Ge Nanowire Epitaxy by CVD: Shape Control, Orientation Selection and Surface Passivation

Hemant Adhikari[1], Prof. Paul C. McIntyre[1], Prof. Christopher E.D. Chidsey[2]

1. Department of Materials Science and Engineering, Stanford University.
2. Department of Chemistry, Stanford University.

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Motivation and Challenges

Continuation of Moore's law: Lithography independent processes feasible for defining minimum feature in device.

Improve interface between high- k and nanowires.
- Control interface states.

Why nanowires?

Why passivation?

Ge Nanowire Epitaxy by CVD: Shape Control, Orientation Selection and Surface Passivation

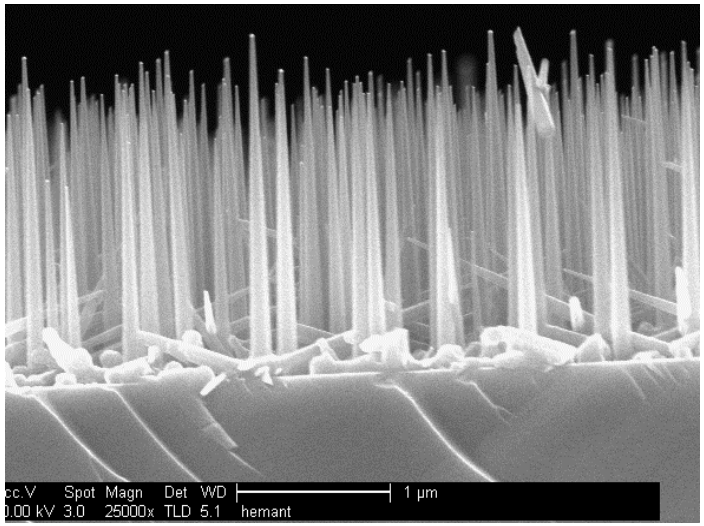
Why Germanium?

Higher intrinsic carrier mobility.
Compatibility with high-k and Si.
Lowest thermal budget among nanowires by CVD.

Why epitaxy? What shape Control? Where orientation Selection?

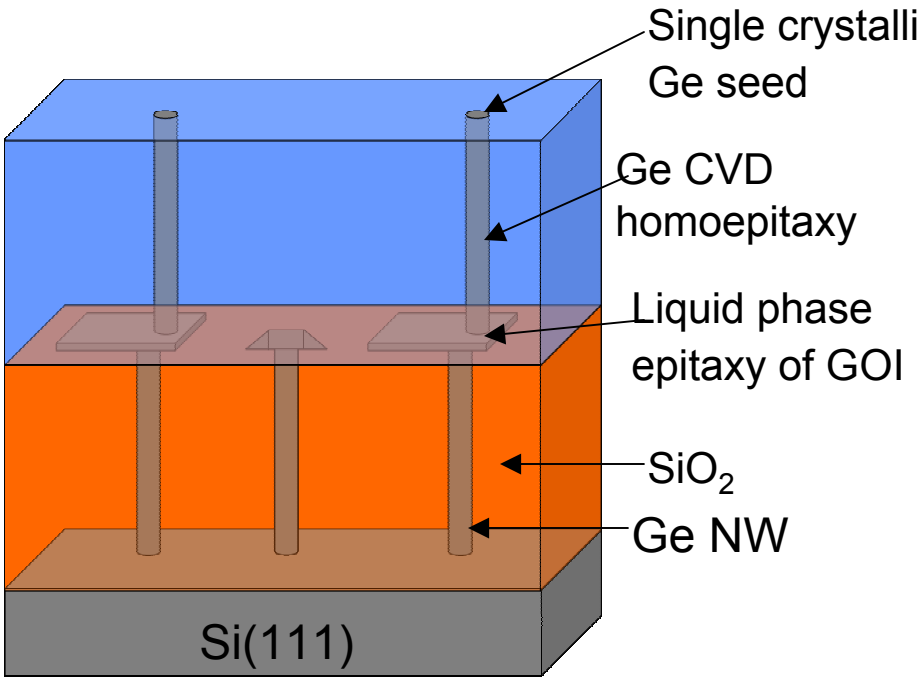
3D nano-electronics:
Vertically aligned nanowires for ultra high density nanoscale device arrays.
Controlled crystalline orientation by epitaxy

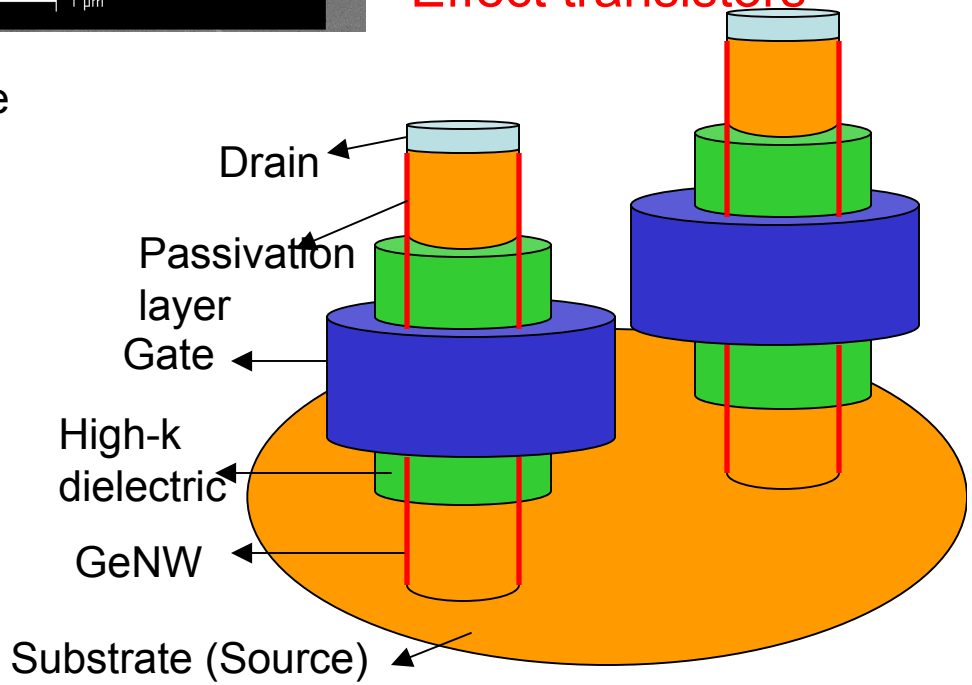
Potential applications:



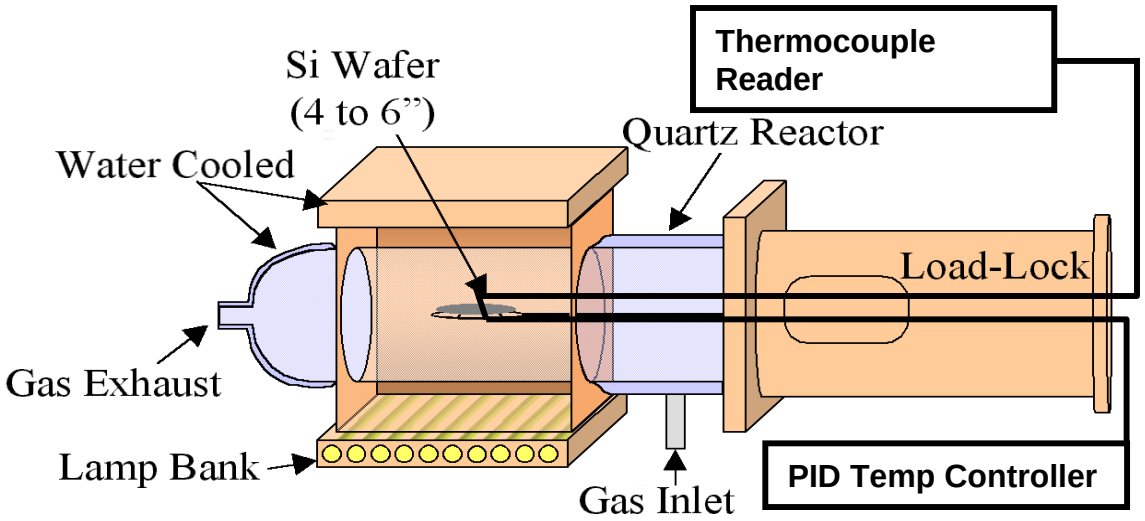
Transfer of Epitaxy

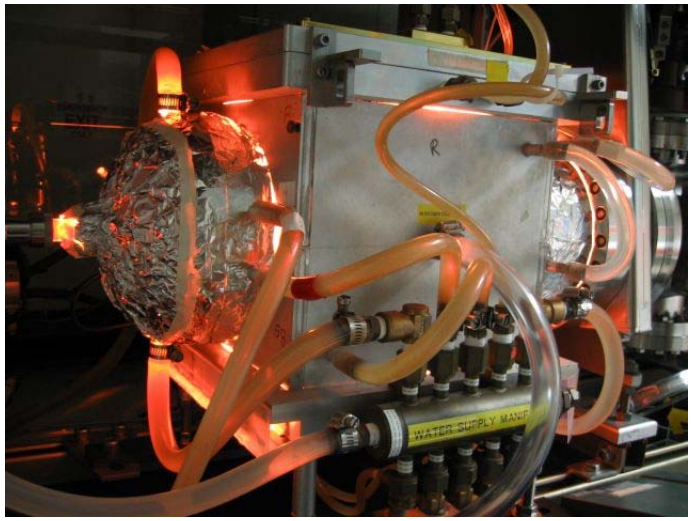
Vertical Field Effect transistors



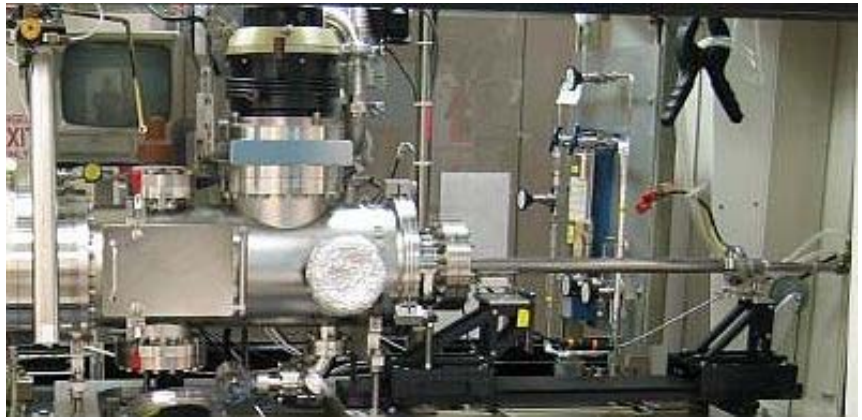


Nanowire Growth Chamber

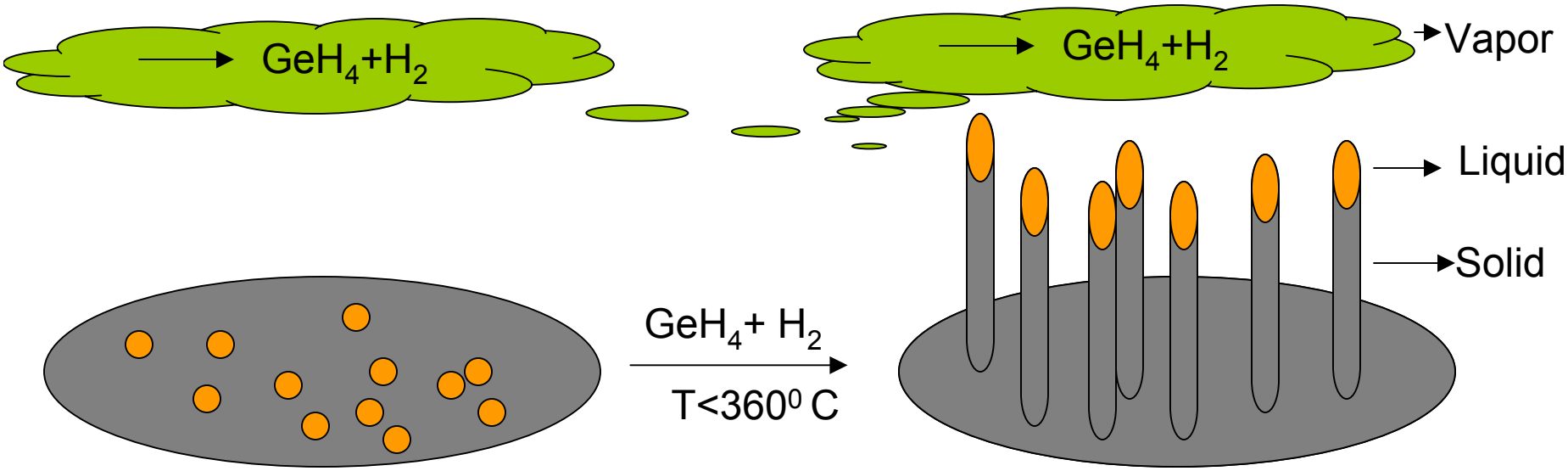




- Converted cold-wall SiGe epi reactor to low temperature NW CVD growth system. (Acknowledgement: Prof. Judy Hoyt)
- Cold wall, lamp heated CVD reactor
  a) 11 independent gas flow channels for different gases (SiH_4, GeH_4, B_2H_6, PH_3, H_2).
  b) accommodate whole wafers (up to ~6" wafers)



Growth mechanism?

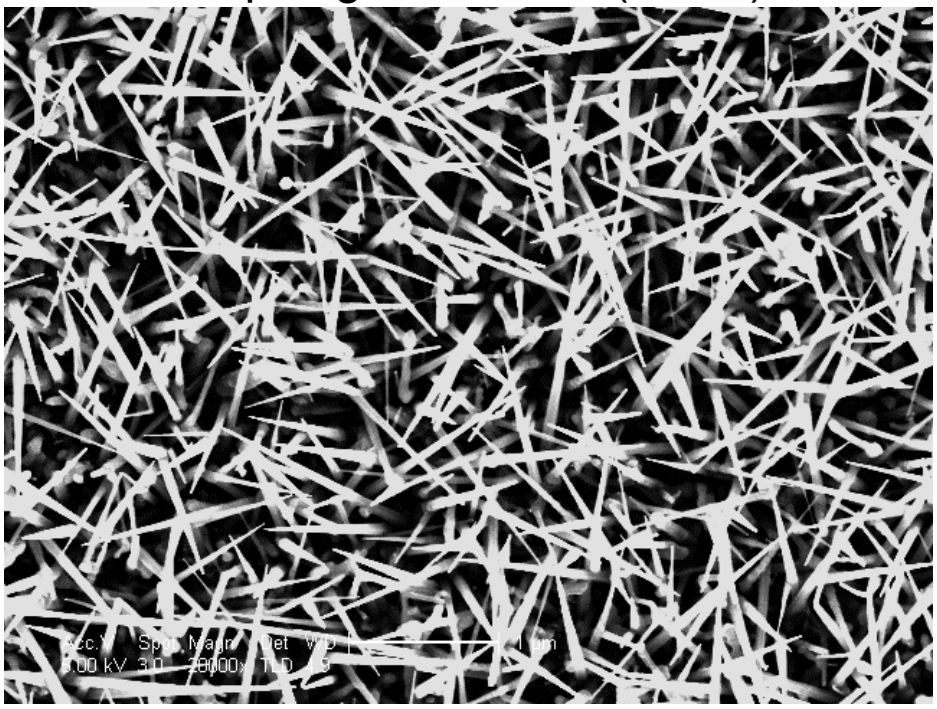


Most cited growth mechanism: VLS

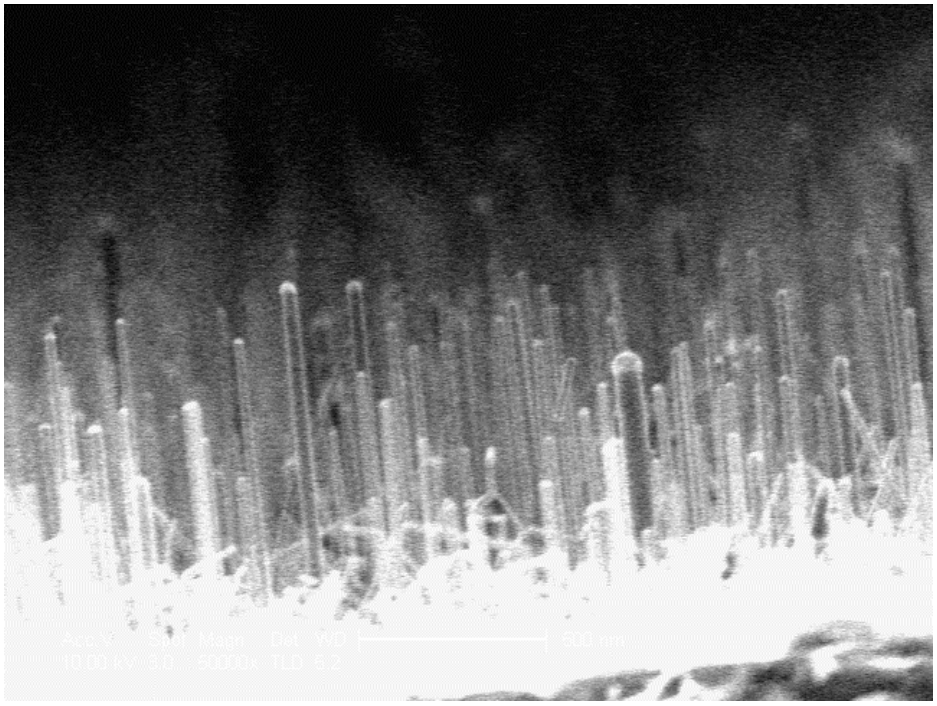
- Catalyst particles at moderately high temperature (much below melting point of pure catalyst).
- As reactive gas species dissolve into the catalyst, melting point is lowered. Forms Ge-Au melt.
- As the catalyst particle gets supersaturated with Ge, it nucleates crystalline Ge. Nanowire grows in length.
- Catalyst particle remains at the top. Nanowire diameter constrained by catalyst size.

SEM images of GeNWs on Si(111) substrate

Tc=350^{0}C, p_{GeH4}=0.273, t=30mins
Sample Prep: **Native oxide**, spin APTES, dip in gold colloids (10nm)



T_c=350^{0}C, p_{GeH4}=1.82, t=15mins
Sample Prep: **HF last Si(111)**, 2nm of evaporated Au.



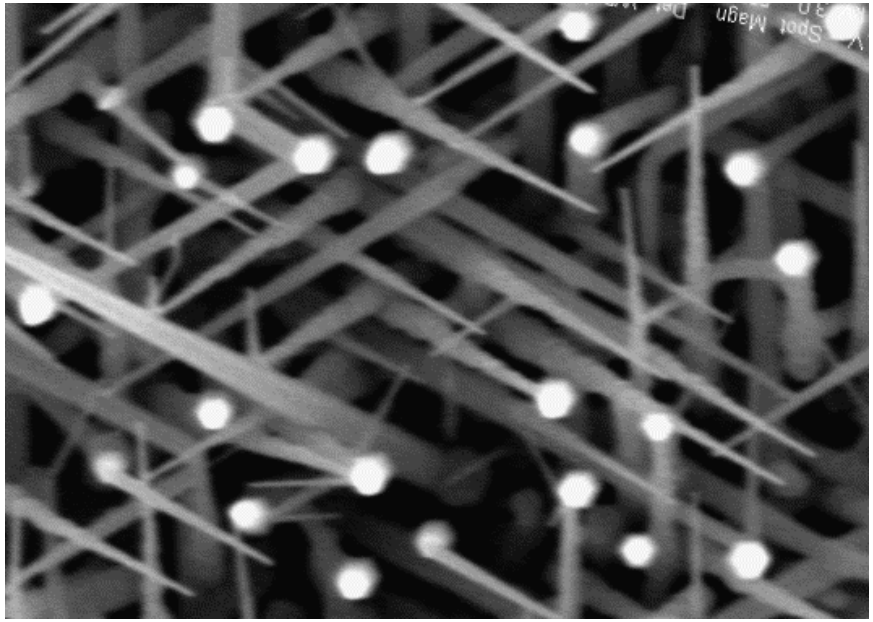
Observations:

- Dense array of randomly oriented GeNWs on Si substrate with native oxide.
- Wires are growing epitaxially on HF last Si(111). It's hard to get epitaxially aligned wires reproducibly on Si(111). Study other substrates which might favor epitaxy.

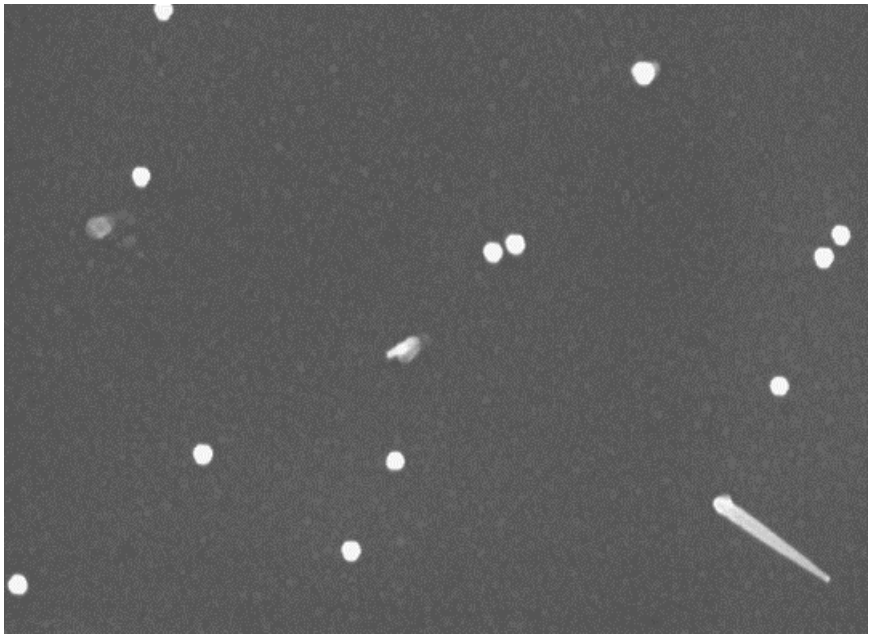
Epitaxial growth of GeNWs on Ge(111) substrate

T_c =350^0 C, P_{tot}= 30 torr, GeH_4= 5 sccm, H_2= 550 sccm, p_{GeH4}=0.273, t=30mins

Sample Prep: Spin APTES, dip in Au colloids 10nm dia



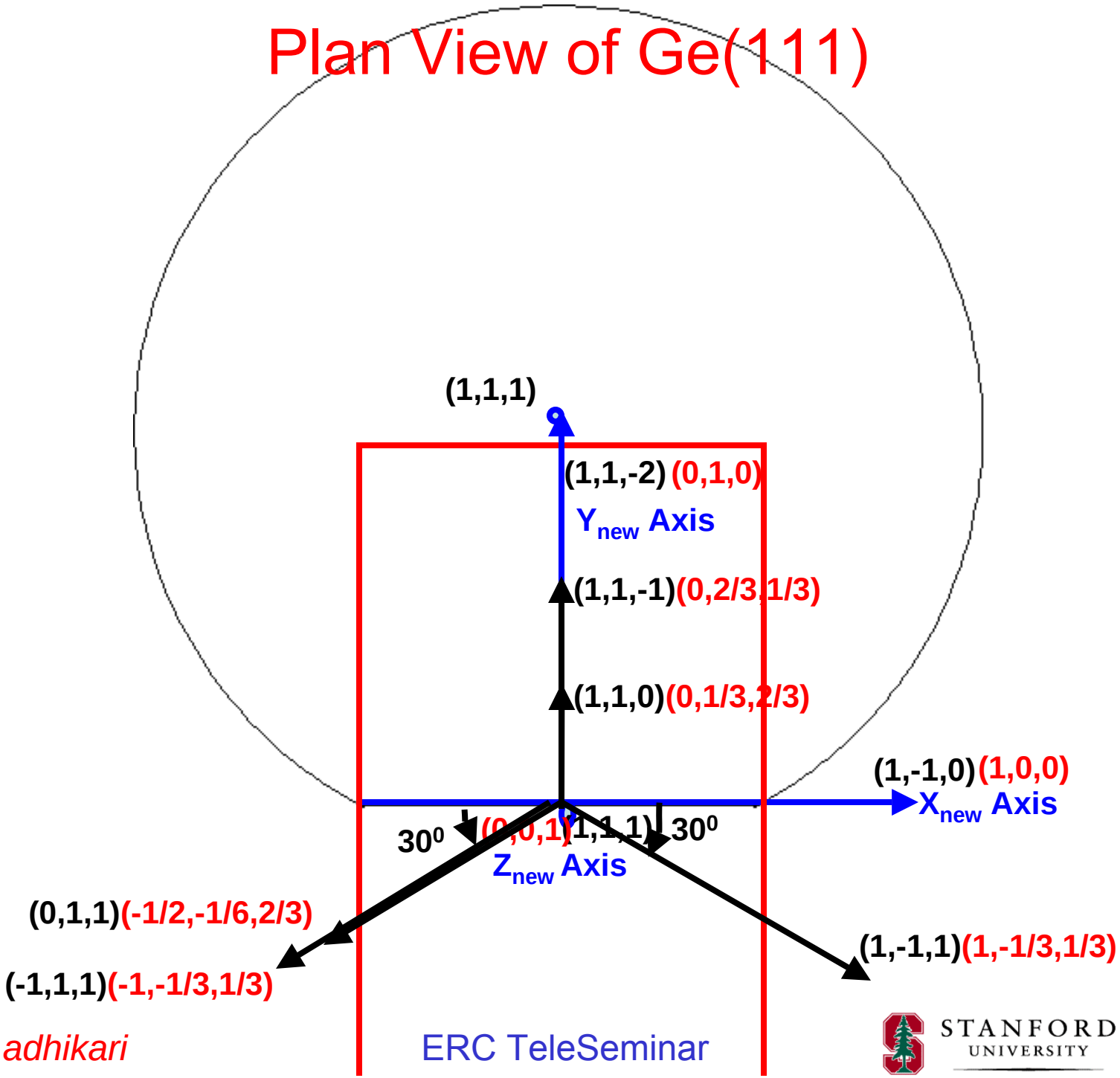
Sample Prep: Spin Au colloids 10nm dia



Observations:

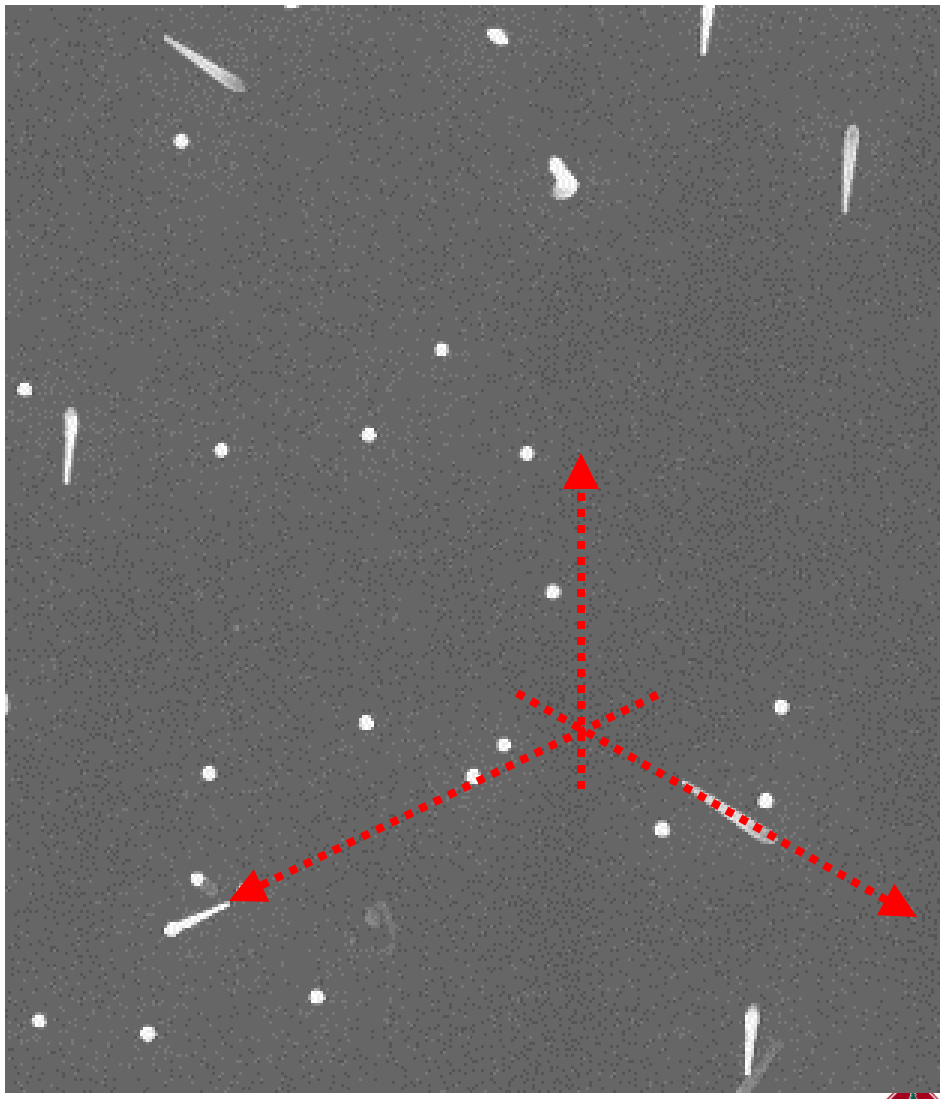
1. Epitaxially aligned nanowires could be grown reproducibly.
2. Most wires seem to be growing vertically up from the substrate. These wires appear as bright spots in plan view. Other wires are growing at roughly 120^{0}C to each other.

Plan View of Ge(111)

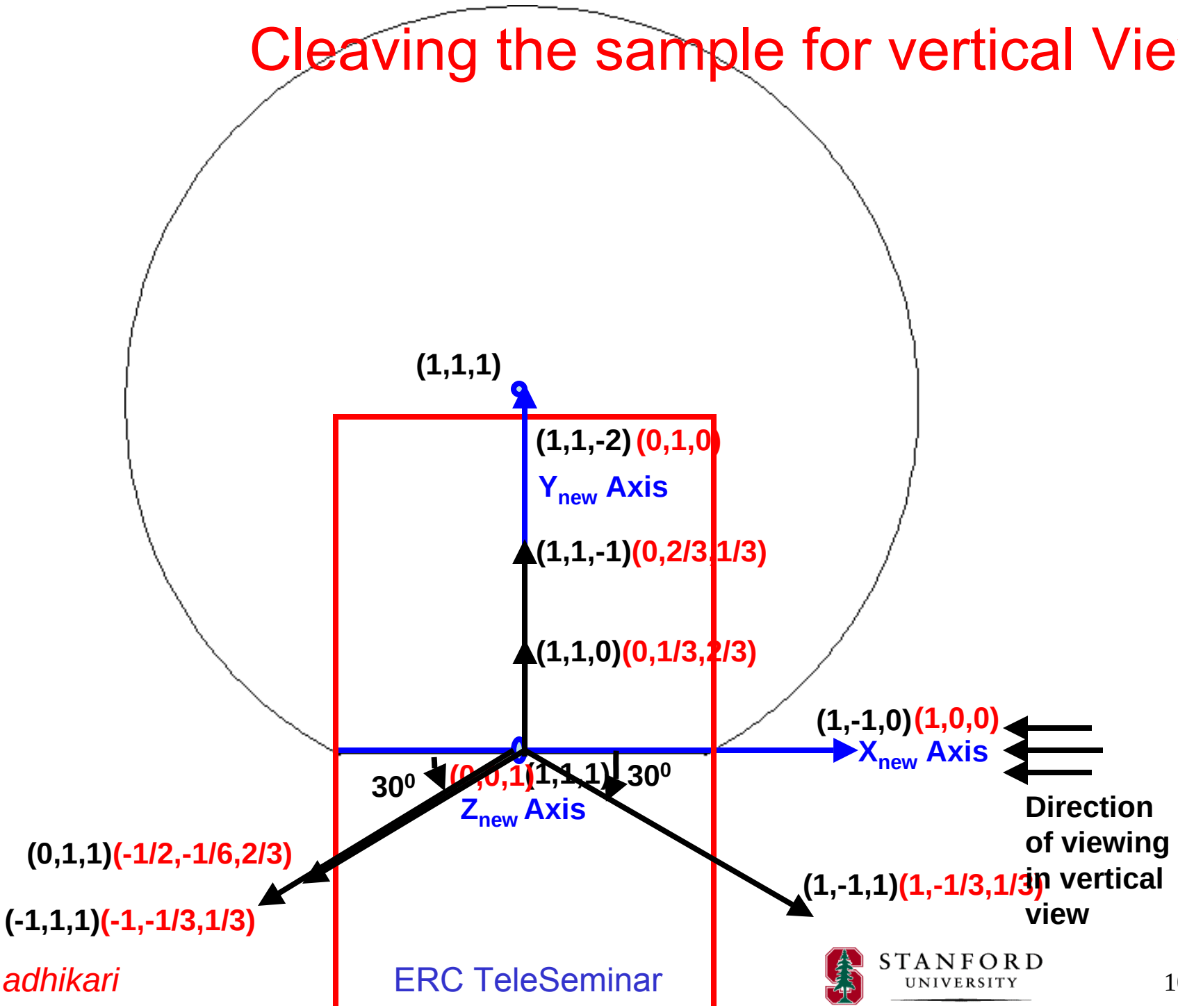


Plan view of GeNWs epitaxially grown on Ge(111)

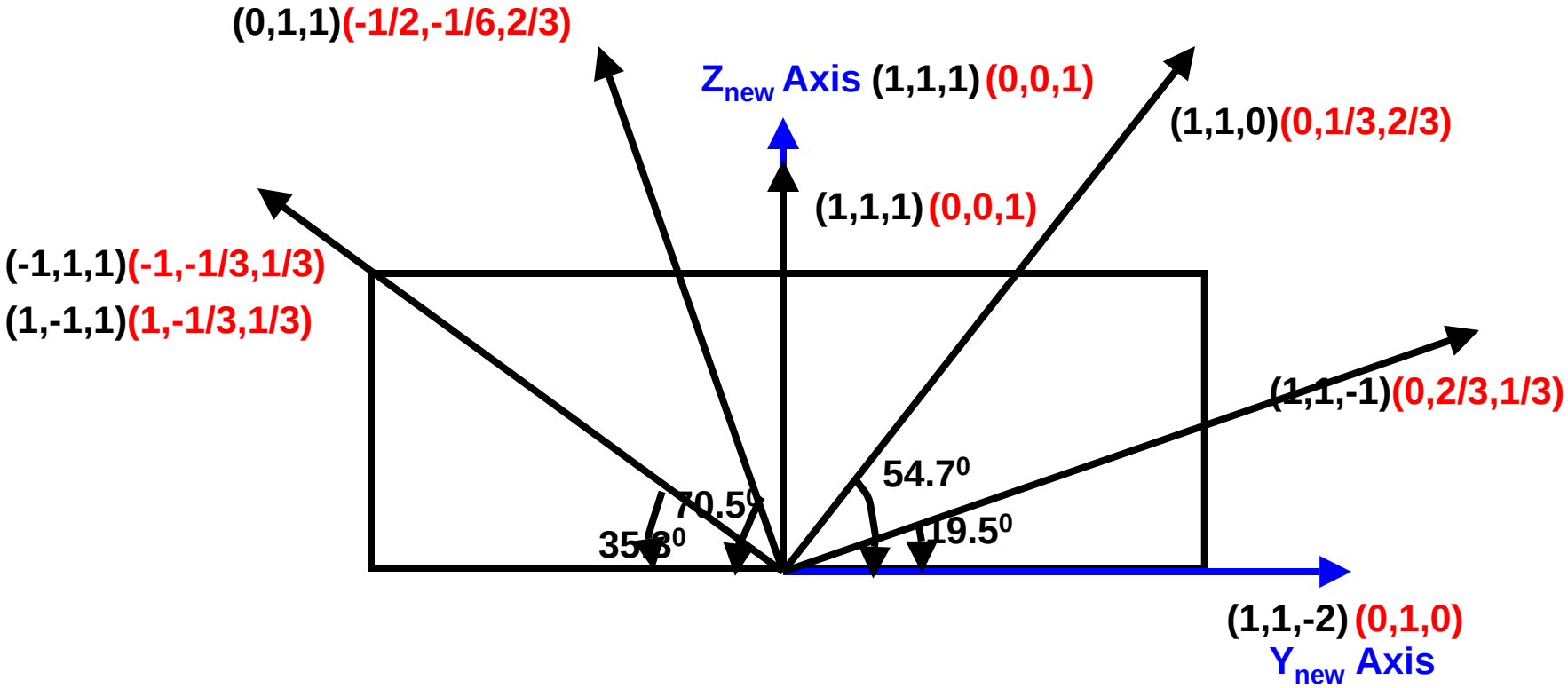
Tc =350^{o} C, P_{tot}= 30 torr, GeH_4= 5 sccm, H_2= 550 sccm, p_{GeH4}=0.273, t=30mins



Cleaving the sample for vertical View



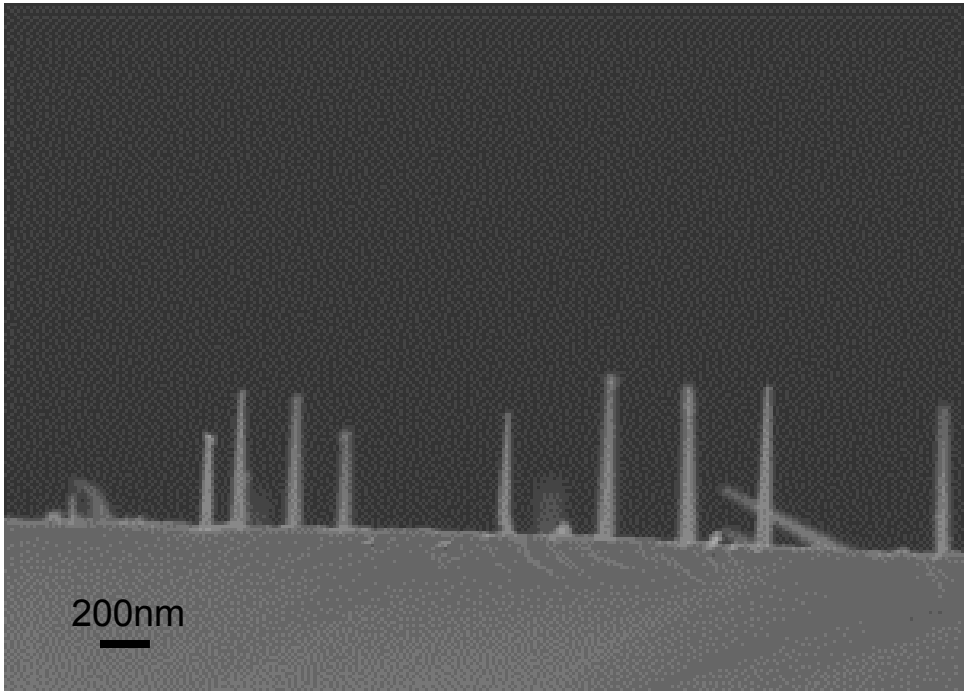
Vertical View on Ge(001)

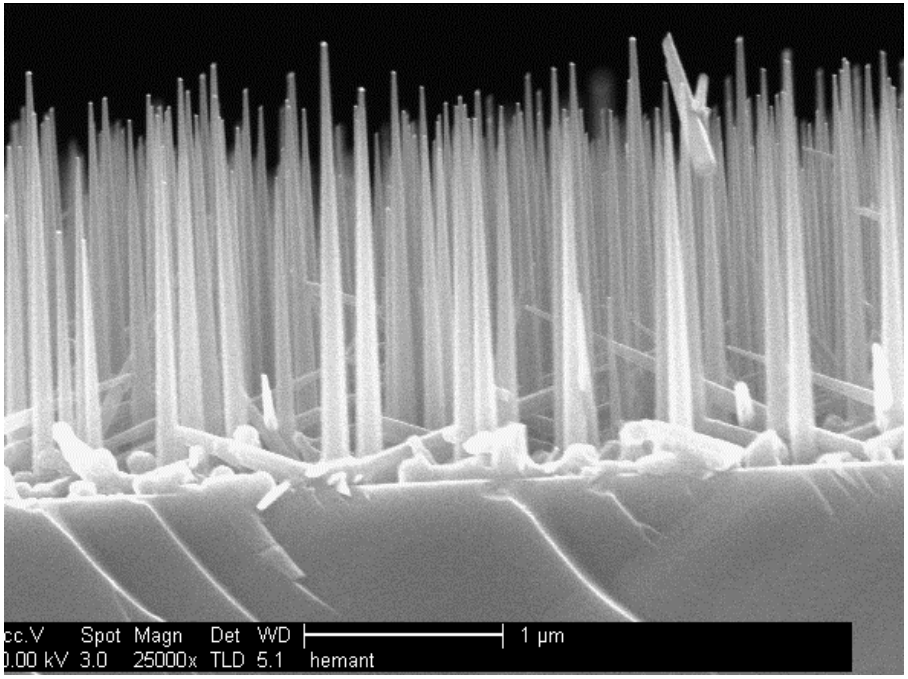


Bottom Line: (111) vertically up and at19.5^0 and 35.3^0. (110) at higher angles.

GeNWs growth on Ge (111) substrate

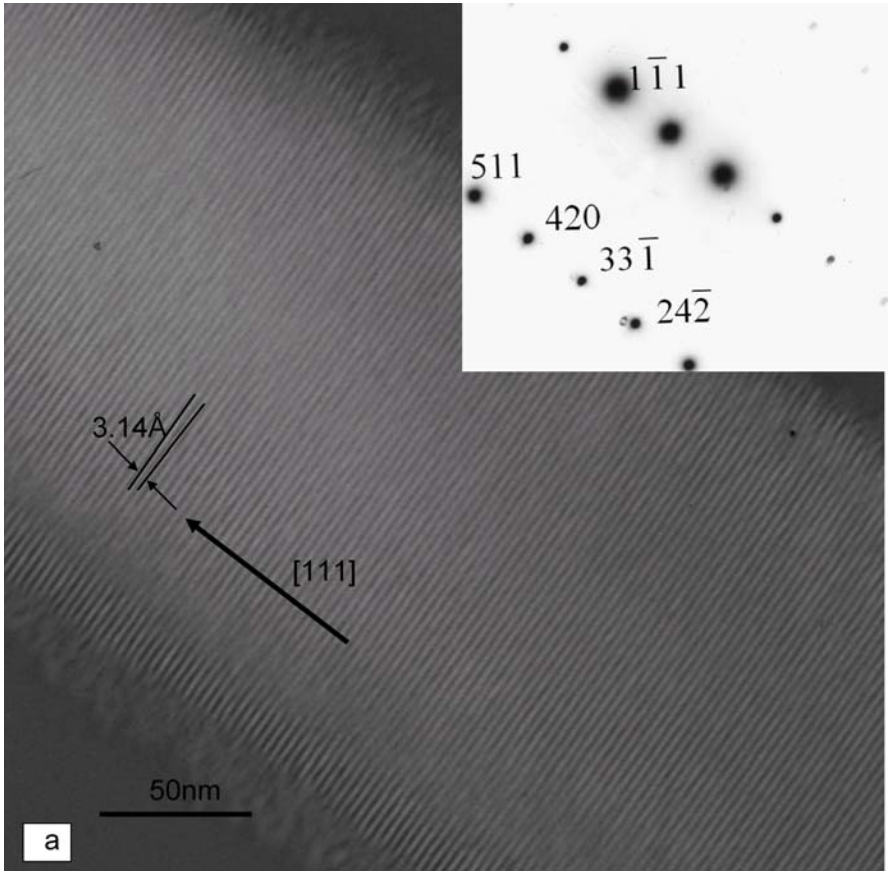
Tc =350^{o} C, P_{tot}= 30 torr, GeH_4= 5 sccm, H_2= 550 sccm, p_{GeH4}=0.273, t=30mins

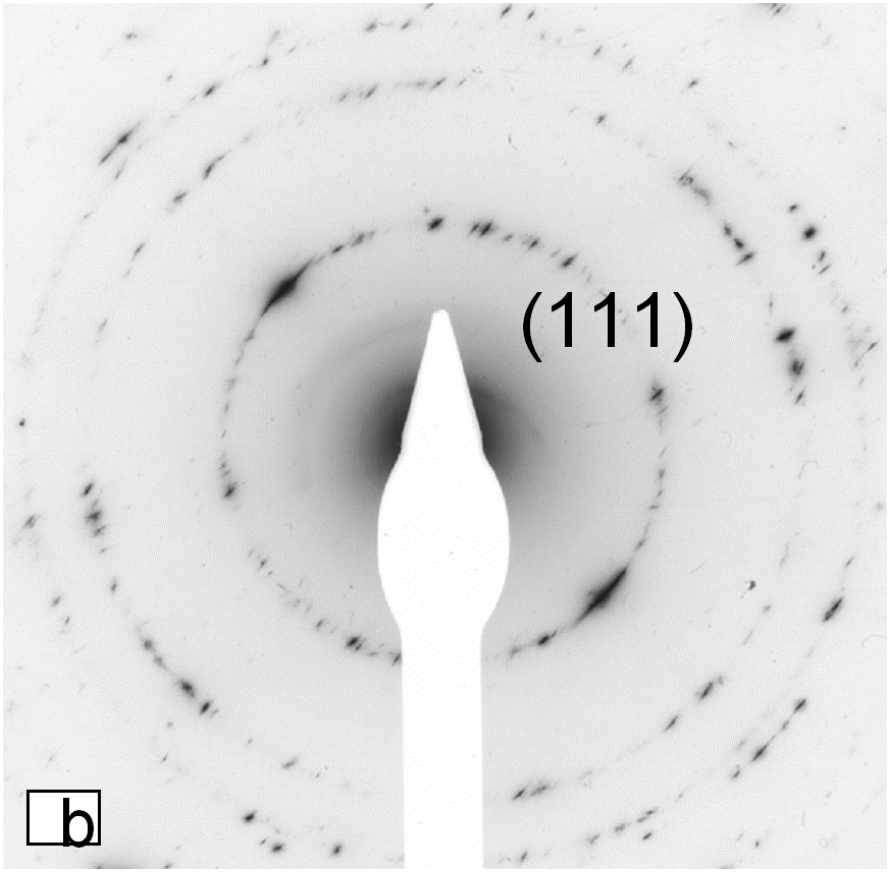




Observation: Most of the nanowires grow vertically. Some nanowires grow along other <111> directions.

Transmission electron microscopy studies of GeNWs on Ge(111)

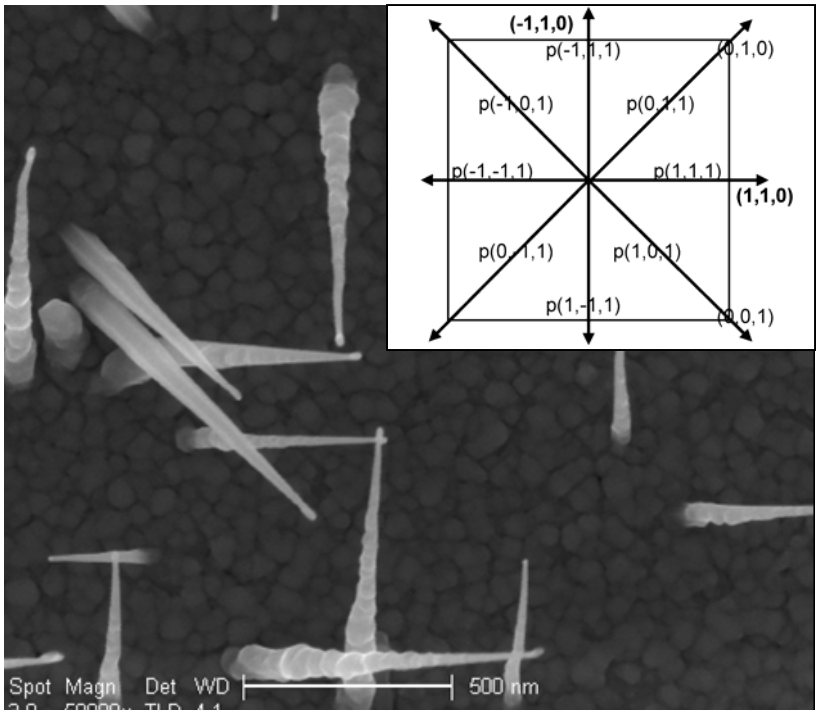


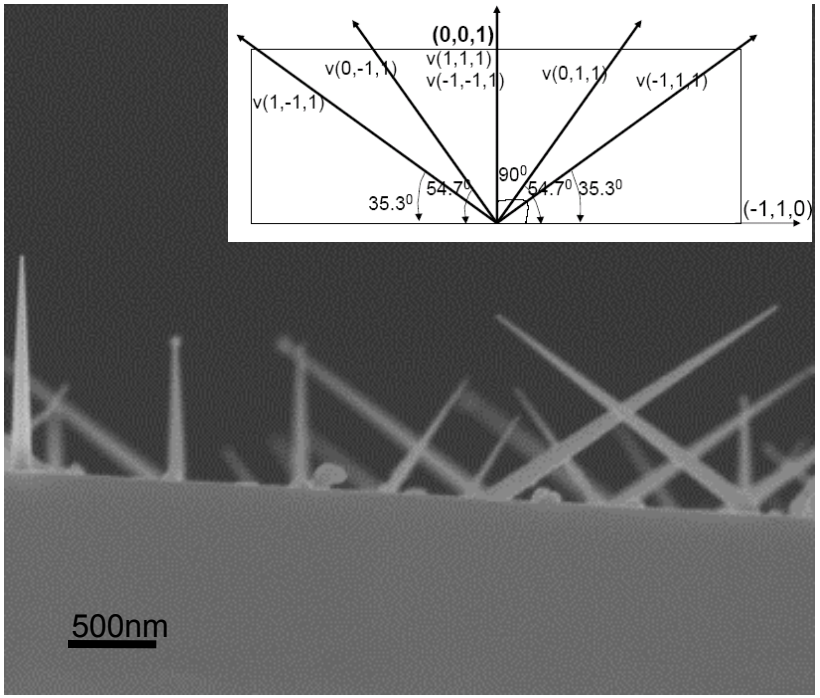


1. GeNWs are single crystalline with no observable defects.
2. Lattice fringe spacing corresponds to the (111) interplanar spacing in Ge.

Epitaxial growth of GeNWs on epi-Ge on Si(001) substrate

Tc =350^{o} C, P_{tot}= 30 torr, GeH_4= 5 sccm, H_2= 550 sccm, p_{GeH4}=0.273, t=30mins



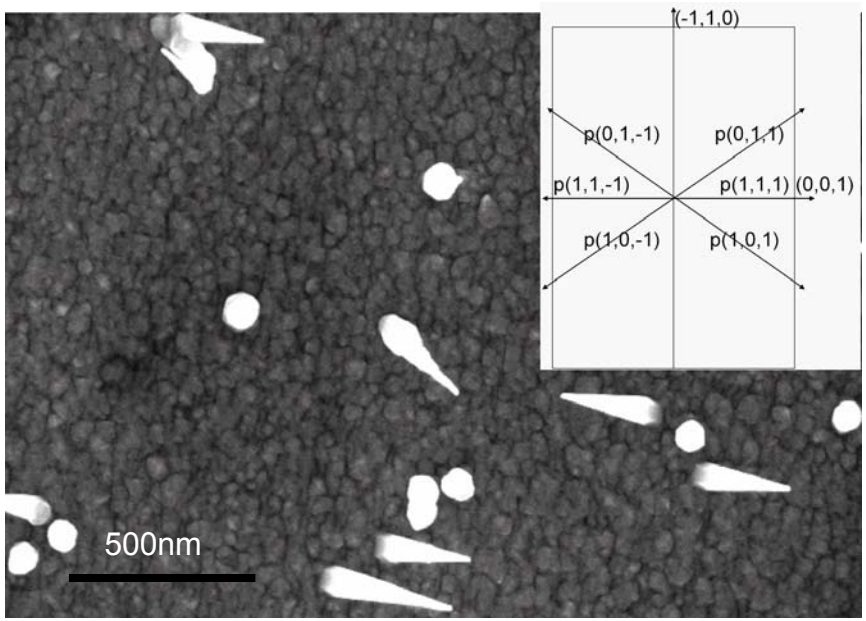


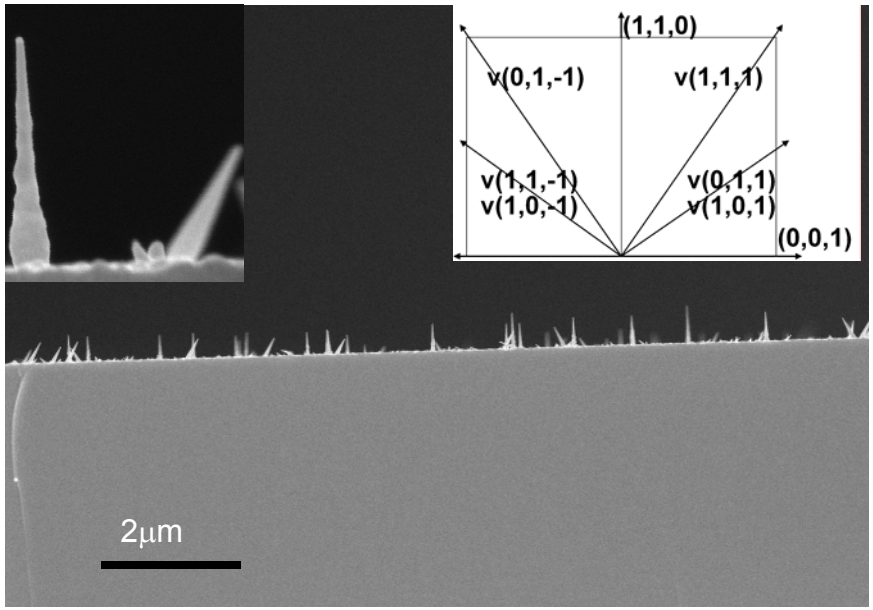
Observation:

1. Most nano-wires grow in (111) directions. Approximately 20% of the nanowires grow in (110) direction.
2. Similar results were obtained on Ge (100) substrates.

Epitaxial growth of GeNWs on Ge(110) substrate

Tc =350^{o} C, P_{tot}= 30 torr, GeH_4= 5 sccm, H_2= 550 sccm, p_{GeH4}=0.273, t=30mins





Observation:

1.Roughly equal number of nanowires grow in vertical [110] direction and the <111> directions.

Conclusions of epitaxial growth of nanowires at one temperature:

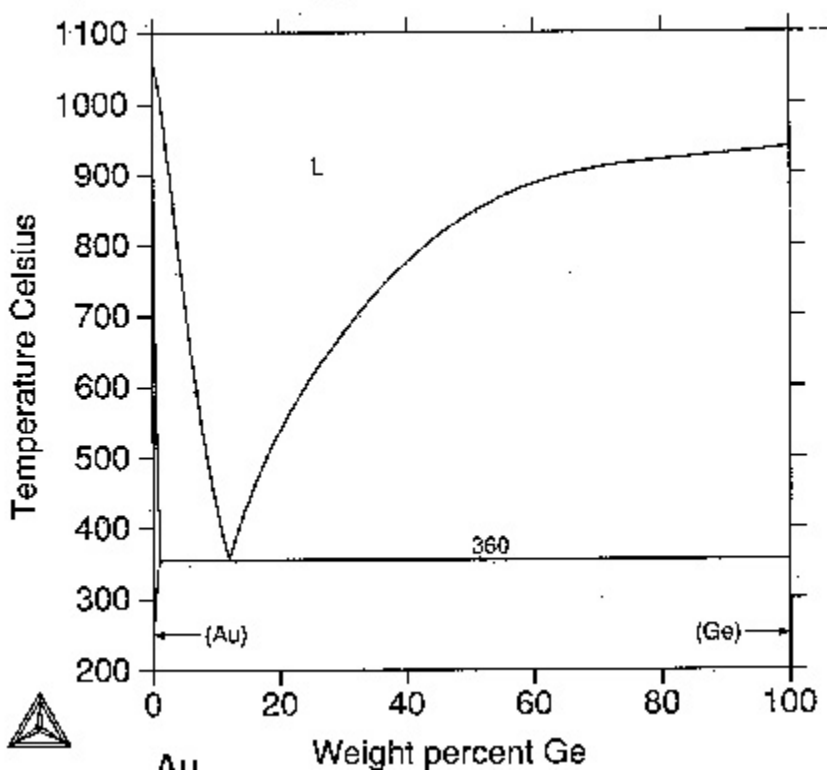
- GeNWs can be grown epitaxially from Ge substrates.

1. Almost all of nanowires align themselves along <111> directions of the substrate when grown on Ge(111).
2. 80% of nanowires grow along <111> and 20% of nanowires grow along <110> on Ge(100) and epi-Ge on Si.
3. Roughly equal no. of nanowires grow along <111> and <110> orientations on Ge(110).

- Nanowires grown at 350^0C are tapered.

1. Tapered nanowires are desirable as field emitters but not preferred for applications in field effect transistors because device characteristics depend on nanowire diameter

Au-Ge phase diagram



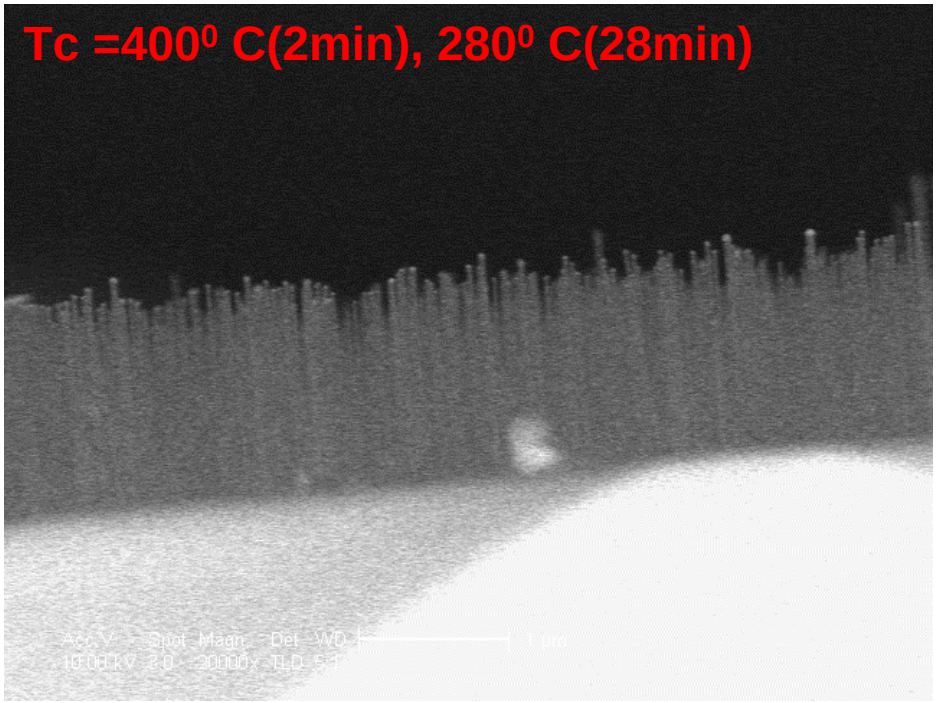
1. Stable growth of single crystalline nanowires far below bulk eutectic temperature.
2. Efficient growth of epitaxial nanowires on or near the bulk eutectic

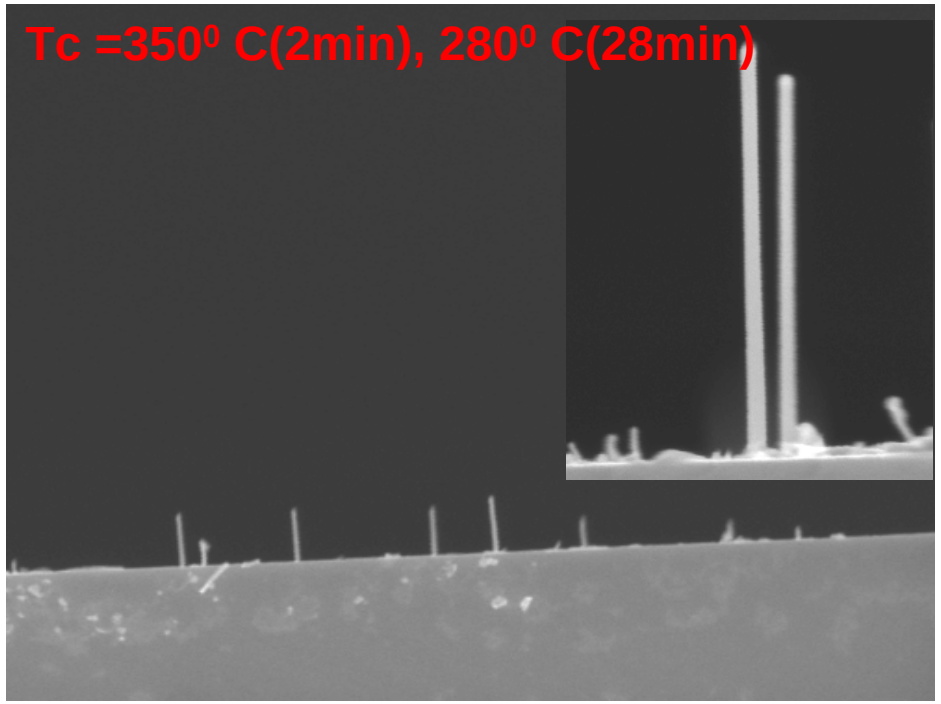
Two-temperature growth on Ge(111)

P_{tot}= 30 torr, GeH_4= 5 sccm, H_2= 550 sccm, p_{GeH4}=0.273, t=30mins

To Avoid Tapering

1. Decreasing reaction temperature reduces taper but decreases epitaxial growth too.
2. Temperature Step: Initiate at higher temperature, grow at lower temperature.





Observations:

1. Wires have (111) growth orientation (vertically up) aligned to (111) direction of the substrate.
2. Wires are non-tapered.

Photoemission studies:

For understanding and controlling the behavior of devices made by GeNWs:

1. Understand the surface chemistry of as-grown and air exposed GeNWs.

- Most of literature reports suggest oxide coverage of as-grown nanowires.
- What are the oxidation states of Ge NW?

2. Investigate the chemical passivation pathways to control the interface states:

- aqueous HF treatment.
- aqueous HCl treatment.
- HCl gas during growth.

X-ray Photoelectron Spectroscopy

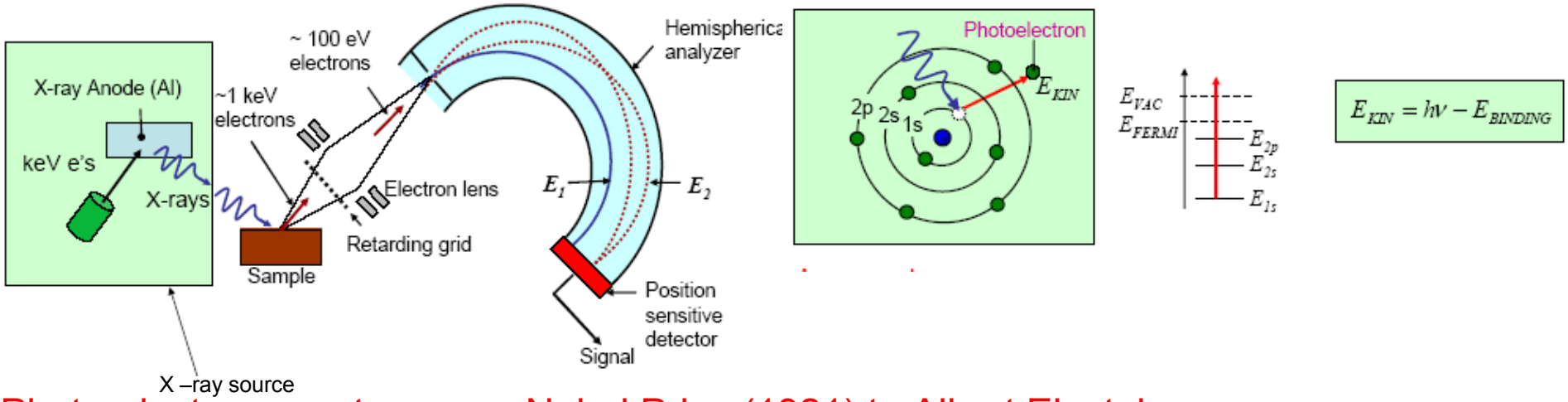
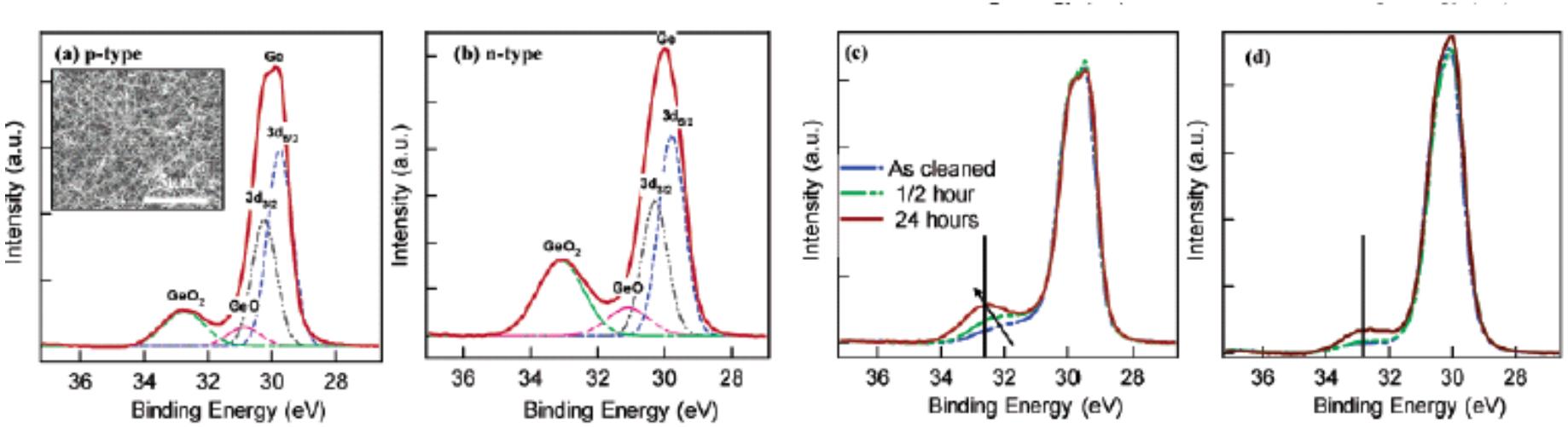


Photo-electron spectroscopy: Nobel Prize (1921) to Albert Einstein.

1. Procedure: The sample is irradiated with x-rays to ionize atoms. It releases core-level photoelectrons. These are collected and analyzed to get a spectrum of emission intensity vs electron binding energy.
2. (a) Since each element has a unique set of binding energies, XPS can be used to identify the elements on the surface.
   (b) peak areas at nominal binding energies can be used to quantify concentration of the elements.
   (c) Small shifts in these binding energies (chemical shifts) provide powerful information about sample *chemical states*.
3. The kinetic energy of the escaping photoelectrons limits the depth from which it can emerge, giving XPS its high surface sensitivity and sampling depth of a few nanometers.

Previous work on surface passivation

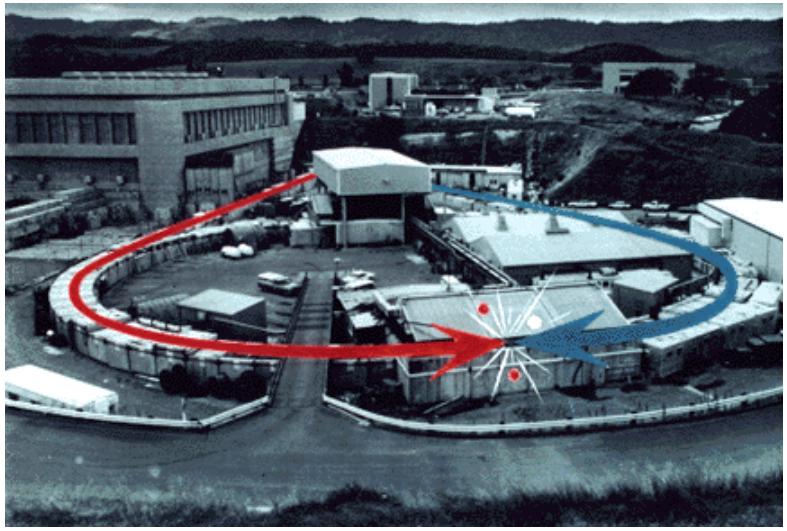


1. The previous work on hot wall grown GeNWs by Dai group (Stanford University).
- Nanowires spectrum taken after 24hr of growth show presence of GeO_2.
- Suggest cleaning with 450^0C annnealing in vacuum. Not very stable termination.

2. Work done on GeNWs grown on SFLS synthesis shows presence of oxide on as grown nanowires.

1.Wang etal, May 2004, Jour.of App. Chem.
2. Hanrath etal, Jun 2004, Jour of App Chem.

Synchrotron Radiation?



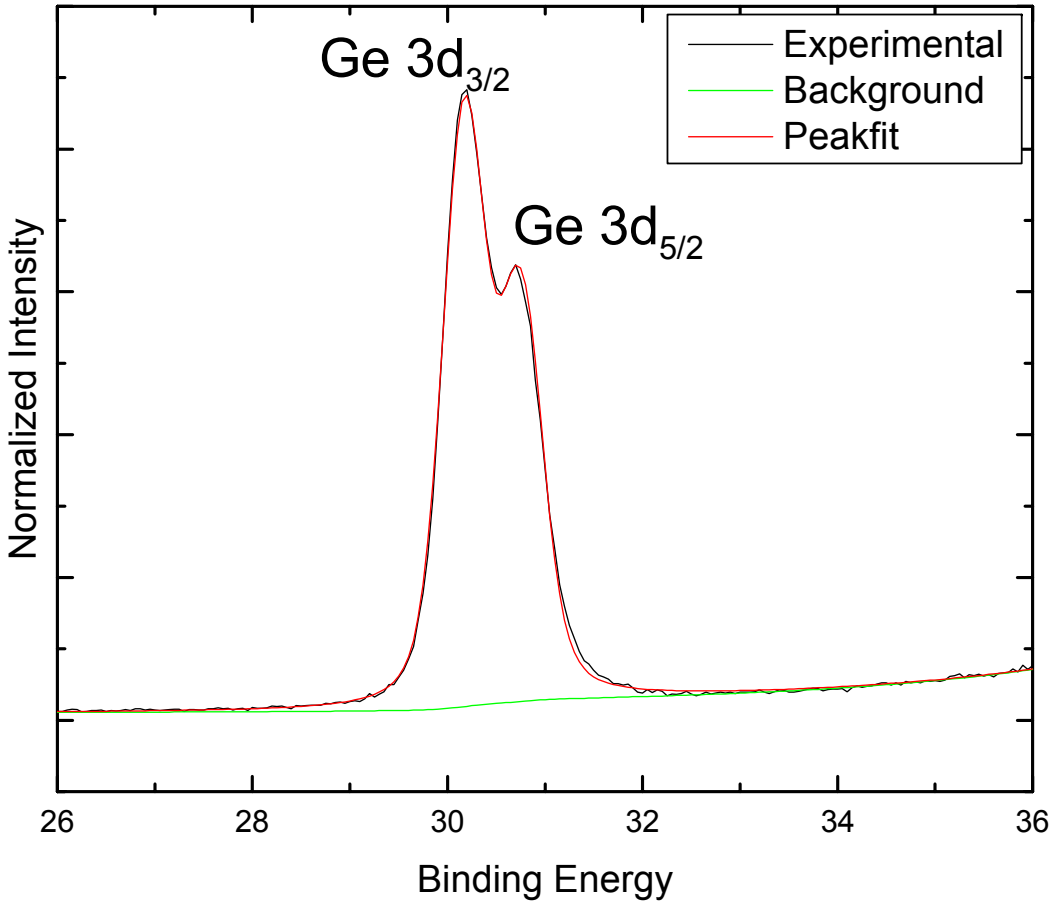
SPEAR (Stanford Positron Electron Accelerating Ring)

1. Synchrotron radiation is an electromagnetic radiation generated by the acceleration of relativistic electrons.
2. The radiation is captured by beamlines which control bandwidth, photon flux , beam dimension, focus etc.
3. Important Characteristics of synchrotron radiations:
   (a) High brightness and intensity, often many times more than with x-rays produced in conventional x-ray tubes.
   (b) The production of a wide range of energy levels.
4. We used lower photon energy of 80eV for Ge peak detection (compared to 1486.6 eV with a monochromatized Al Kα source in a conventional XPS setup) : hence **higher surface sensitivity** and **higher resolution**.

Photoelectron spectrum (using a synchrotron source) of as-grown germanium nanowires

T_c =350^0 C, P_{tot}= 30 torr, GeH_4= 5 sccm, H_2= 550 sccm, p_{GeH4}=0.273, t=30mins

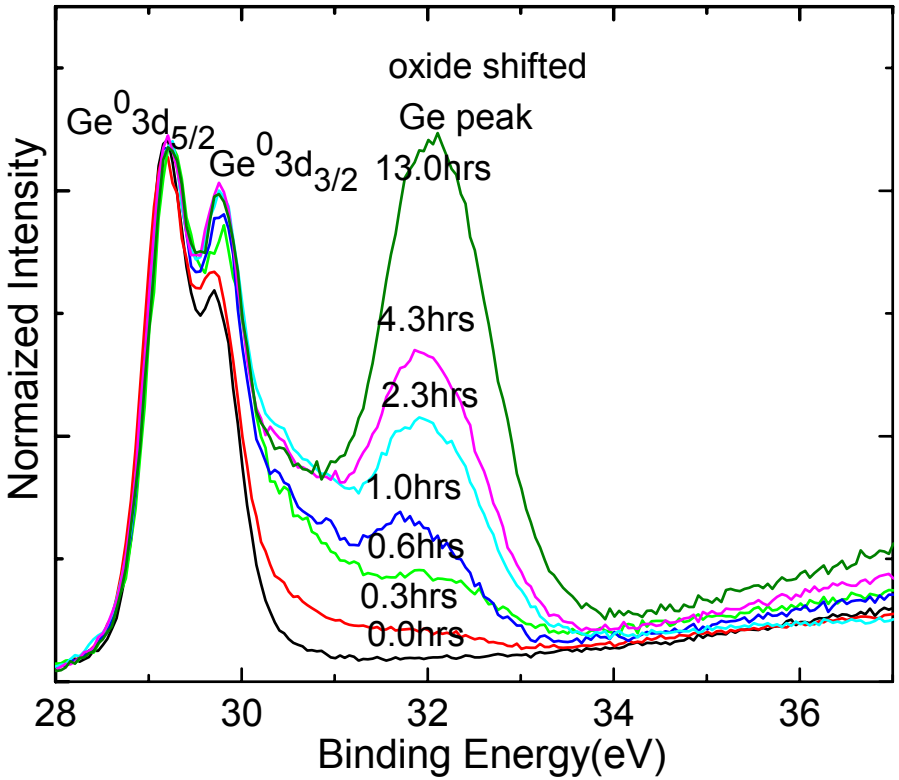
Sample Prep: Spin APTES, dip in Au colloids 10nm dia

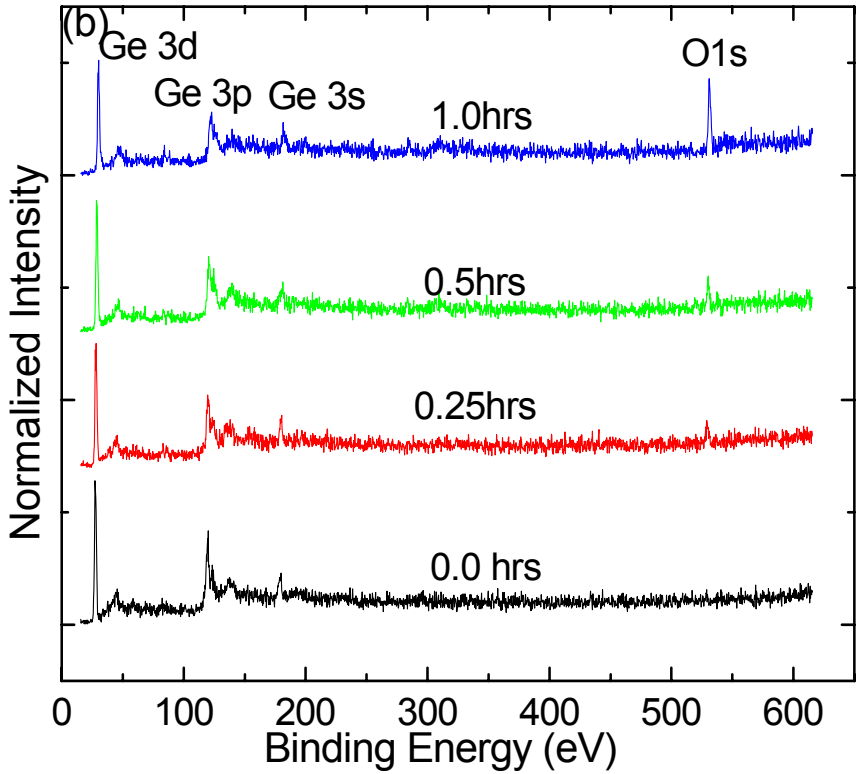


Observation:

1. As grown nanowires don't have any oxide shifted Ge 3d peak. This suggests that wires are **hydrogen terminated** immediately after growth.

Photoelectron spectrum of germanium nanowires showing growth of oxide in air



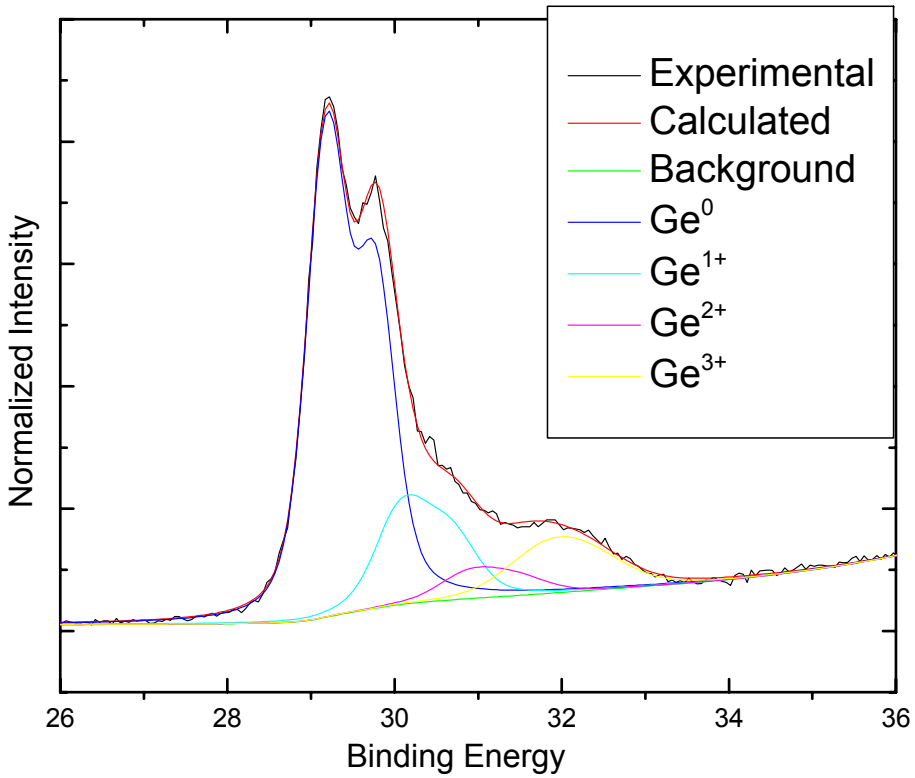


Observations:

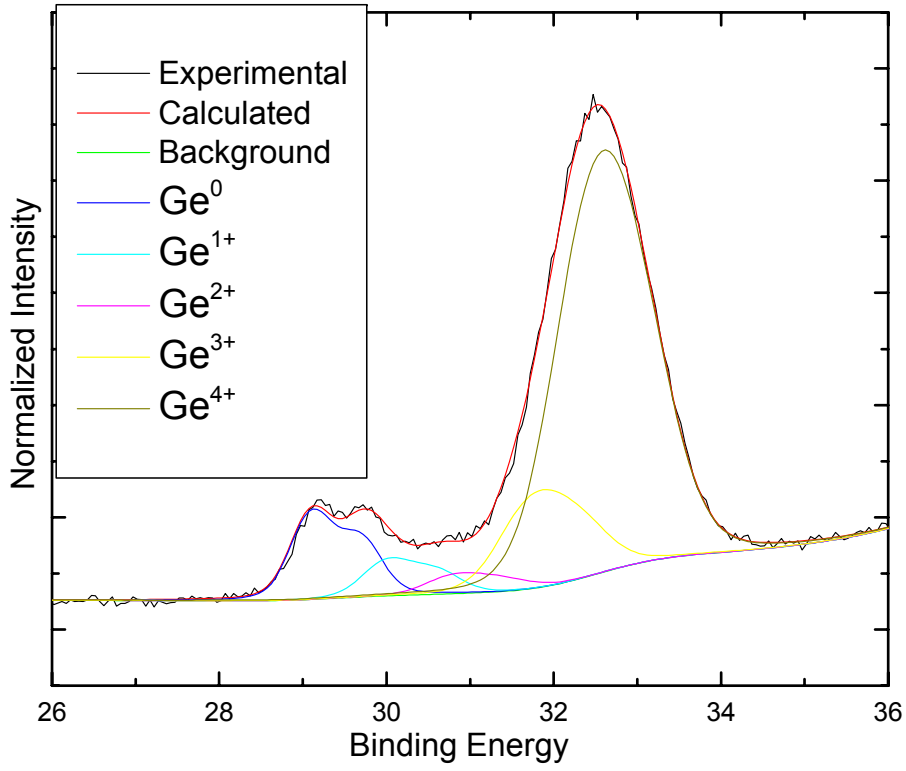
1. As grown nanowires don't have any oxide shifted Ge 3d peak. This suggests that wires are hydrogen terminated immediately after growth.
2. Oxide-shifted Ge peak starts appearing and increases when wires are exposed to atmosphere implying that **wires are progressively growing oxide**.

Peak fitting for determination of oxidation state

GeNWs exposed to air for 33 mins



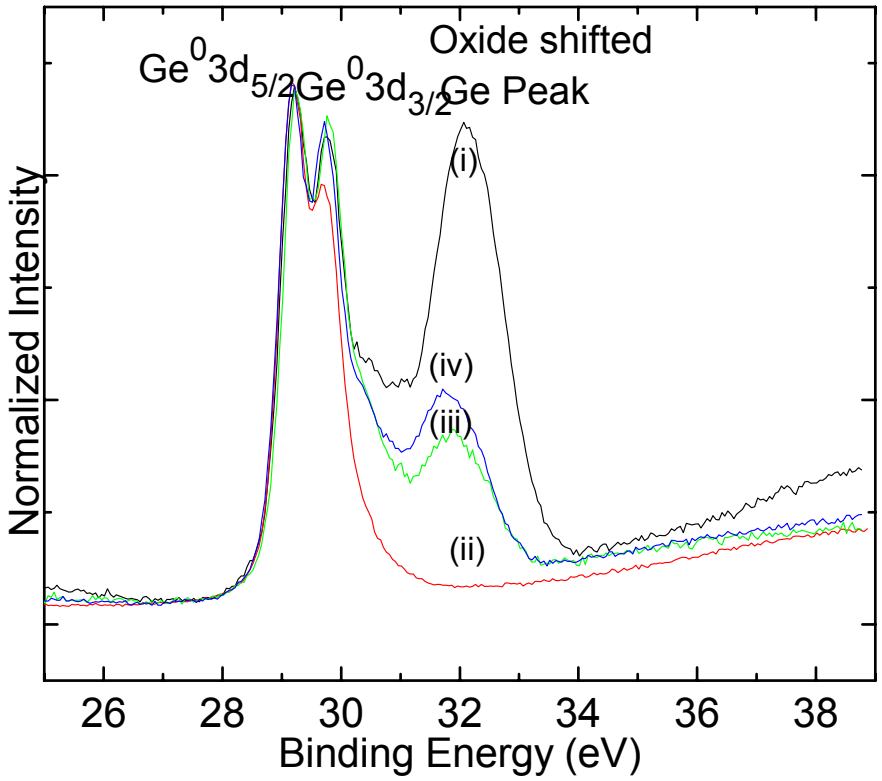
GeNWs exposed to UV light for 10mins

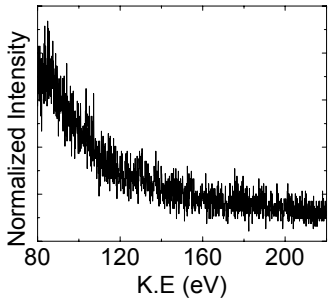


Observations:

1. Oxide grown on nanowires exposed to air (when covered with Al foil) can be completely fitted to Ge^{0}, Ge^{1+}, Ge^{2+}, Ge^{3+}.
2. Oxide-shifted Ge peak for GeNWs exposed to UV light has a predominant Ge^{4+} component.

Photoelectron spectrum (using a synchrotron source) of germanium nanowires after aq. HF treatment



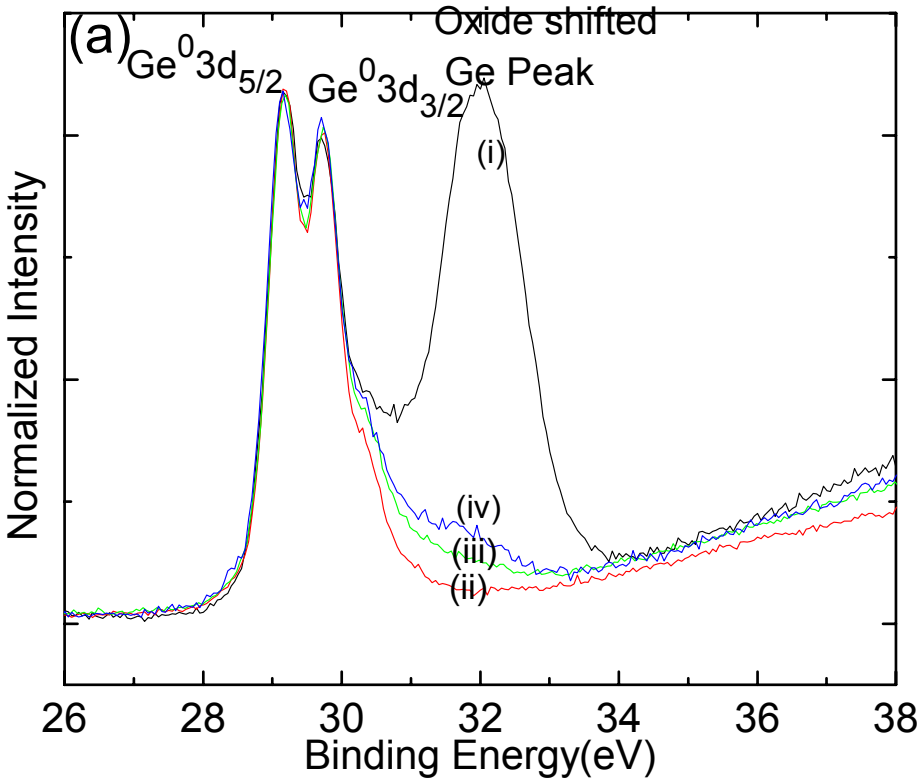


(i) GeNWs after 4 hours of exposure to air
(ii) the same GeNWs immediately after aqueous HF treatment;
(iii) growth of oxide in HF treated GeNWs after 18 mins of air exposure;
(iv) growth of oxide on HF treated GeNWs after 70 mins of air exposure

Observations:

1. The oxide grown on nanowires can be almost completely removed by an aq. HF treatment. This leaves the wires H-terminated.
2. The hydrogen termination achieved with aq. HF treatment in less stable than H-termination achieved during the growth because of H_2 environment.

Photoelectron spectrum of germanium nanowires after aq. HCl treatment

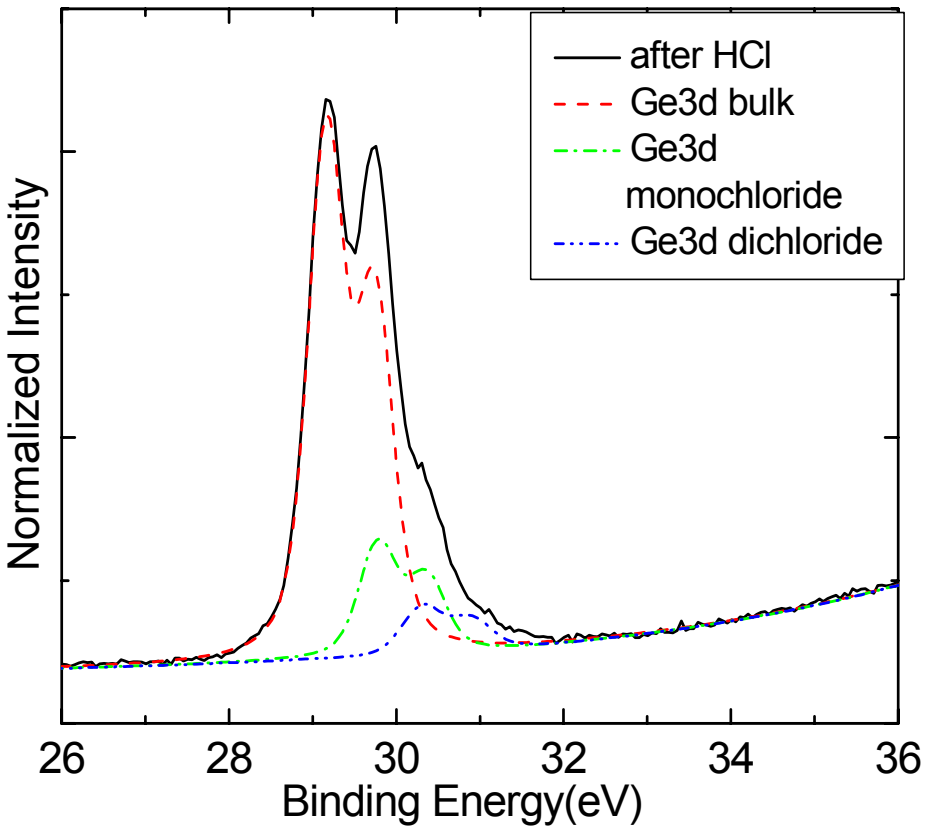


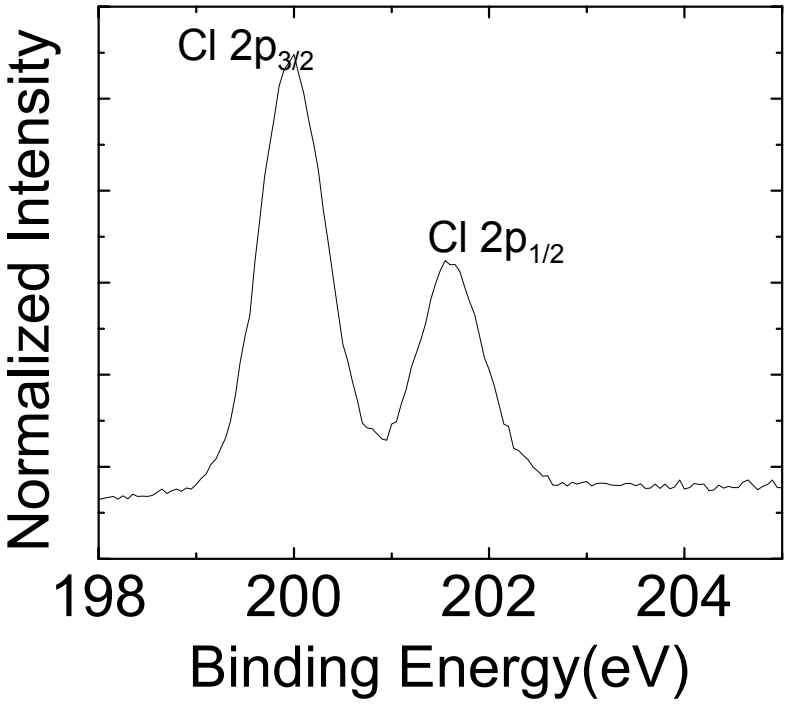
(i) GeNWs after 13 hours of exposure to air
(ii) the same GeNWs immediately after aqueous HCl treatment;
(iii) growth of oxide in HCl treated GeNWs after 78 mins of air exposure;
(iv) growth of oxide on HCl treated GeNWs after 160 mins of air exposure

Observations:

1. The oxide grown on nanowires can be completely removed by an aq. HCl treatment.
2. The passivation achieved with **aq. HCl treatment is more stable against oxidation** than either as grown samples or aq.HF treated samples.

Photoelectron Spectrum of Germanium Nanowires after aq. HCl treatment





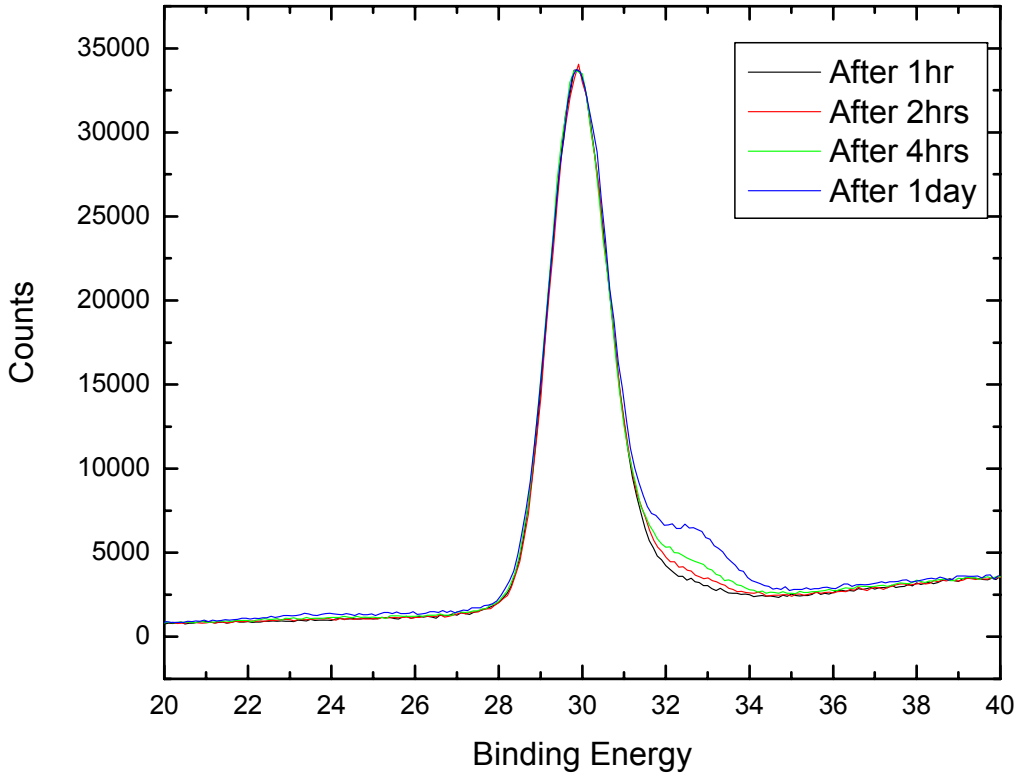
Observation:

1. The aqueous HCl treatment leaves the **wires Cl-terminated**. (As against H-terminated in case of aq. HF treatment)

GeNWs grown with HCl flowing during growth

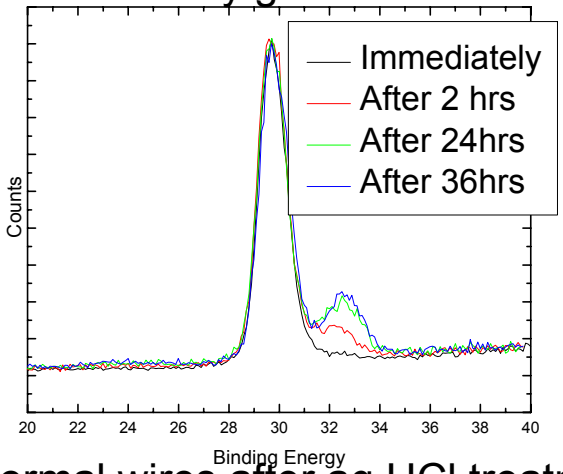
Tc =350^{0}C, P_{tot}= 30 torr, GeH_4= 5 sccm, H_2= 550 sccm, HCl=5sccm, t=30mins

Sample Prep: Spin APTES, dip in Au colloids 10nm dia

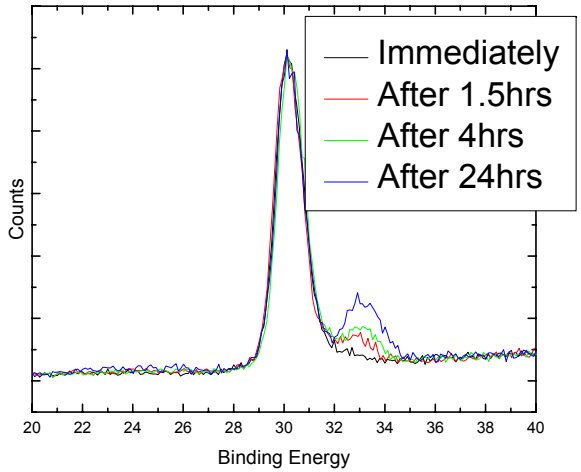


Comparison of Ge3d spectra obtained by various passivation mechanism by conventional XPS

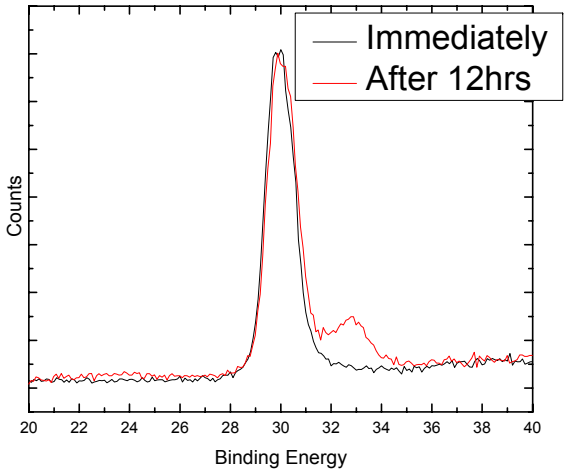
GeNWs normally grown without treatment



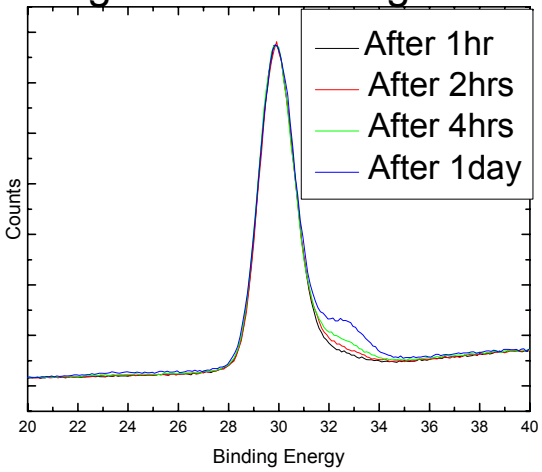
Normal wires after aq.HF treatment



Normal wires after aq.HCl treatment



Wires grown with HCl gas during growth



Nanowires grown with HCl during growth provide very stable passivation.

Conclusions

1. Nanowire growth:

- Epitaxially oriented germanium nanowires can be grown on Ge substrates.
- Two temperature process gives uniform diameter epitaxial nanowires.

2. Surface passivation:

- Wires immediately after the growth are hydrogen terminated. They progressively grow oxide with time when exposed to atmosphere.
- The oxide grown on nanowires can be removed by aq. HF and aq. HCl treatment. The most stable passivation is obtained by flowing HCl along with GeH_4 during growth.

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Conversion of Coordinates for the new coordinate system for Ge(111)

$$\begin{pmatrix} 1 & 1 & 1 \\ -1 & 1 & 1 \\ 0 & -2 & 1 \end{pmatrix} \cdot \begin{pmatrix} u1 \\ u2 \\ u3 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} x1 \\ x2 \\ x3 \end{pmatrix}$$

$$\begin{pmatrix} u1 \\ u2 \\ u3 \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} & 0 \\ \frac{1}{6} & \frac{1}{6} & -\frac{1}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} \end{pmatrix} \cdot \begin{pmatrix} x1 \\ x2 \\ x3 \end{pmatrix}$$

$$\begin{pmatrix} u1 \\ u2 \\ u3 \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} & 0 \\ \frac{1}{6} & \frac{1}{6} & -\frac{1}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} \end{pmatrix} \cdot \begin{pmatrix} 1 \\ -1 \\ 0 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$$

$$\begin{pmatrix} u1 \\ u2 \\ u3 \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} & 0 \\ \frac{1}{6} & \frac{1}{6} & -\frac{1}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} \end{pmatrix} \cdot \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

x1,x2,x3= Original coordinates
u1, u2, u3= New coordinates

X1	X2	X3	U1	U2	U3
1	1	1	0	0	1
1	1	-1	0	2/3	1/3
1	-1	1	1	-1/3	1/3
-1	1	1	-1	-1/3	1/3
1	-1	0	1	0	0
1	1	0	0	1/3	2/3
0	1	1	-1/2	-1/6	2/3