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Growth of (In,Ga)-(As,P) Nanowires by MOCVD

J.G. Cederberg, A.A. Talin,
D.P. Nelson, K.C. Cross,
G. Subramania
Sandia National Laboratories

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Outline

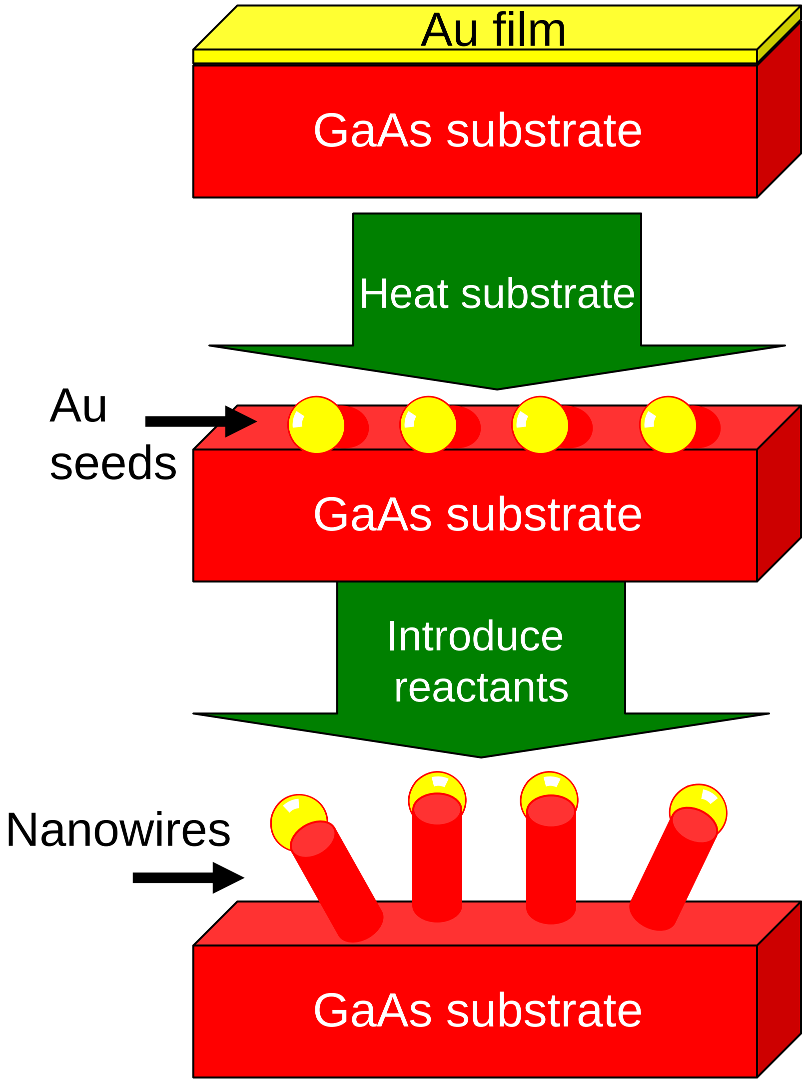
- Motivation
- Process details
- Initial growth demonstration of (In,Ga)-(As,P) nanowires
- Morphology sensitivity of GaAs nanowires
  - Effects of growth temperature and AsH_3 partial pressure
- Nanowire growth model
- Oriented growth of GaAs nanowires
- Controlled size and placement of GaAs nanowires
- Doping issues for (In,Ga)(As,P) nanowires
- Conclusions

Motivation

- Properties of materials modified by reducing dimensions (2D to 1D to 0D)
  - e.g. quantum wells, carbon nanotubes, quantum dots
- New physics and applications may be enabled by nanostructures
  - Photonics
  - Electronics
  - Sensors
- Reduced dimensions could allow integration of dissimilar materials
  - Eliminate defects due to lattice mismatch

Nanowire Growth

- Use Vapor Liquid Sold(VLS)/Vapor Solid Solid (VSS) technique
  - Use Au as “catalyst” for nanowire growth
  - Dispersed by anneal above growth temperature
- Use metal-organic chemical vapor deposition (MOCVD) to introduce reactants
- Nanowires can propagate normal to many crystal planes

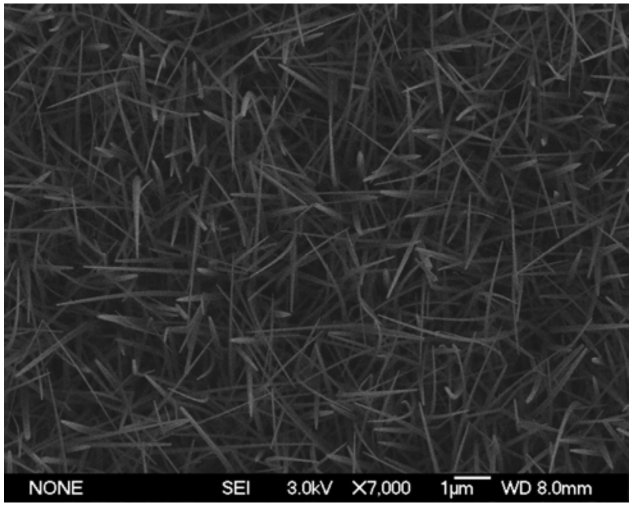


Initial Growth Conditions

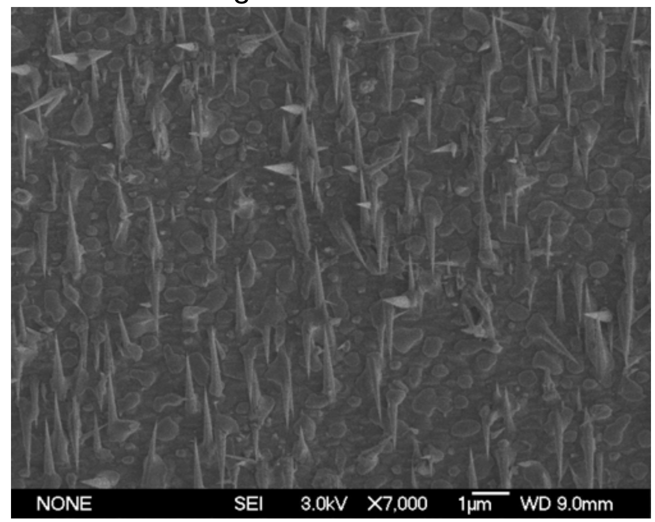
- Growth performed in vertical rotating disk growth chamber held at 70 Torr using H_2 ambient.
- Use GaAs substrates covered with 1 ± 0.5 nm of Au
- Au dispersed by heating sample under AsH_3 to 650°C for 10 min
- Cooled to nanowire growth temperature
- Introduced appropriate gases
  - triethylgallium, trimethylindium, arsine, or phosphine
- All samples grown for 50 min

Nanowires growth on GaAs(100)

GaAs 450°C, AsH_3 PP = 0.07 Torr, CVD7925

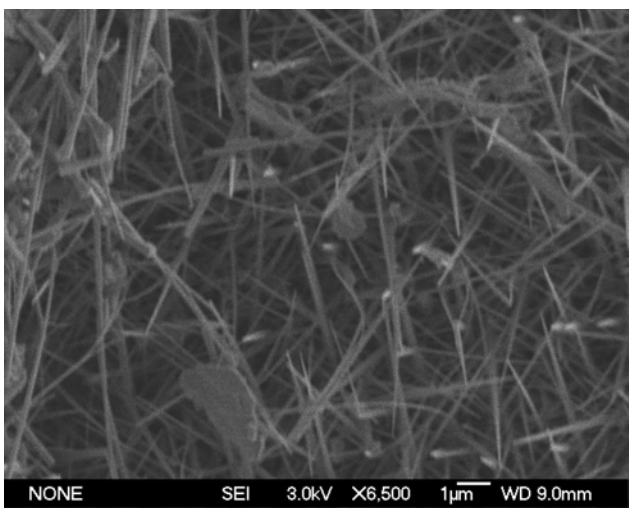


GaP 450°C, PH_3 PP = 0.14 Torr, CVD7908

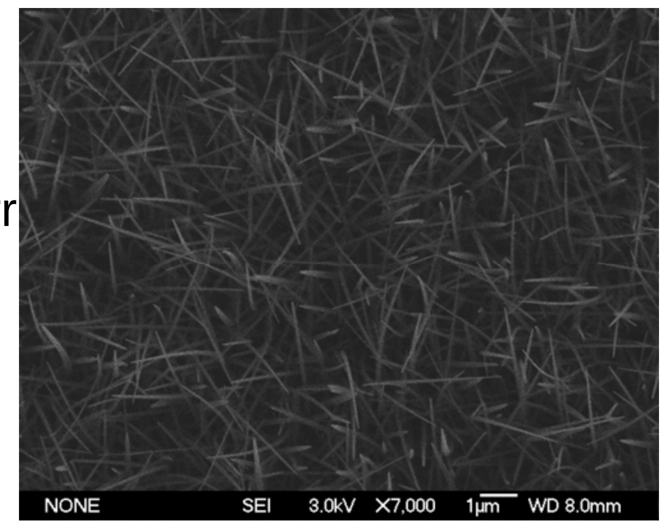


P_{TEGa} = 1.4E-4 Torr

InAs 400°C, AsH_3 PP = 0.07 Torr, CVD7905



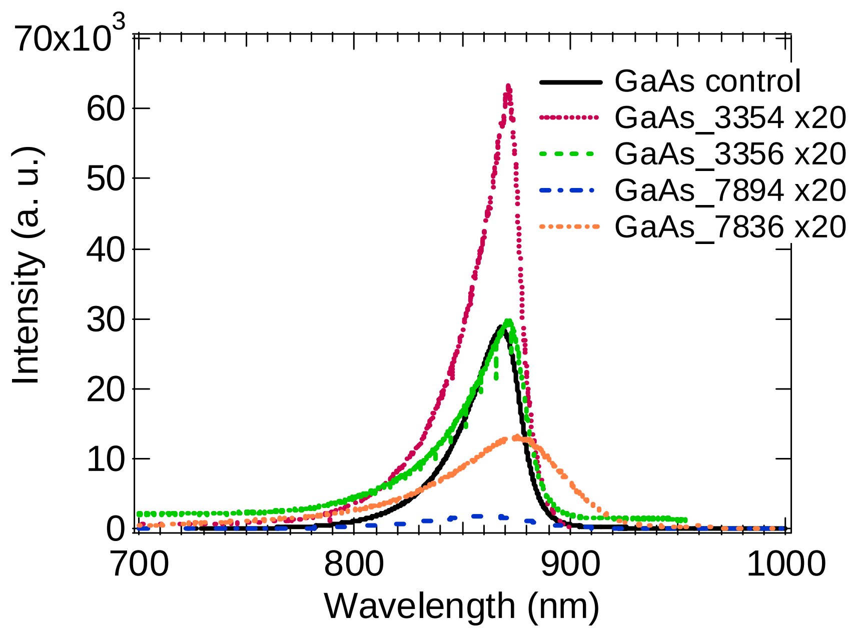
InP 450°C, PH_3 PP = 0.17 Torr, CVD7900

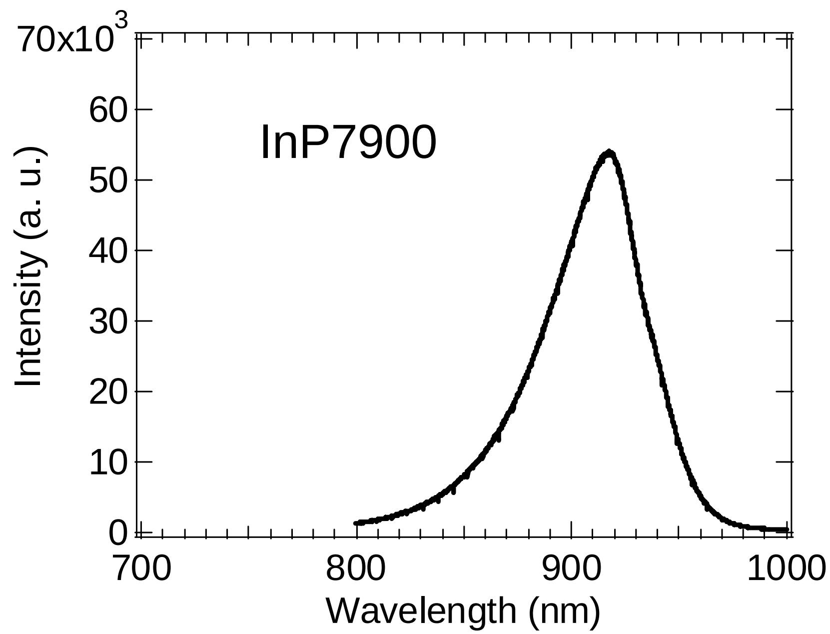


P_{TMIn} = 1.4E-4 Torr

Photoluminescence from GaAs and InP nanowires

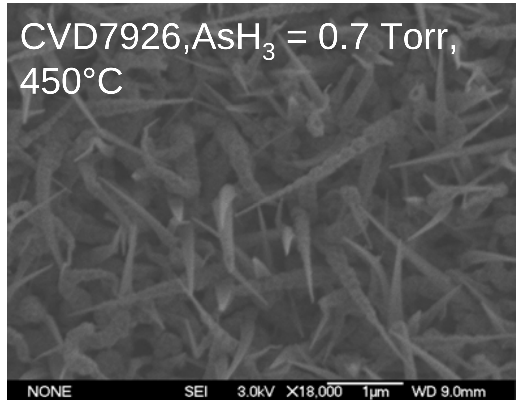
- Observed room temperature PL from InP and GaAs nanowires
  - Resonances correspond to bandgap energies for bulk films
    - Suggests are nanowires are too large to observe quantum effects
  - FWHM for resonance is broader than for bulk films
    - InP nanowires have 88 meV FWHM, undoped planar InP has 39 meV FWHM
- Small signal from nanowires expected given small amount of material

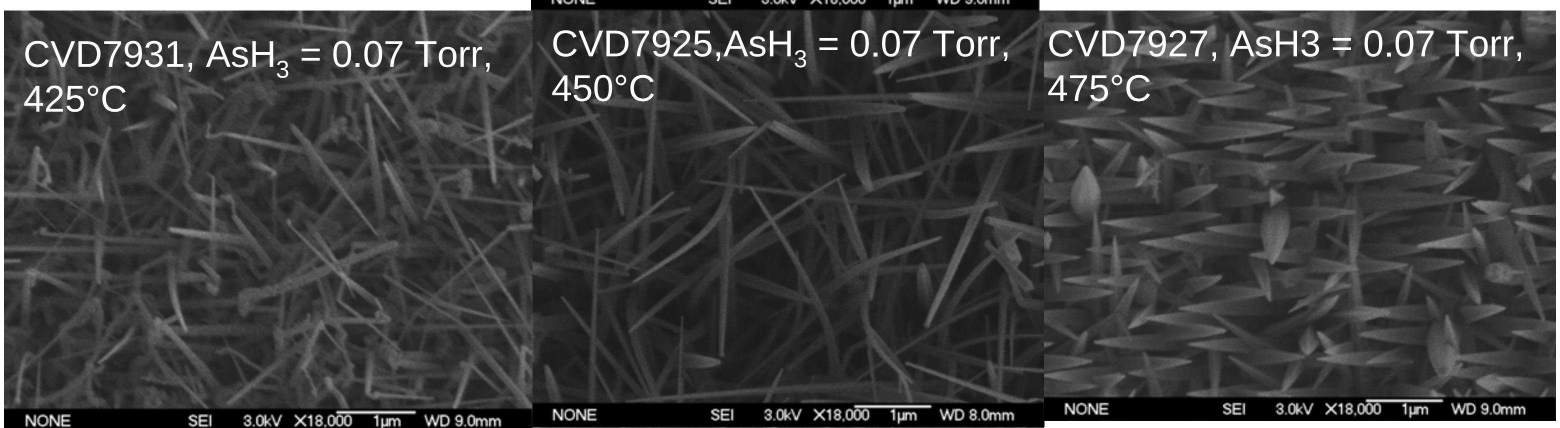


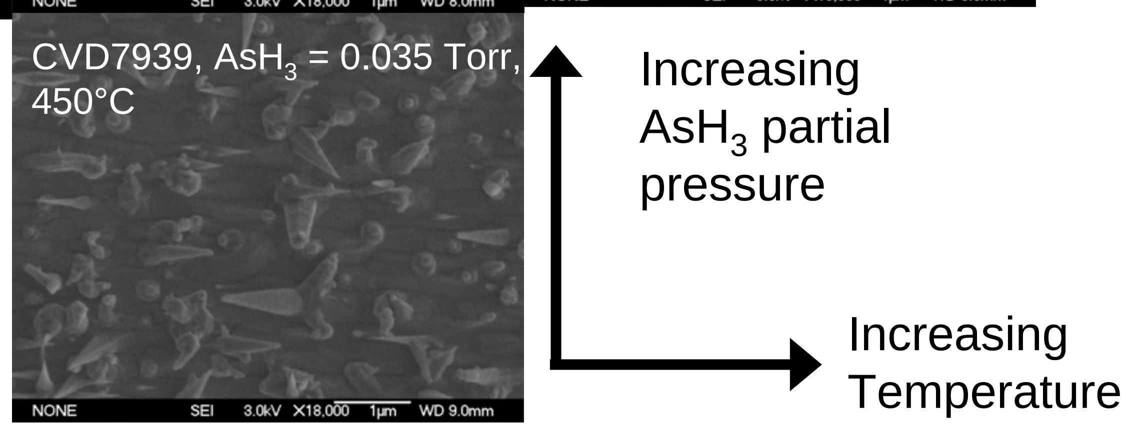


Process Sensitivity for GaAs Nanowires

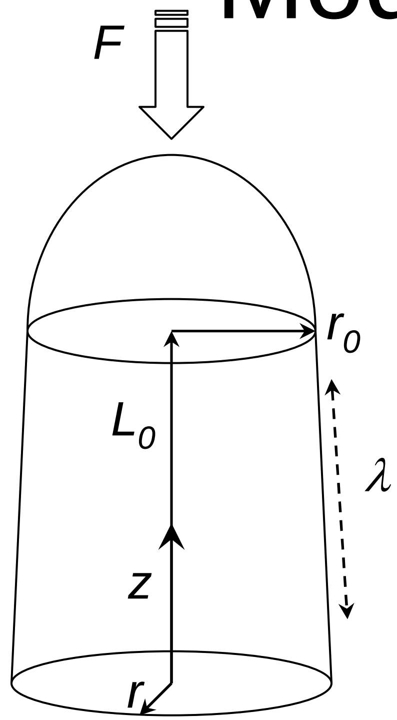
P_{TEGa} = 1.4E-4 Torr
for all experiments







Model of nanowire tapering



First order ODE with initial condition $r = r_0$ at $z/L_0 = 1$

$$\frac{dV}{dt} = 2\pi r^2 Fv + 2\pi r \lambda Fv$$ Rate of nanowire growth

$\lambda = (D_{III}\tau)^{1/2}$

$$\frac{dV}{dt} = \pi r^2 \frac{dz}{dt} + 2\pi r z \frac{dr}{dt}$$ Volume derivative with respect to time

$$\pi r^2 \frac{dz}{dt} + 2\pi r z \frac{dr}{dt} = (2\pi r^2 + 2\pi r \lambda) Fv$$ Eliminate time derivative of volume

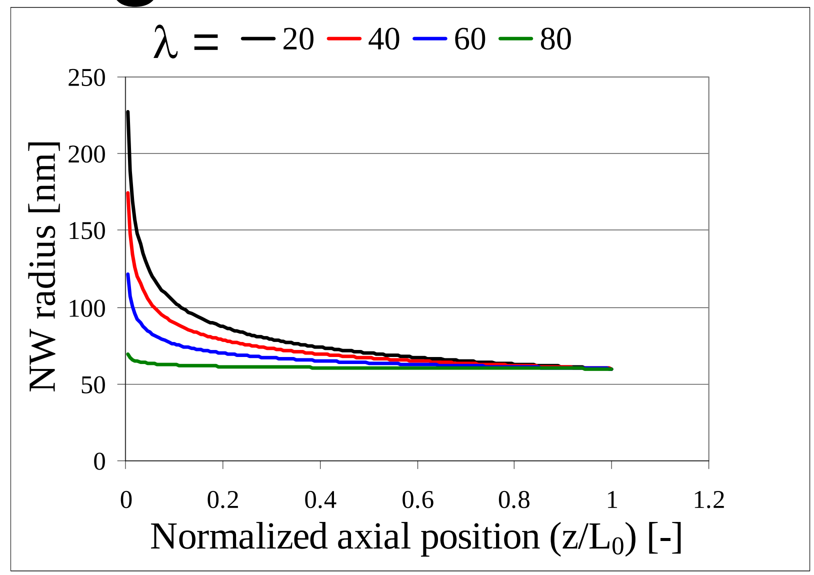
$$\frac{dr}{dz} + \frac{r}{z}\left(\frac{R_z - 2Fv}{2R_z}\right) = \frac{1}{z}\frac{Fv\lambda}{R_z}$$ Divide by dz/dt and rearrange

$$r(z) = \frac{2\lambda Fv}{R_z - 2Fv} + \left(r_0 - \frac{2\lambda Fv}{R_z - 2Fv}\right)\left(\frac{z}{L_0}\right)^{-\frac{R_z - 2Fv}{2R_z}}$$

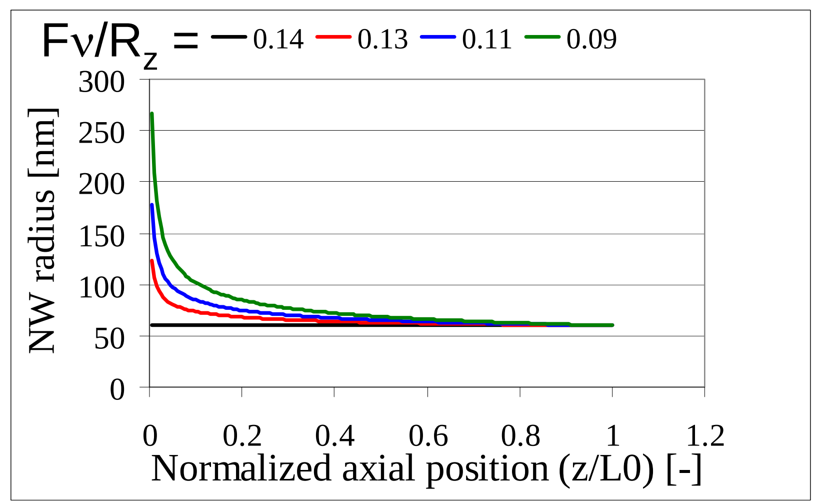
Effect of model parameters on tapering

- Two parameters impact radial profile
  - Vary diffusion length (λ) through temperature or hydride partial pressure
  - Vary group III flux/axial growth rate ratio ($F\nu/R_z$) through temperature (evaporation)
- Model doesn't include deposition on nanowire sidewalls
  - Can't predict the sidewall faceting observed at high temperatures and high hydride partial pressures

$F\nu/R_z$ = constant

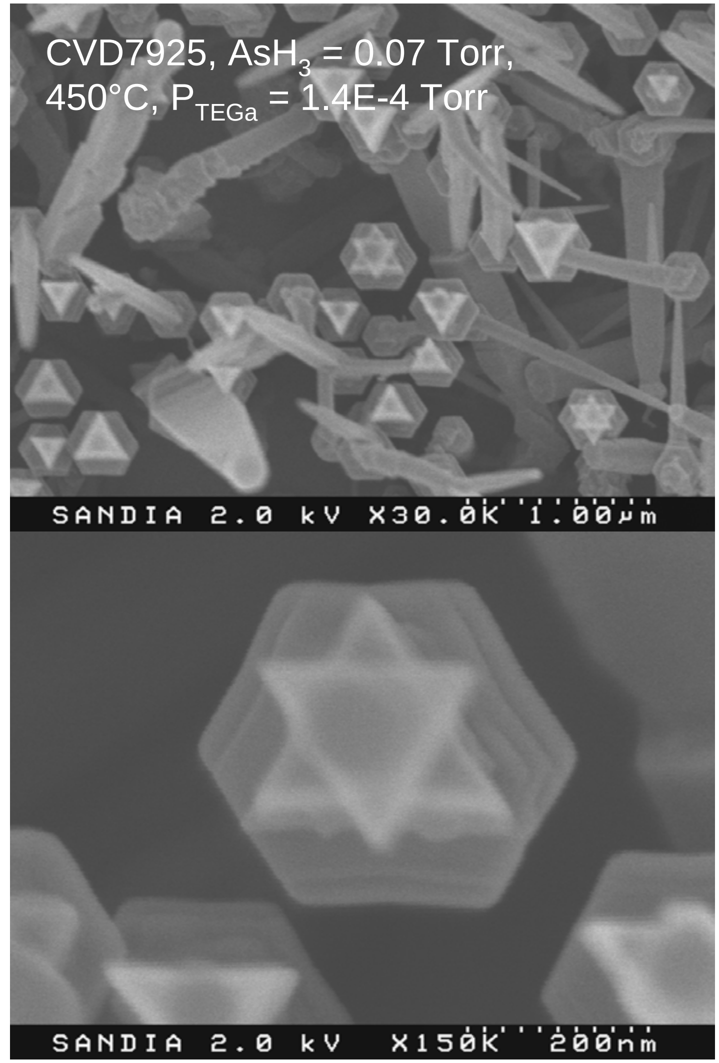


λ = constant



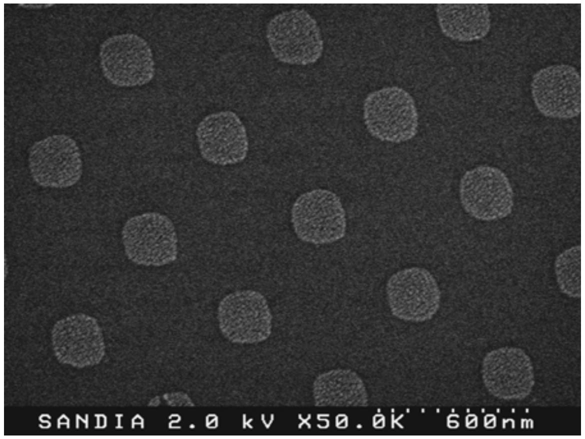
Oriented Growth of GaAs Nanowires on (111)As substrates

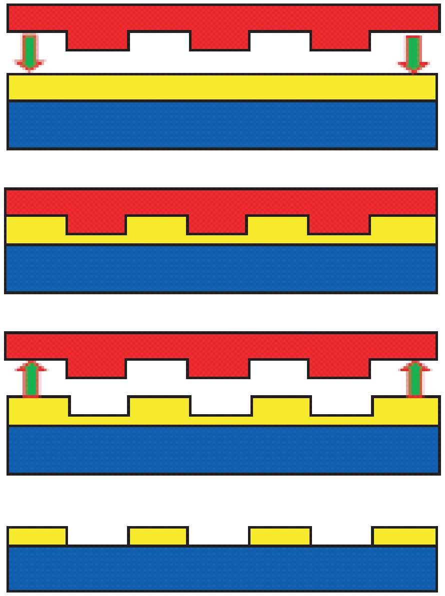
- Performed growth on (111)As utilizing coalesced Au films following previous recipe
- Nanowires start growth normal to (111)As surface
  - Shows that growth proceeds by 60° rotation of crystal planes
  - Suggests that nanowires are wurzite (hexagonal) instead of zinc blende (cubic)
  - Form kinks that allow propagation in other directions



Nano-Imprint Lithography (NIL) – a route to controlled nanowire size and placement

- NIL allows periodic features to be generated
- Forms mask for Au deposition and liftoff to form localized seeds

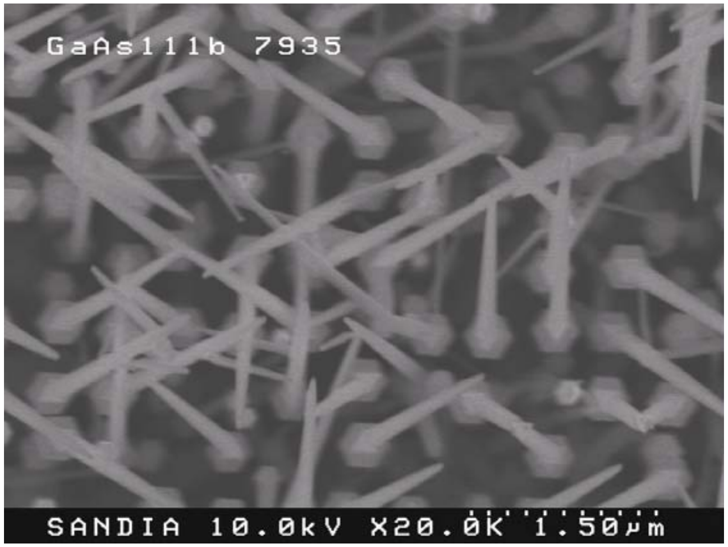




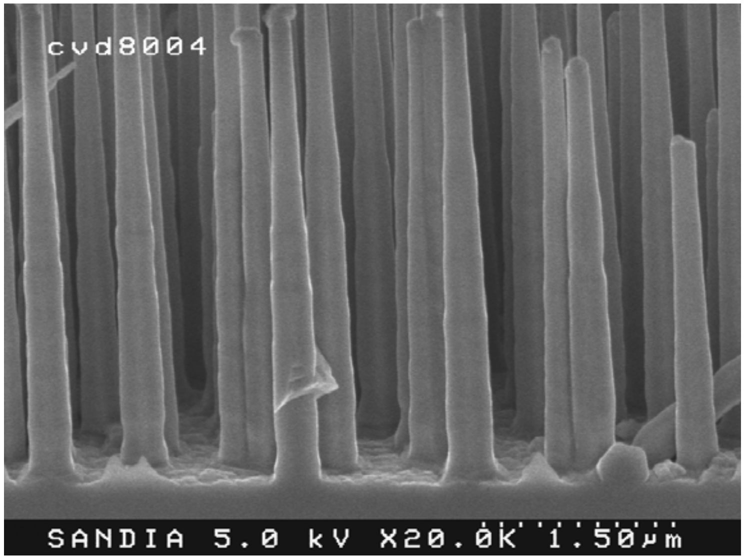
From L.J. Guo,
J. Phys. D, **37**,
(2004), R123

NIL seeded nanowires

3 nm Au



1 nm Au



Doping issues with VLS/VSS Nanowires

- Devices require independent control of Fermi level
  - Accomplished through doping
- Temperatures used for VLS/VSS growth is dominated by background impurities
  - Carbon is primary background impurity in MOCVD at low growth temperatures
  - Exacerbated due to incomplete cracking of metal-organics
- Perform SIMS analysis on planar films due to difficulties doing chemical analysis on nanowires

Background impurities in III-V films

- Planar GaAs grown at 450°C is dominated by intrinsic carbon background
  - 1E19 cm^{-3}
- PL doesn't show bandgap reduction expected for heavily p-type GaAs
- Suggests that GaAs nanowires are compensated ($N_a = N_d$)
  - Carbon acting like both donor and acceptor
  - SEM images of nanowires show charging effects at high magnifications
- Slightly higher growth temperature (500°C) removes compensation allows planar films to be doped n-type at 5E17 cm^{-3} with Si.

- Planar InP grown at 450°C shows also shows carbon concentration
  - 4E17 cm^{-3}
- TMIn decomposes more efficiently at low temperatures
- Carbon is probably a donor in InP
- <u>*Speculate*</u> that InAs will have similar background doping level
  - Carbon is a donor in InAs
- Charging of InAs and InP nanowires not an issue

Conclusions

- (In,Ga)-(As,P) nanowires can be synthesized by MOCVD using VLS/VSS technique
- Tapering of GaAs nanowires depends on arsine partial pressure and growth temperature
- Growth on (111)As substrates results in preferential growth of orthogonal nanowires
- NIL seed formation on (111)As substrates is a route to control of nanowire orientation and placement
- Controlled doping of GaAs nanowires is a challenge due to high background carbon levels
- Doping of InP and InAs nanowires appears easier