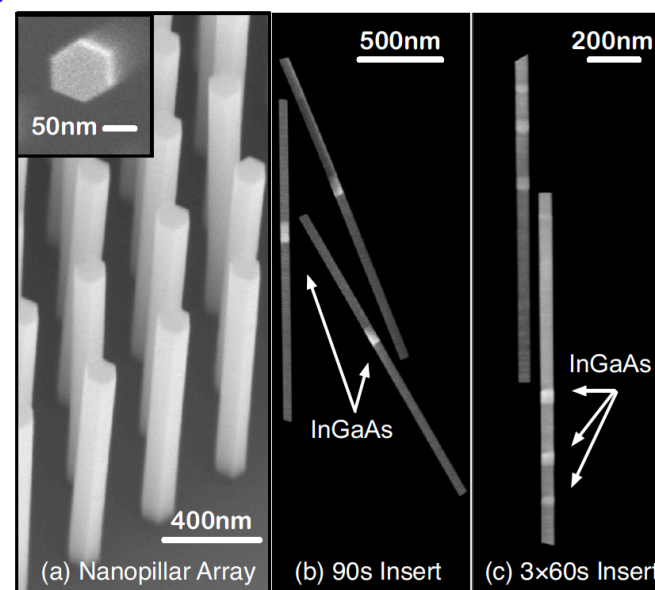
InGaAs heterostructure formation in catalyst-free GaAs nanopillars by selective-area metal-organic vapor phase epitaxy

J. N. Shapiro,^{a)} A. Lin, P. S. Wong, A. C. Scofield, C. Tu, P. N. Senanayake, G. Mariani, B. L. Liang, and D. L. Huffaker^{b)}

Department of Electrical Engineering and California Nano-Systems Institute, University of California at Los Angeles, Los Angeles, California 90095, USA

- (111)B GaAs + SiO₂ mask
- e-beam + RIE: s=300nm, d=80nm
- TMGa, TMIIn, TBAs
- Carrier gas: H₂
- T = 720° C
- P = 60 Torr
- Nominal₍₁₀₀₎ = 0.35 ML/s
- V/III_{GaAs} = 9, V/III_{InGaAs} = 50,

- GaAs / InGaAs 10-2-2-5' growth
- 30" Growth interrupts at heterointerfaces
- Scanning Tunneling Microscopy
- Energy Dispersive X-ray Spectroscopy



SEM

HAADF STEM

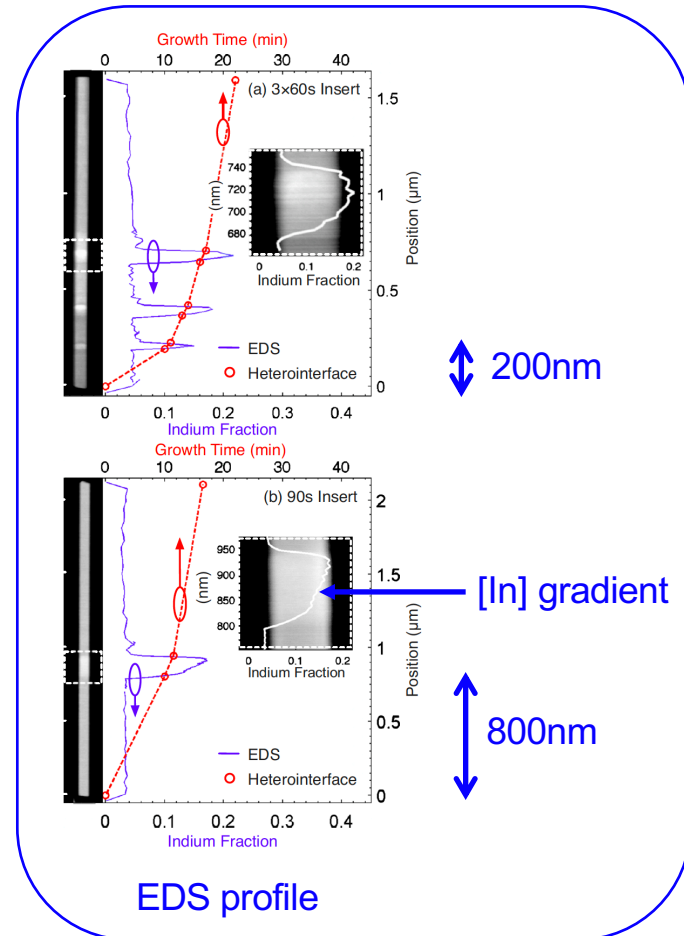
In content
from EDS

19%

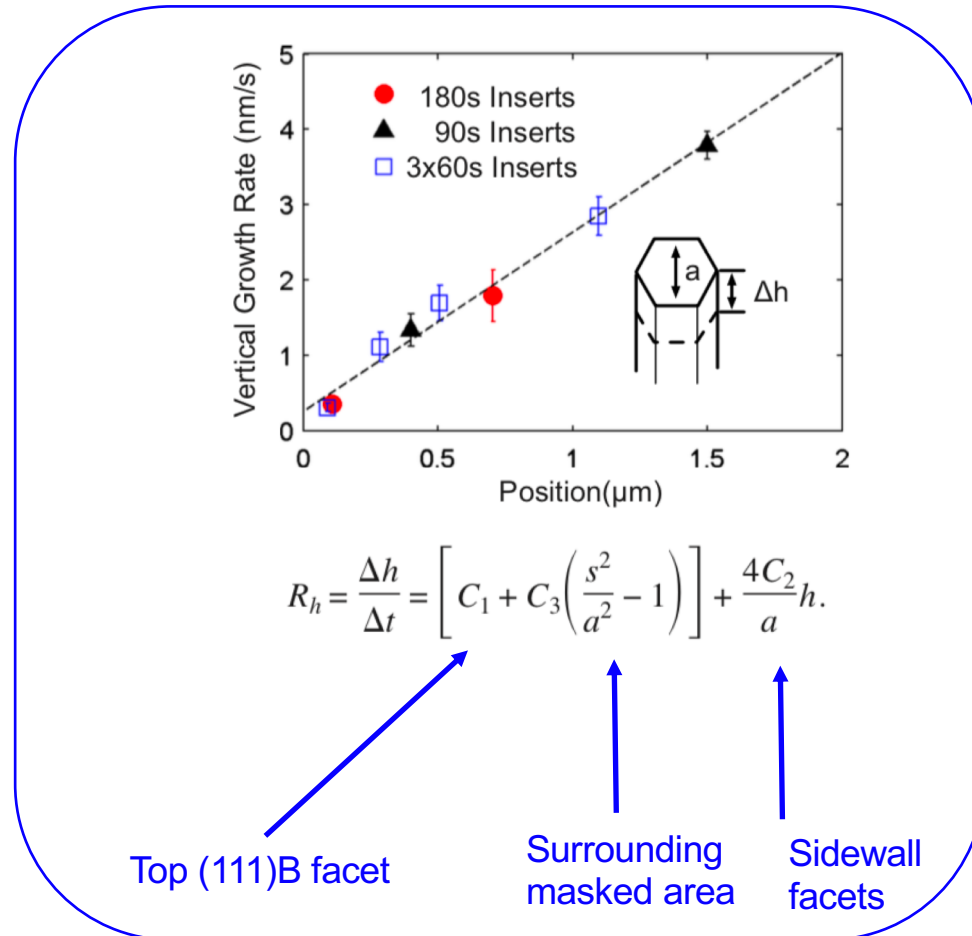
16%

13%

Selective and non-planar epitaxy



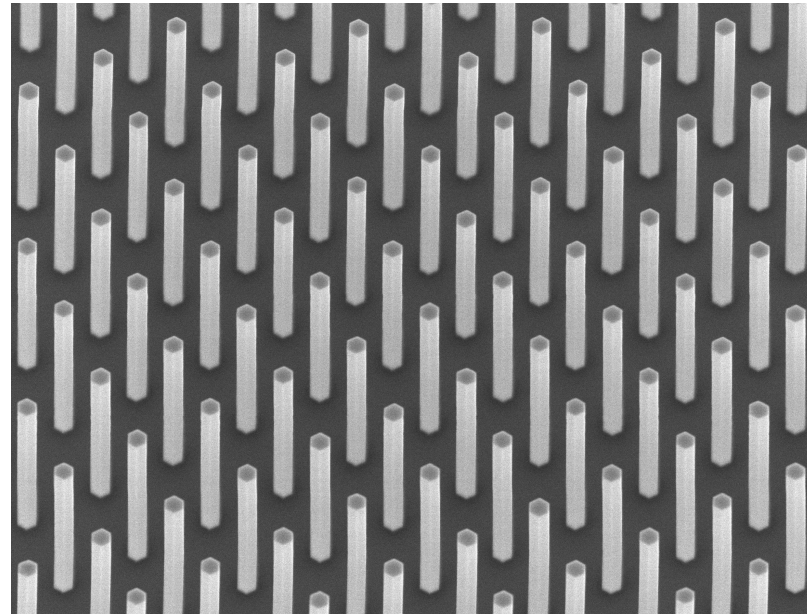
Shapiro *et al.* APL 2010



Ikejiri *et al.*, Nanotechnology 2008

Selective area growth of n-GaAs NWs

- Background & motivations
- Selective area MOVPE
for n-GaAs nanowire (NW) arrays
- Shape and uniformity of GaAs NWs arrays
 - N-type doping precursor
 - Growth temperature T_s
- GaAs NWs based p-i-n diodes
- Summary and perspectives



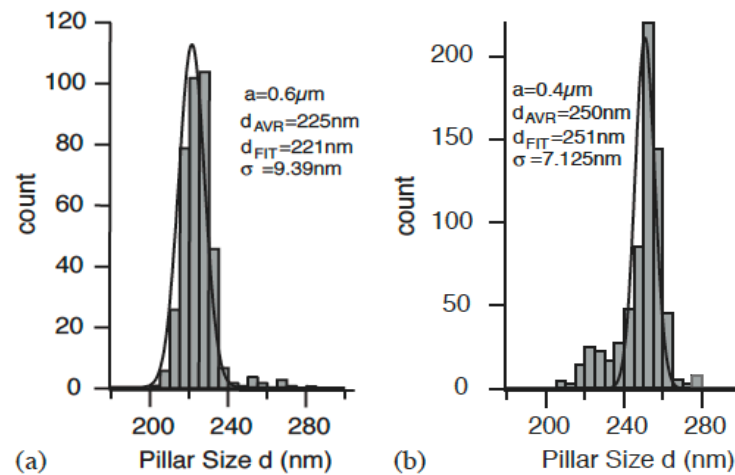
Acknowledgements

D. Mikulik, P. Romero Gomez,
L. Güniat, C. Jürgensen,
A. Fontcuberta i Morral, B. Dwir, E. Kapon

Laboratory of Semiconductor Materials, School of
Engineering, School of Basic Sciences

Background and motivations

- Nanowire arrays Solar Cells (NWSCs) & nanophotonics (PhCs...) demand high uniformity NWs
- Undoped GaAs & InAs NW arrays with high uniformity achieved by MOVPE SAG (1,2)

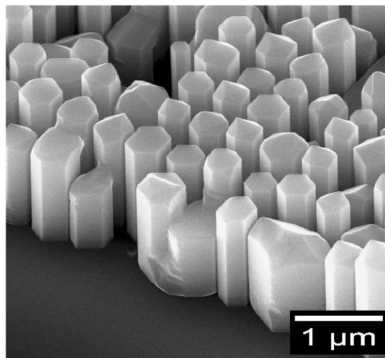


- (1) SD/D ~ 3% J.Motohisa *et al.*, Physica (2004)
- (2) SD/D ~ 7% K.Tomioka *et al.*, J. Cryst. Growth (2007)

Background and motivations

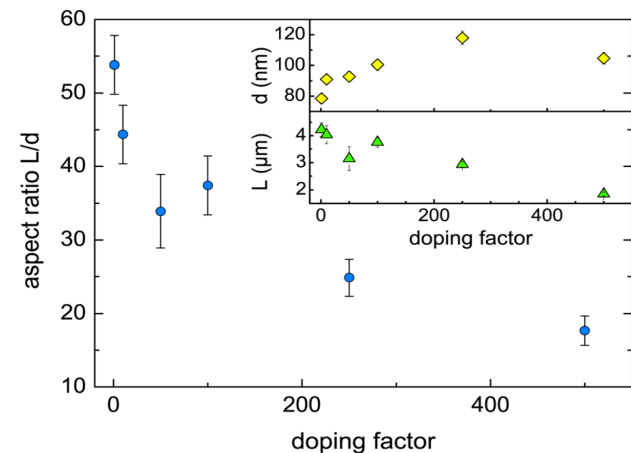
- Si_2H_6 as n-type dopant precursor affects the shape and uniformity of GaAs & InAs NW arrays :

Irregular GaAs:Si NWs arrays



K.Sladek *et al.*, J. Crystal Growth 312 (2010)

Reduced aspect ratio in InAs:Si NWs



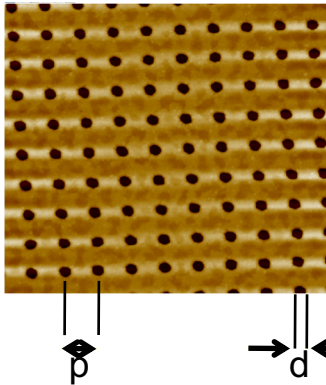
7-15%

S. Wirths *et al.*, J. Appl. Phys. 110 (2011)

Do we have a valid precursor for uniform n-GaAs NW arrays ?

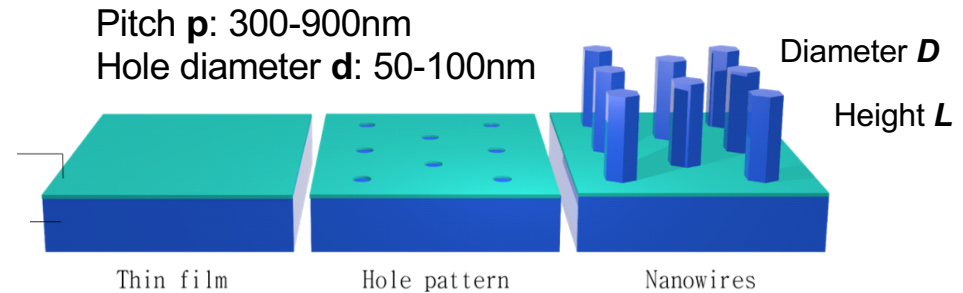
Substrate preparation & growth parameters

AFM of SiO₂ mask



SiO₂ 30nm mask
GaAs (111)B wafer

$d=50\text{nm}$
 $p=300\text{nm}$

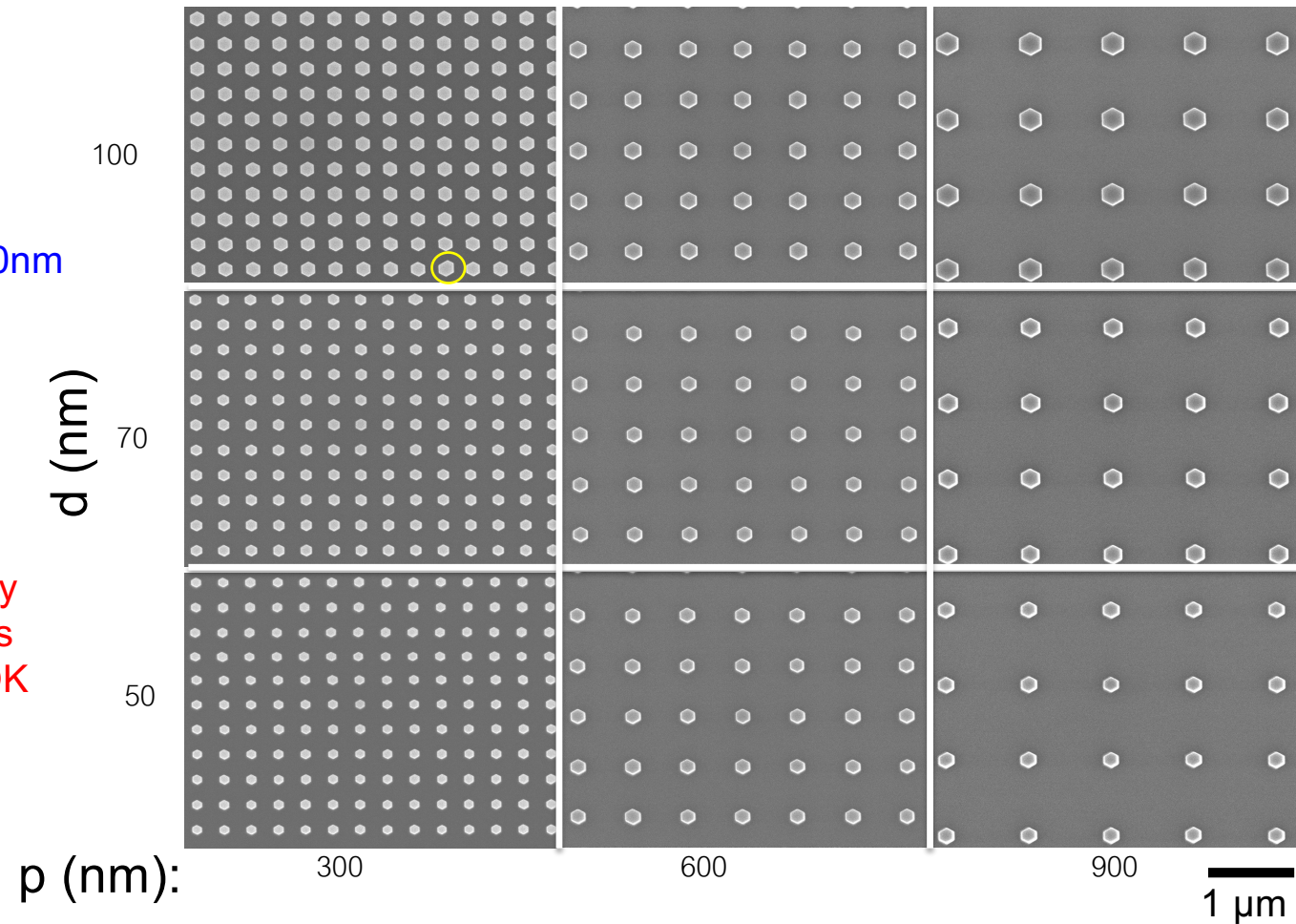


- N₂ ambient (2.4l/mn, 20mbars)
- Deoxidation: 4mn @ 870° C under AsH₃
- T_s: 750 - 850° C, V/III: 100-600
- TMGa, AsH₃: GaAs ~ 0.04nm/s on (100)
- Si₂H₆ (10⁻⁴ in N₂), IV/III: 10⁻⁴ - 10⁻²

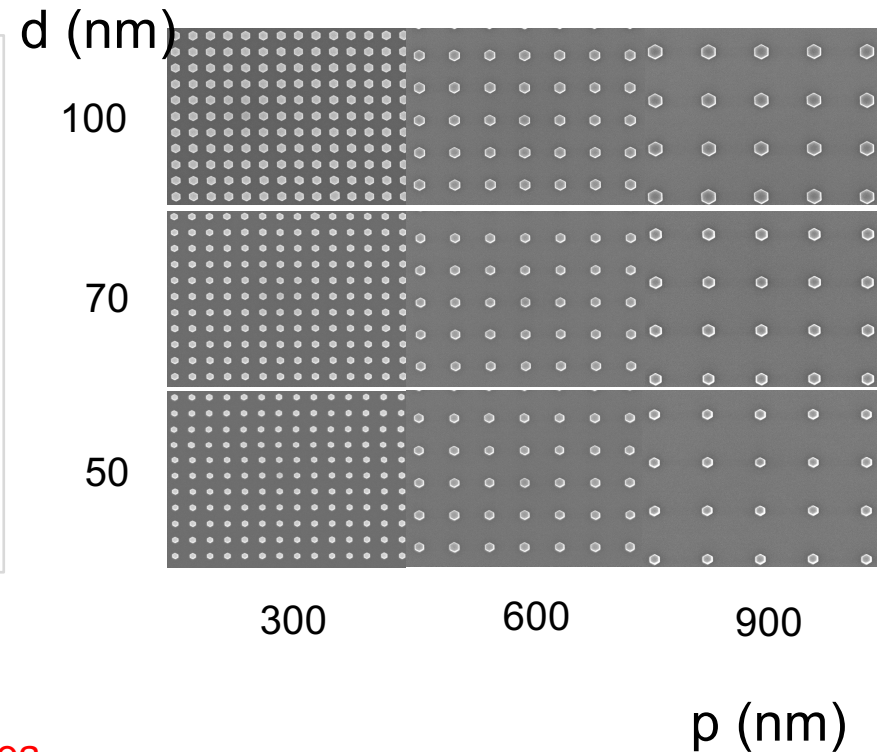
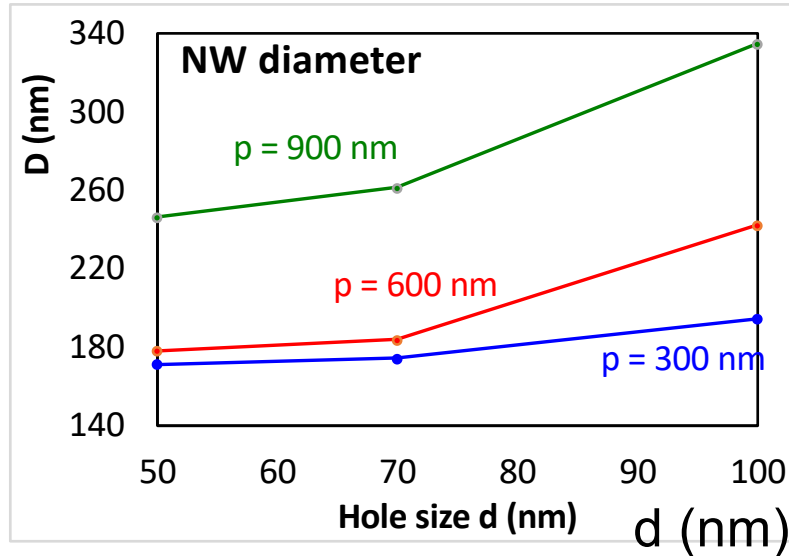
Top view SEM of n-GaAs arrays grown on (d,p) matrix

- $T_s = 850^\circ \text{C}$
- $V/\text{III} = 586$
- $\text{IV}/\text{III} = 4 \cdot 10^{-3}$
- Nom. thick. $T_n = 40\text{nm}$

- ✓ Perfect selectivity
- ✓ Hexagonal pillars
- ✓ Eye uniformity OK

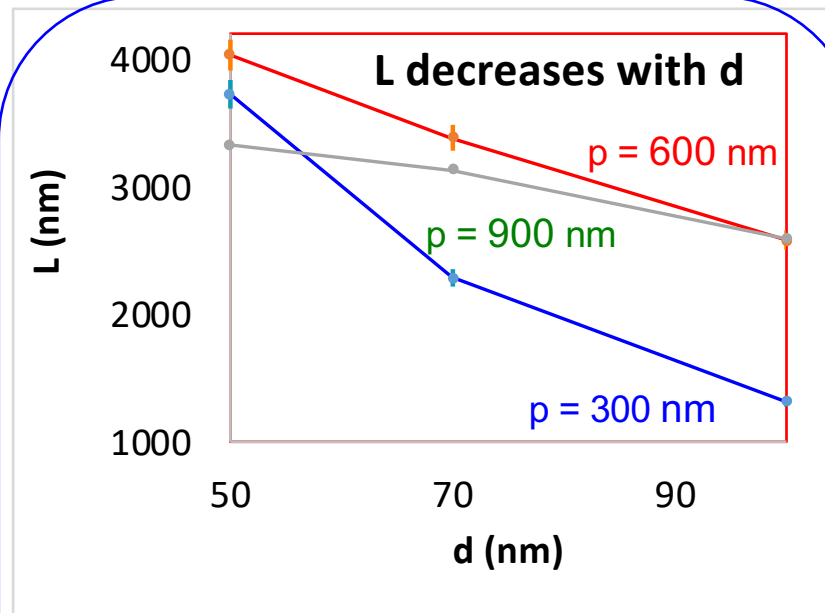
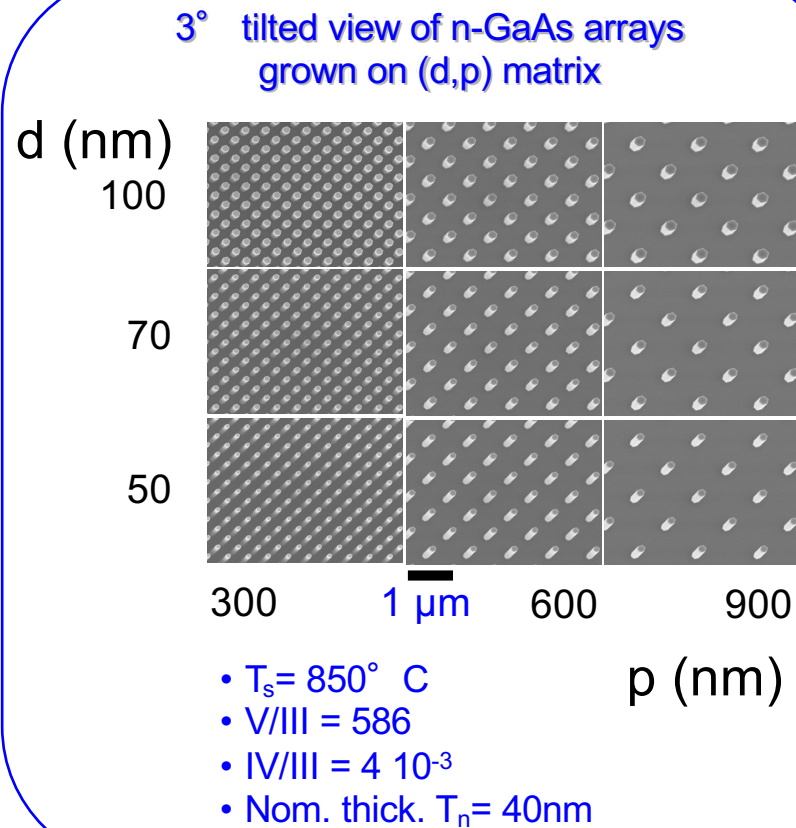


Influence of mask geometry on NW diameter



- ✓ D increases with p
- ✓ Precursors collected from masked area

Influence of mask geometry on NW length



- ✓ Eye uniformity OK
- ✓ L decreases with d
- ✓ L max at p=600nm

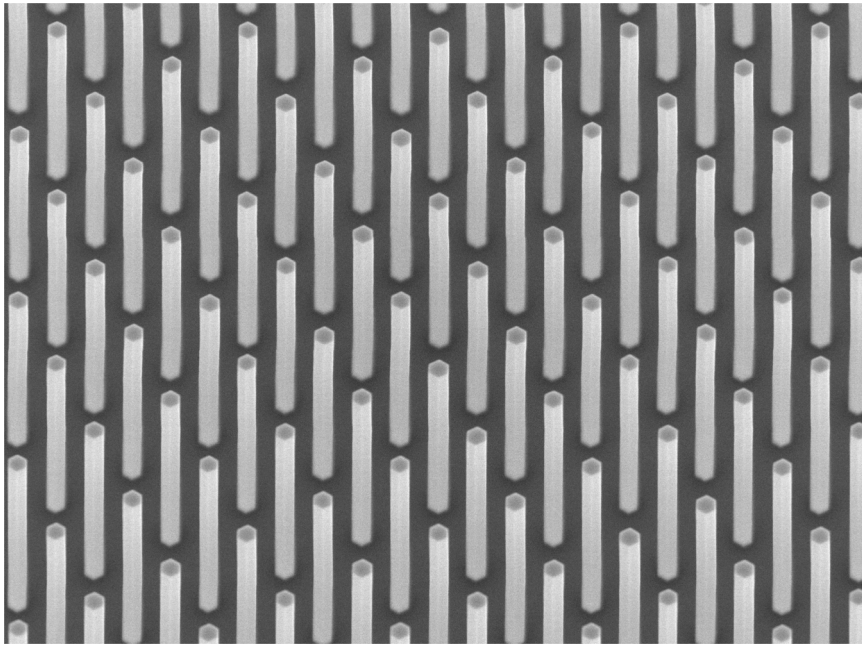
Uniformity of GaAs:Si NWs array

$T_s = 850^\circ \text{C}$, $\text{IV/III} = 4 \cdot 10^{-3}$

$p = 600 \text{nm}$
 $d = 50 \text{nm}$

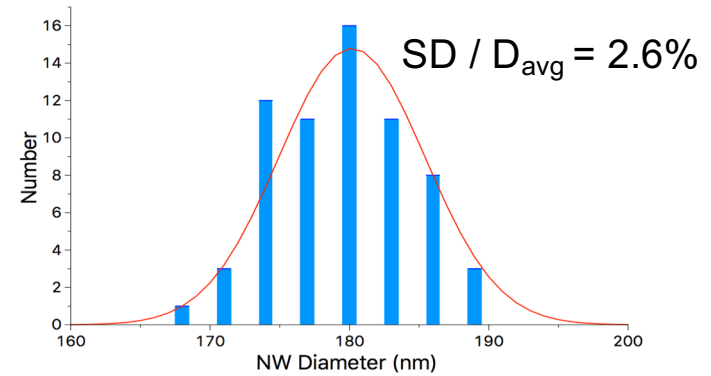
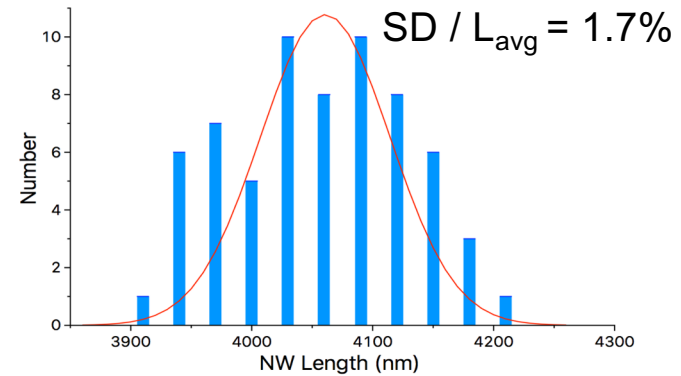


$D_{\text{avg}} = 180 \text{nm}$
 $L_{\text{avg}} = 4090 \text{nm}$



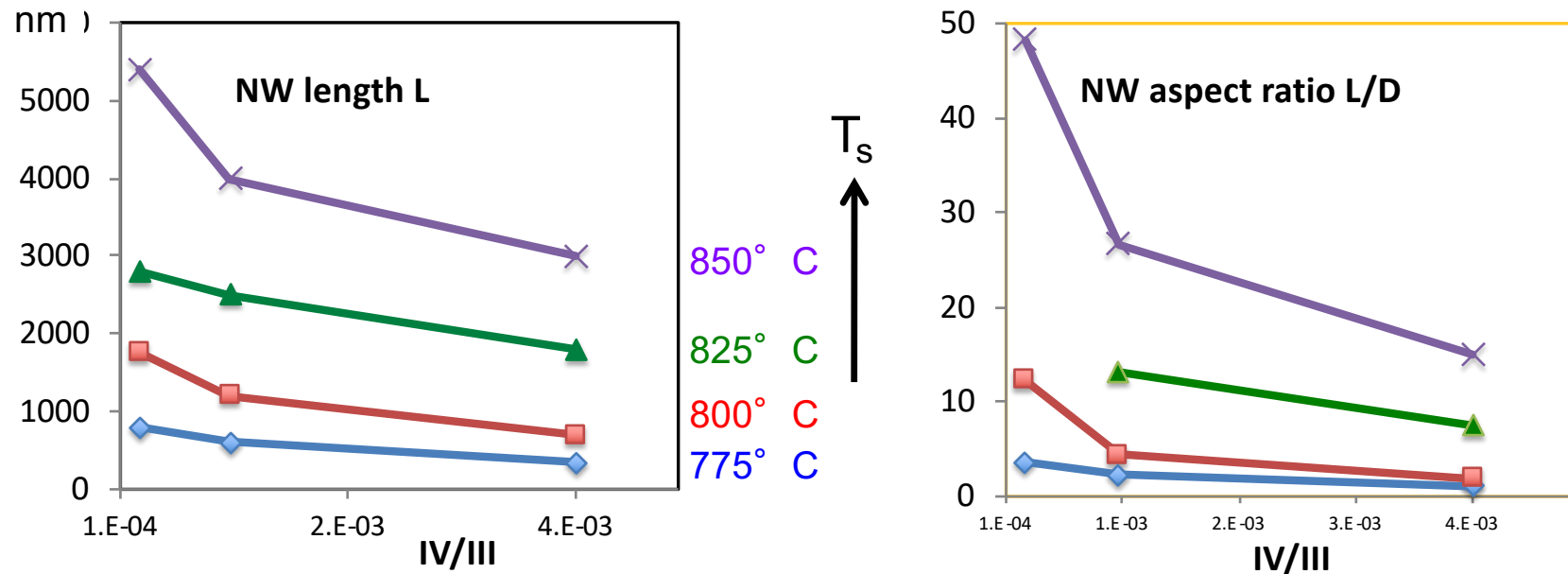
$\alpha = 15^\circ$

$SD = \text{Standard Deviation}$



Previous state of the art: SD/L : 5-10 %, SD/D : 1.6-4.5%, J. Jin *et al.*, Appl. Mat. Interfaces 2016

Effect of Si_2H_6 flow on GaAs:Si NW dimensions

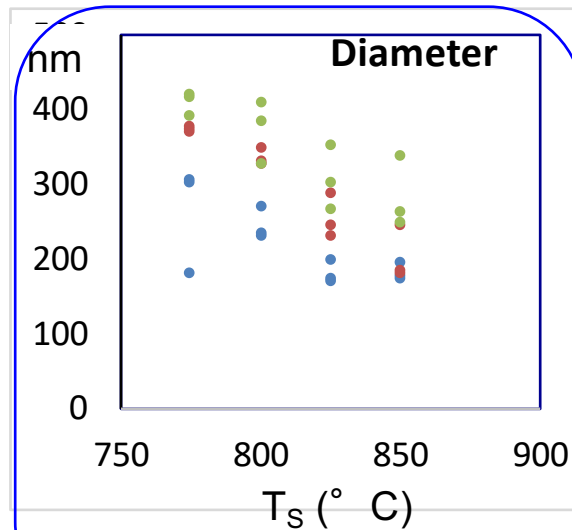


Si_2H_6 flow

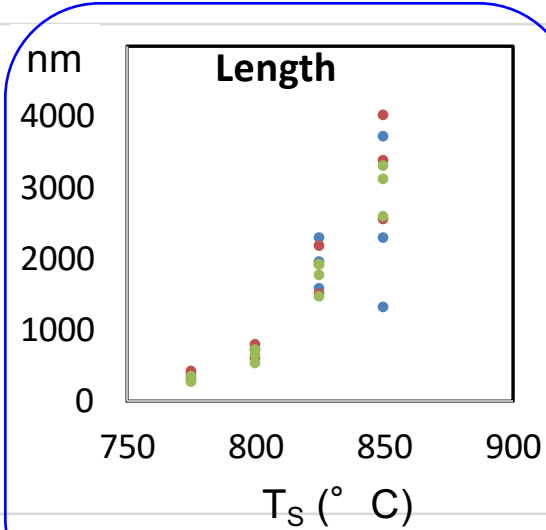
- **reduces** the growth rate on the top (111)B facet
- **increases** the growth rate on the lateral {110} facets
- **reduces** the NW aspect ratio
- **Similar behaviour** reported on InAs:Si NWs *

* S. Wirths *et al.*, J. Appl. Phys. 110 (2011)

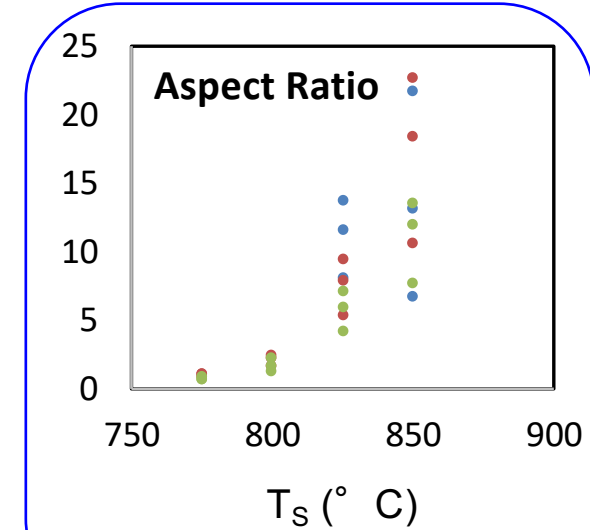
Effect of growth temperature on n-GaAs NW dimensions



D decreases with T



L increases with T



AR increases with T

IV/III: $4 \cdot 10^{-3}$

T_s : 775-850° C

• 300nm

p: • 600nm

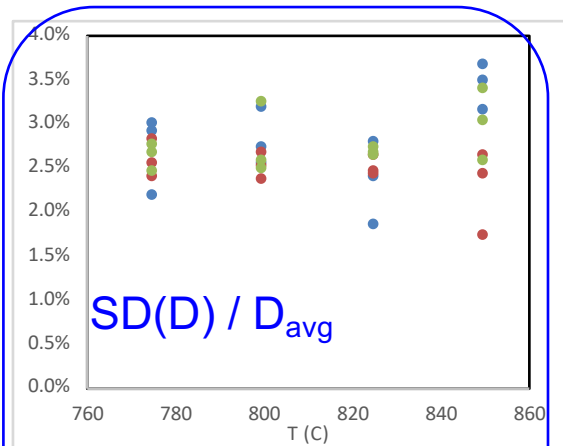
• 900nm

d: 50, 70, 100nm

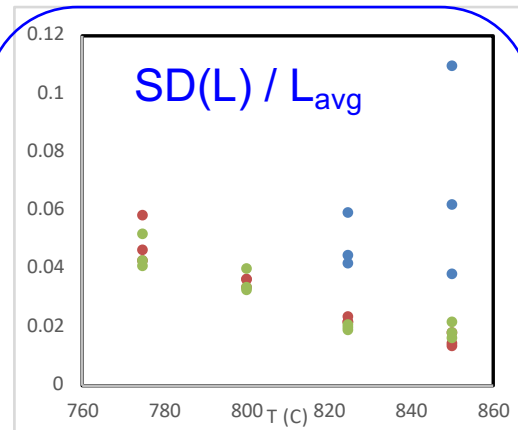
Increasing substrate temperature:

- **increases** axial growth rate (top (111)B facet)
- **reduces** lateral growth rate (side {110} facets)
- **increases** aspect ratio

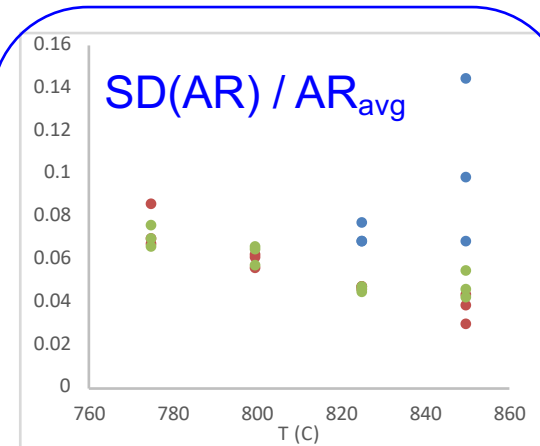
Effect of growth temperature on n-GaAs NW uniformity



Diameter uniformity
stable



Height uniformity
improves



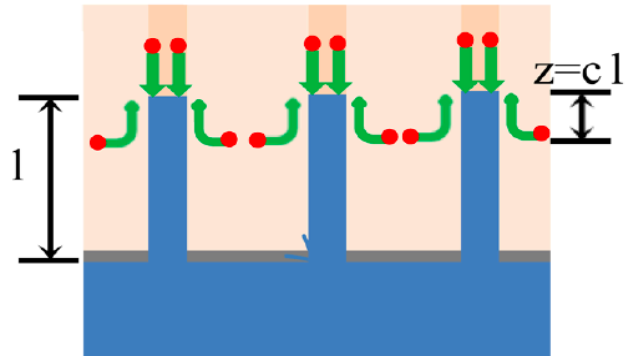
Aspect ratio uniformity
improves

IV/III: $4 \cdot 10^{-3}$
 T_s : 775 - 850° C

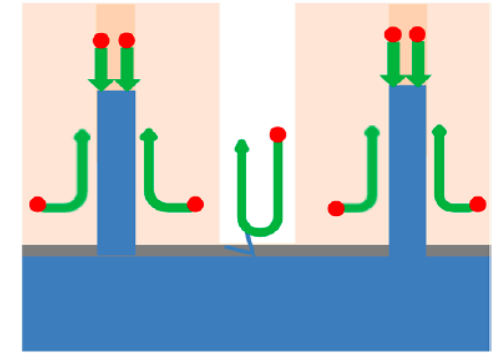
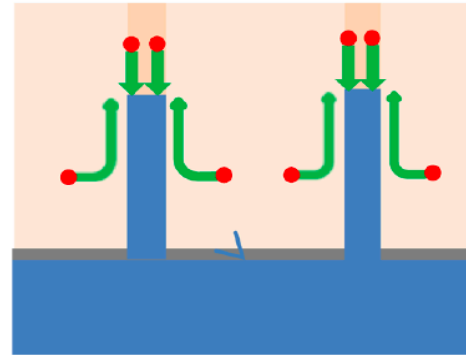
p: • 300nm
• 600nm
• 900nm

except for $p=300nm$

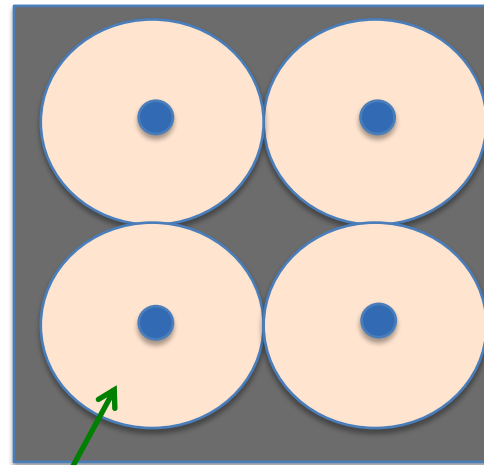
NW array uniformity and precursor collection surface



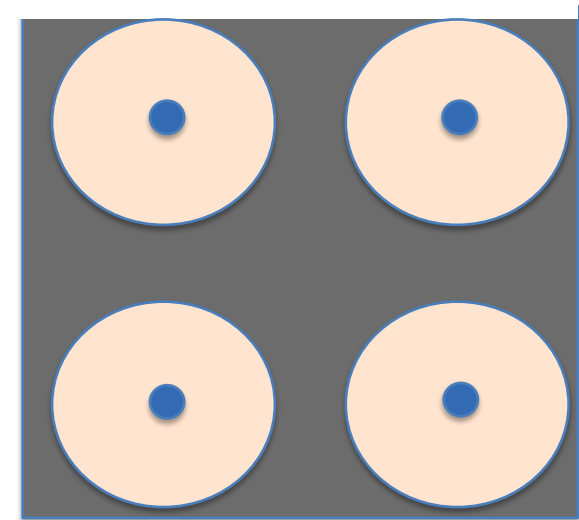
J. Jin *et al.*, Appl. Mat. Interfaces 2016



NW uniformity may be influenced by overlap transition in precursor collection areas

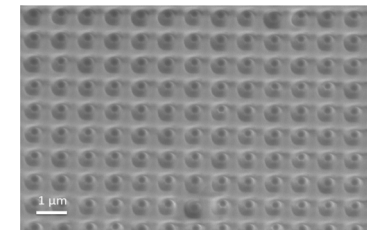
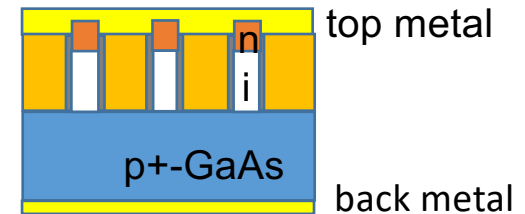
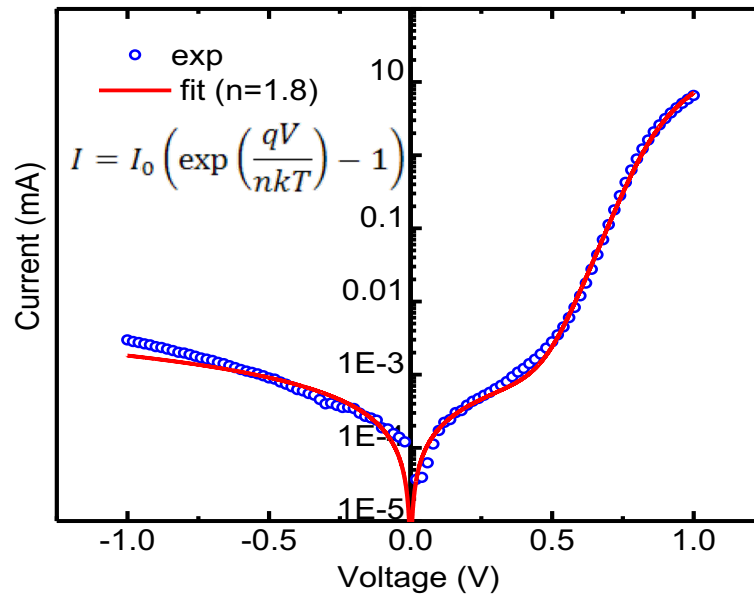


MO collection area



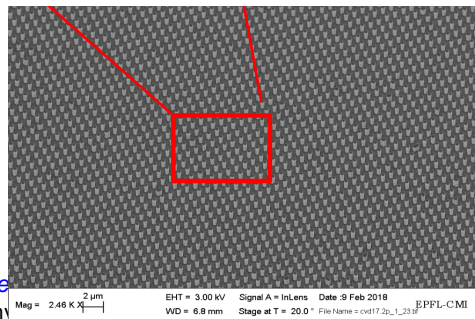
Proof of concept: p-i-n junction GaAs NWs arrays

Courtesy of J. Leuthold, ETHZ



After contact layer deposition

Diode behaviour confirms
effective n-type doping



Selective area MOVPE of GaAs NWs: a summary

- Very high uniformity n-GaAs NWs arrays
in the 775-850° C growth temperature range
- Dramatic influence of Si₂H₆ on NW morphology
- n-GaAs NWs integrated in p-i-n diodes for solar cells
- Future: NWs + QDs for improved QD light extraction