Non-destructive gold removal from germanium nanowire samples

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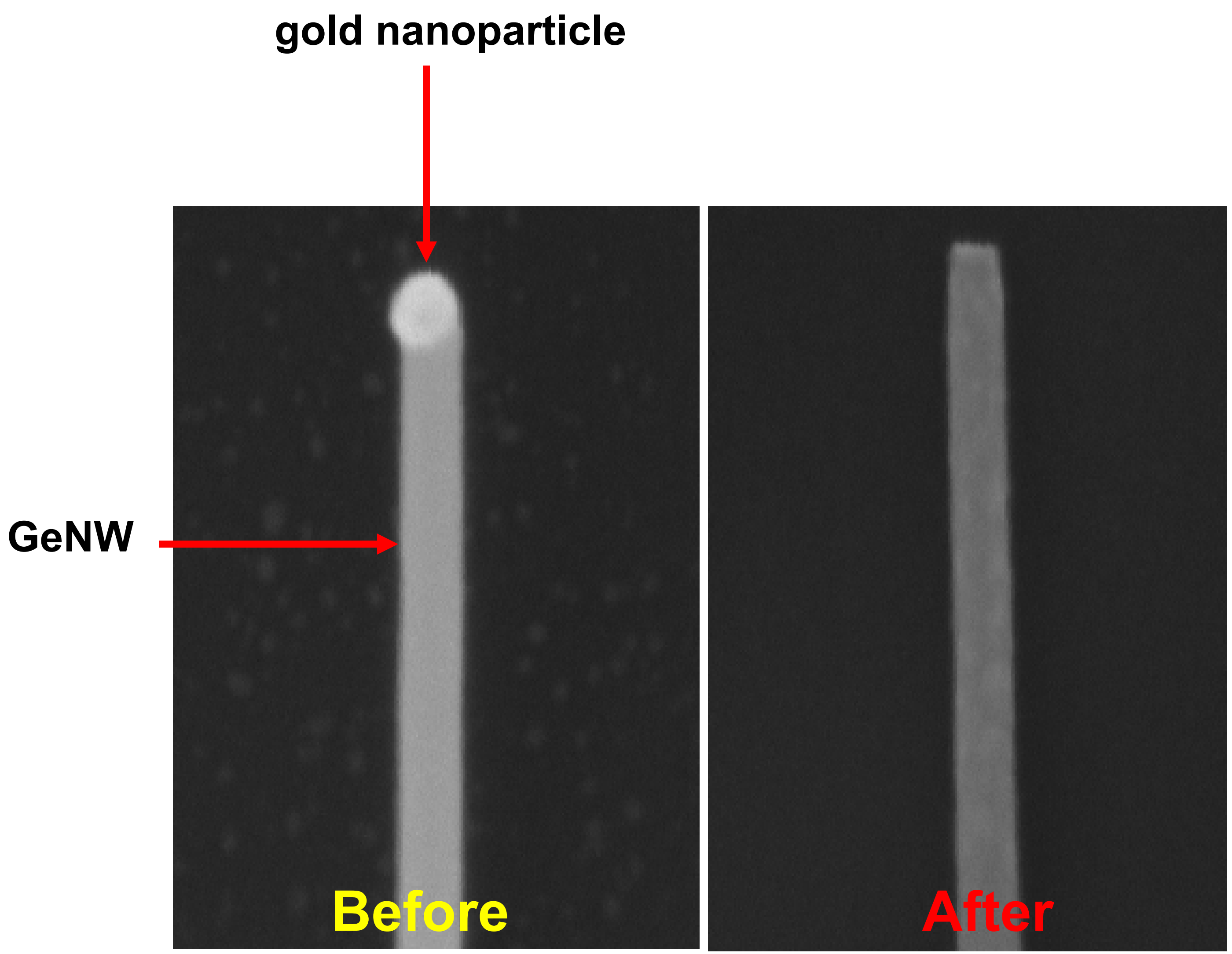
Outline

- **introduction**
- GeNW growth from gold nanoparticles
- effect of gold in germanium and silicon processing
- gold removal procedure
- chemical characterization of GeNW surfaces before and after gold removal
- effectiveness of the gold removal procedure
- conclusion



- **Non-destructive gold removal from the tips of GeNWs**
- **May be useful for planar Si and Ge surfaces**

Environmental impact of GeNW electronic materials

- GeNW in-situ growth reduces process waste of expensive bulk materials
- single crystal growth at lower processing temperature
- unknown semiconductor manufacturing process integration of gold cataylzed GeNWs

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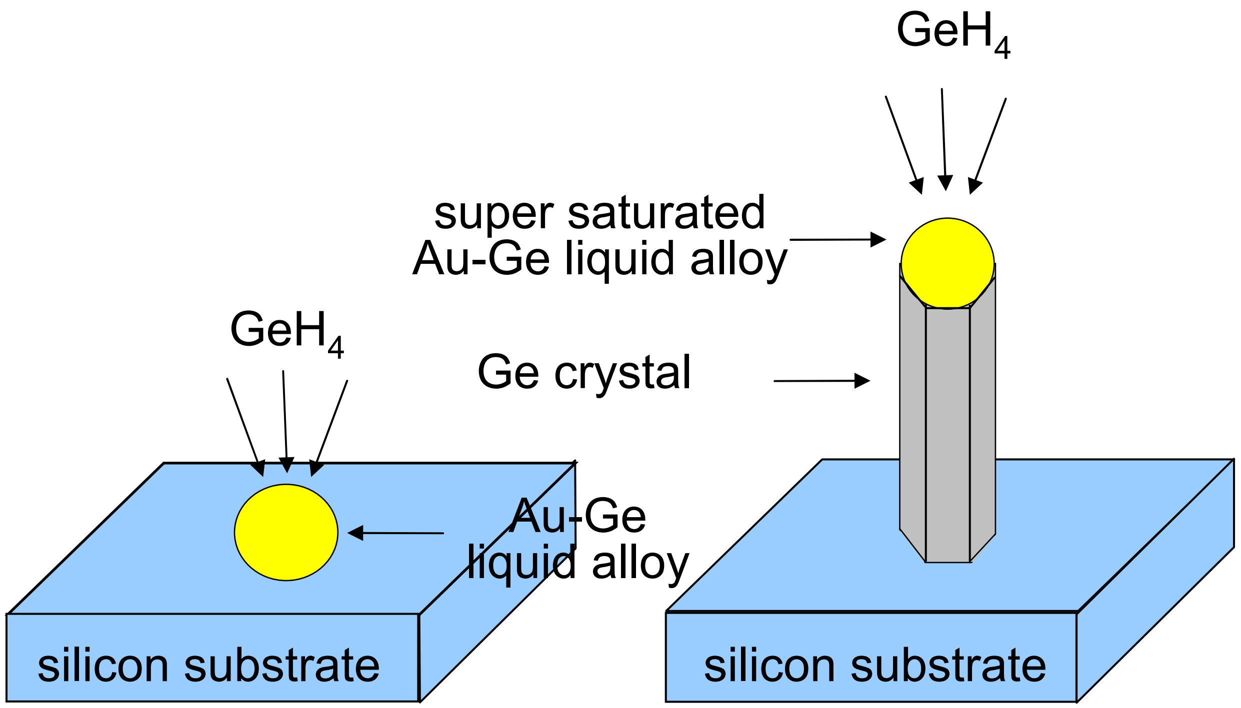
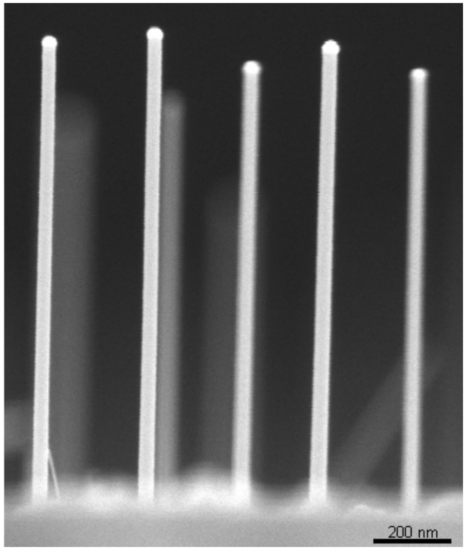
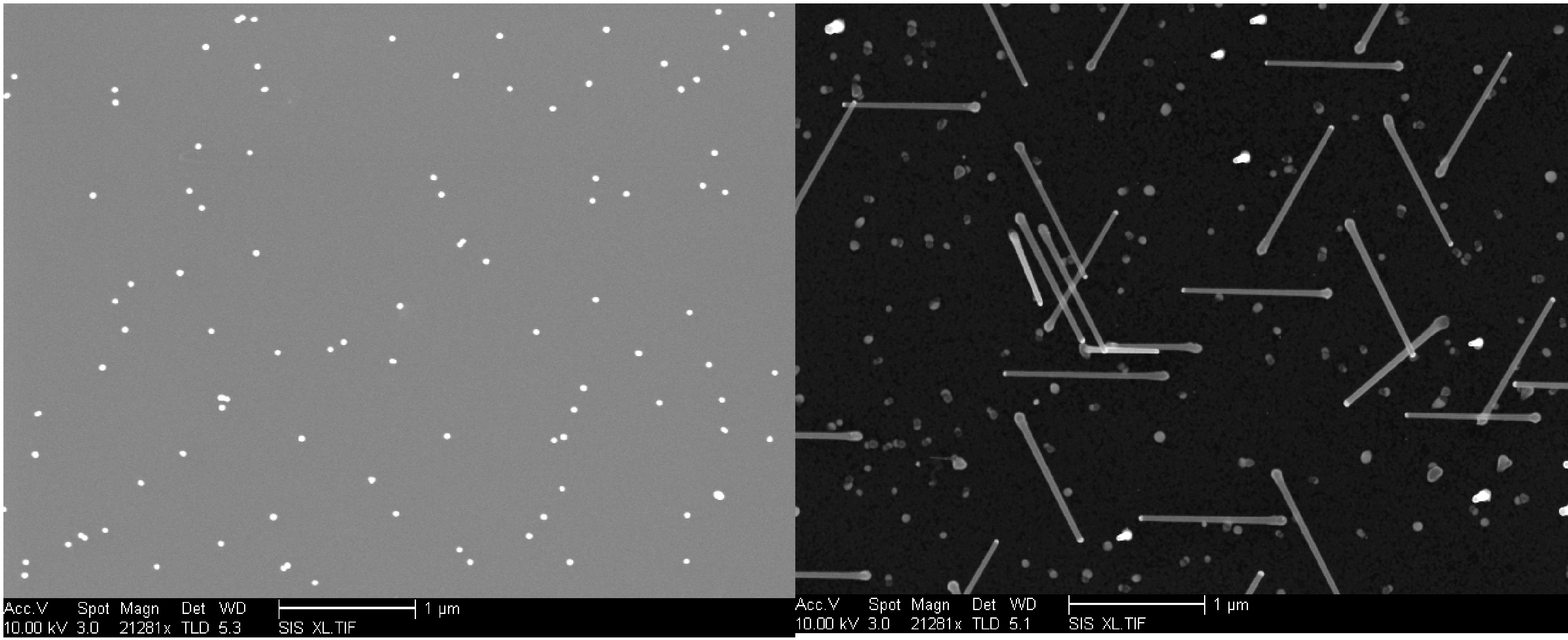
Gold catalyzed crystal growth from precursor gas





R.S. Wagner, W.C. Ellis Appl. Phys. Lett. 4 89, (1964)

Epitaxial Growth of GeNW from gold nanoparticles on Si <111>



GeNW grown by heating linker free 40 nm gold colloids to 400°C for 2 minutes followed by 280° C for 18 minutes with 0.430 Torr GeH_4(g) and 29.6 Torr H_2 (g).

Woodruff, J. H.; Ratchford, J. B.; Goldthorpe, I. A.; McIntyre, P. C.; Chidsey, C. E. D.;

***Nano Lett.*, 2007; 7(6); 1637-1642.**

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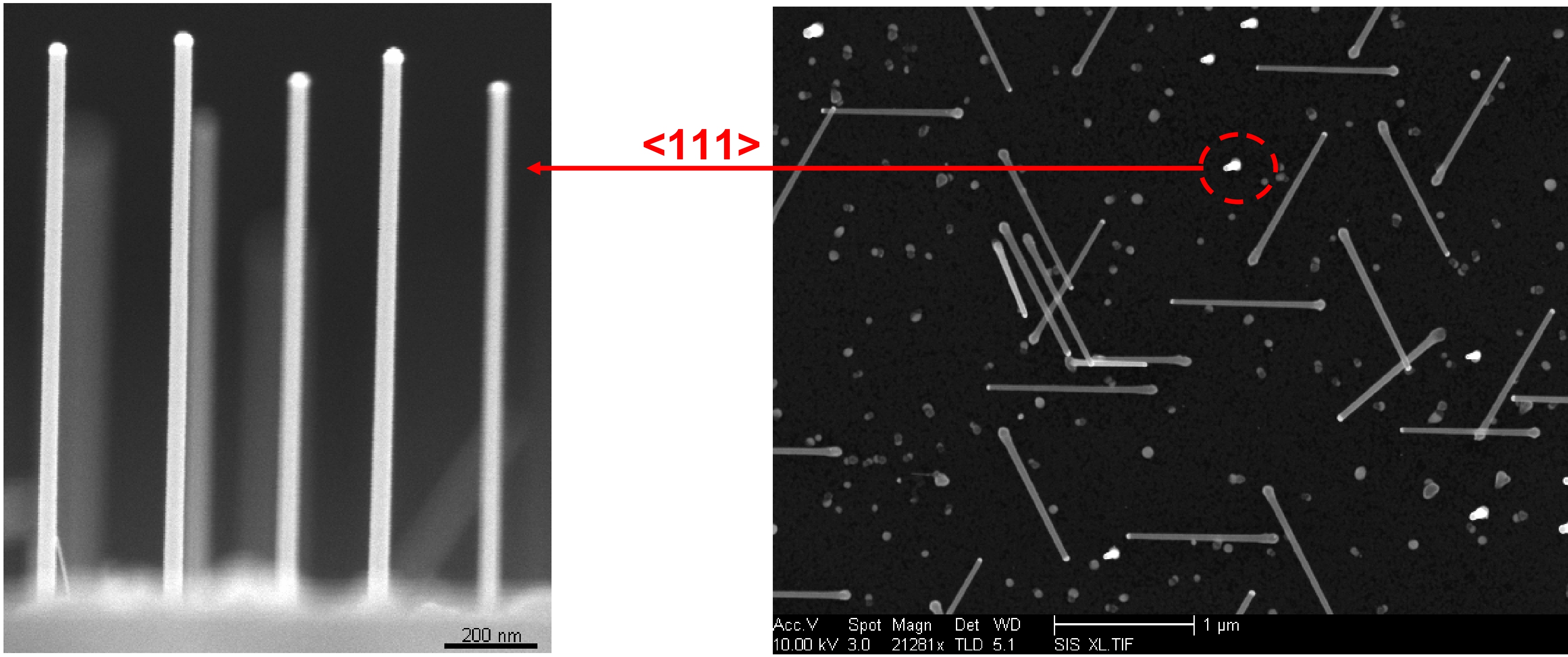

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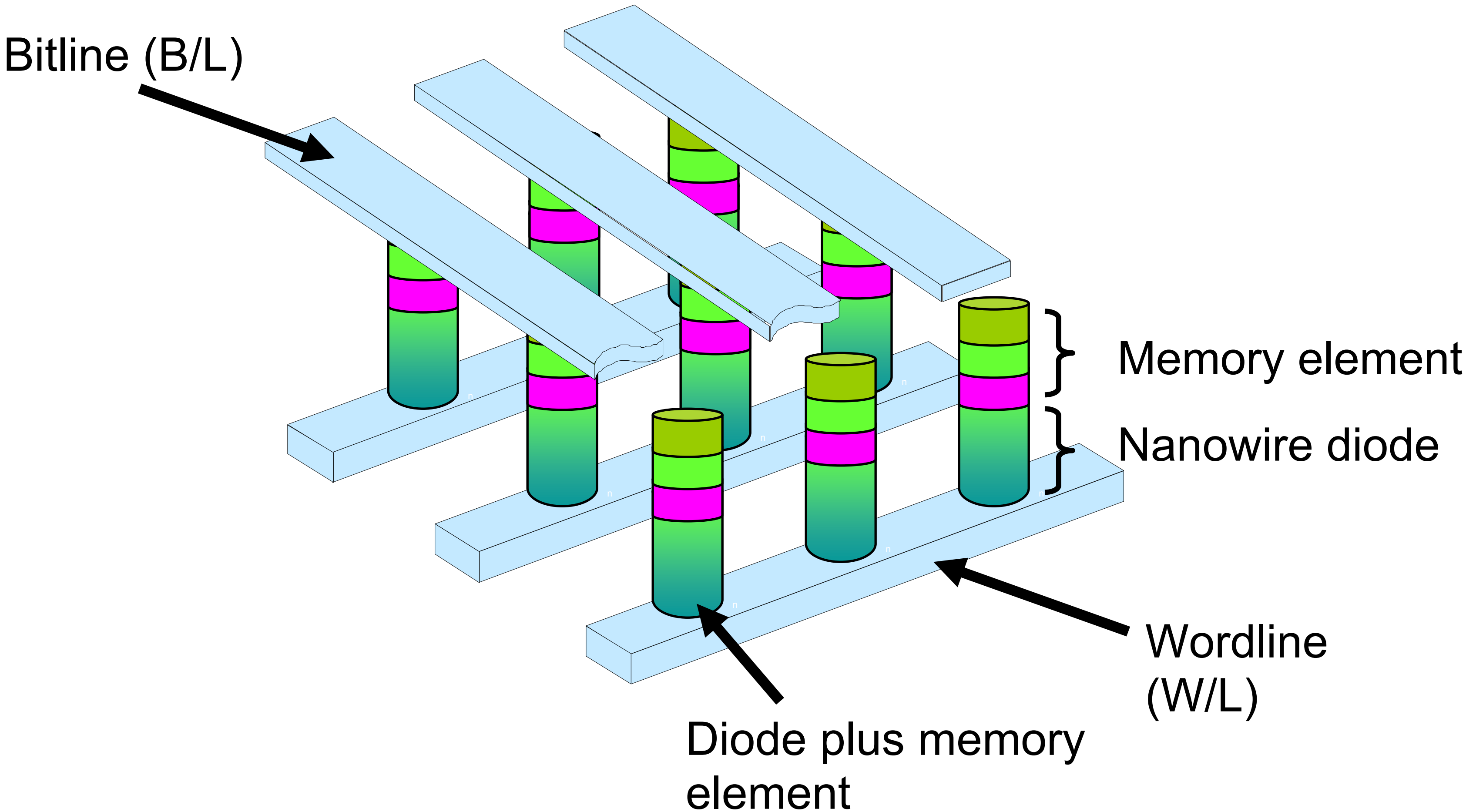
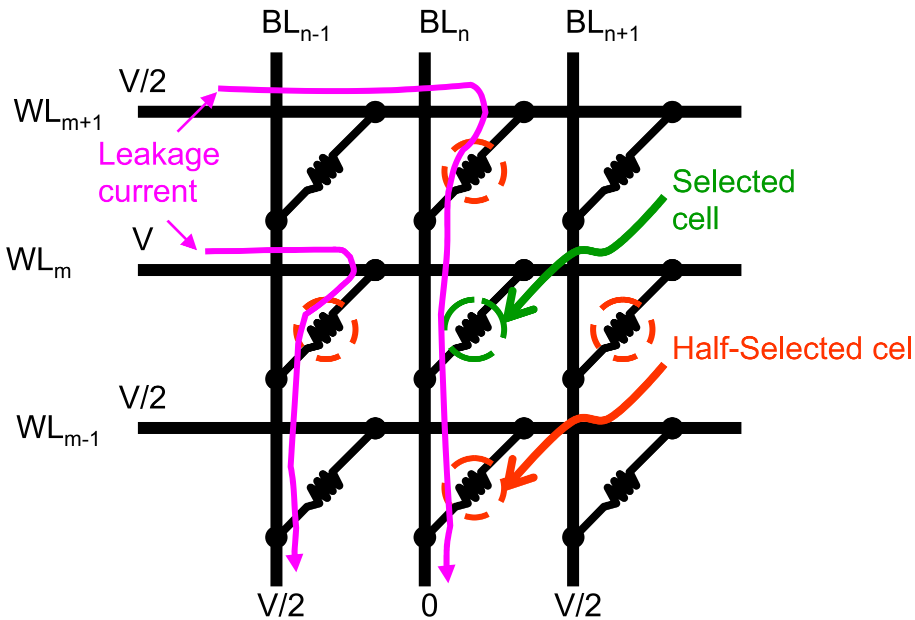
High Density Cross-Point Memory with GeNW Diode

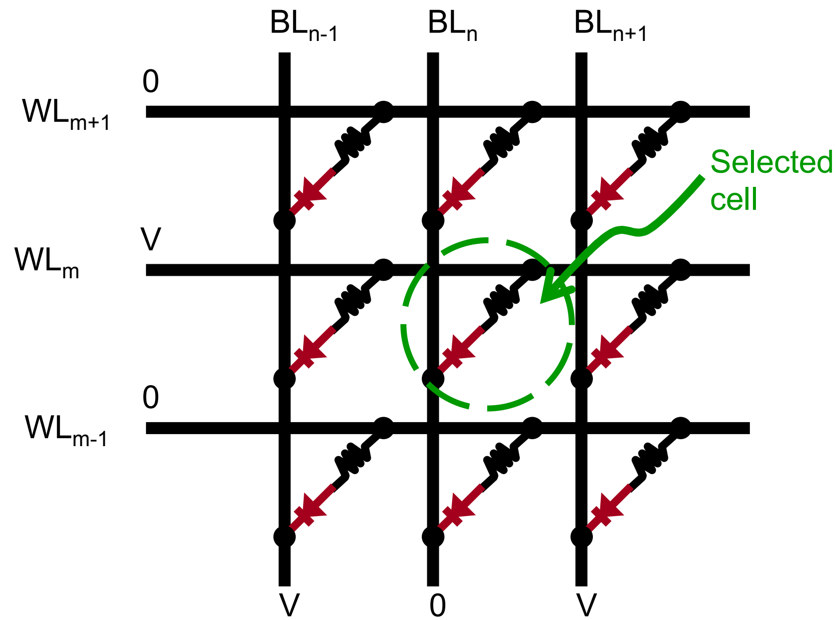


Yuan Zhang, et.al. "An Integrated Phase Change Memory Cell With Ge Nanowire Diode For Cross-Point Memory" presented 13 Jun. 2007 at 2007 Symposium on VLSI Technology, Kyoto, Japan.

Cross-Point Memory Cell Selection



Without Diode



With Diode

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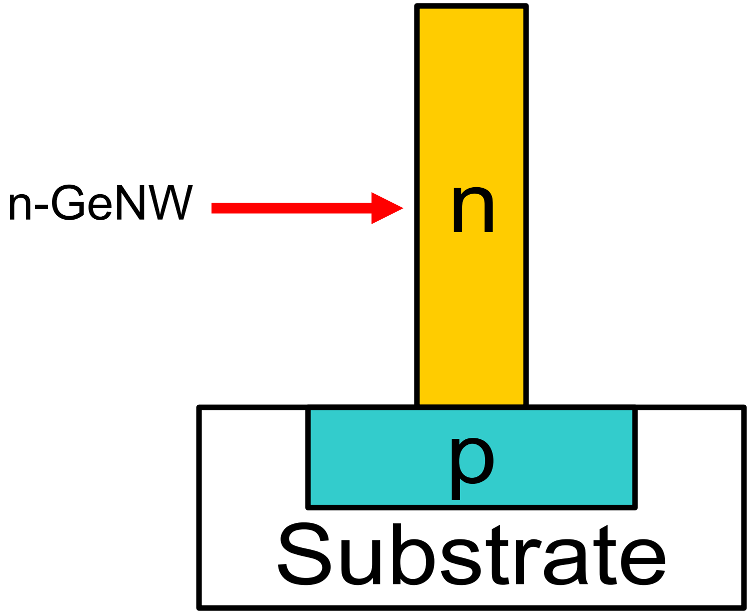
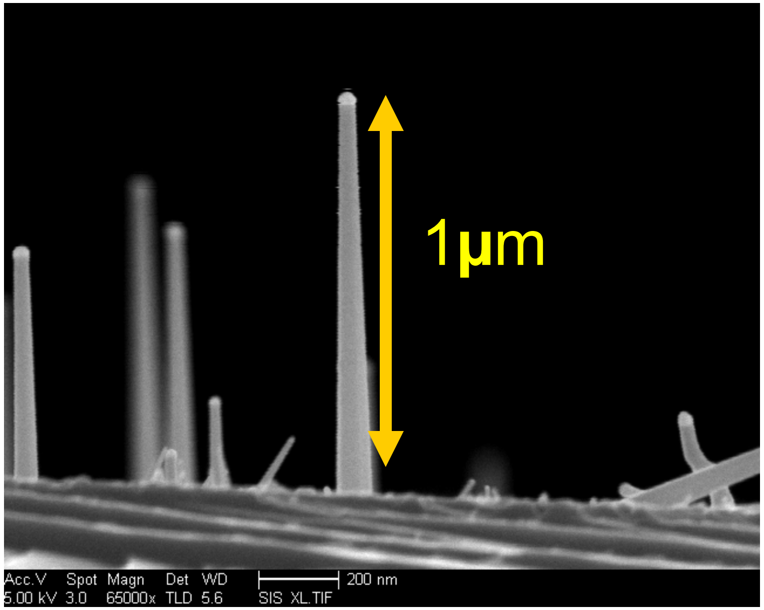
GeNW diode

- In-situ phosphorus-doped Ge nanowire standing on p-type Si(111) substrate.
- wafer level processsing
- GST-GeNW diode memory cell has ON/OFF ratio =~100





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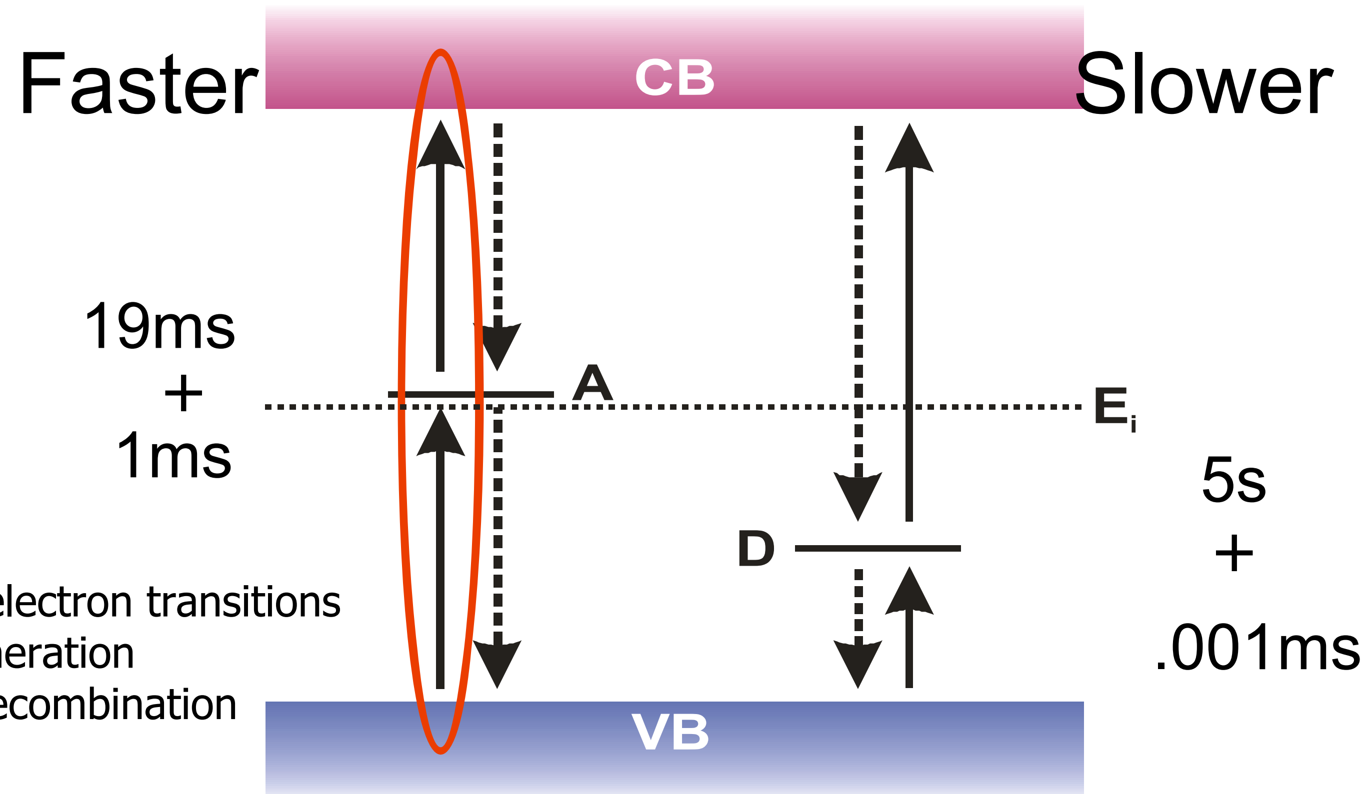
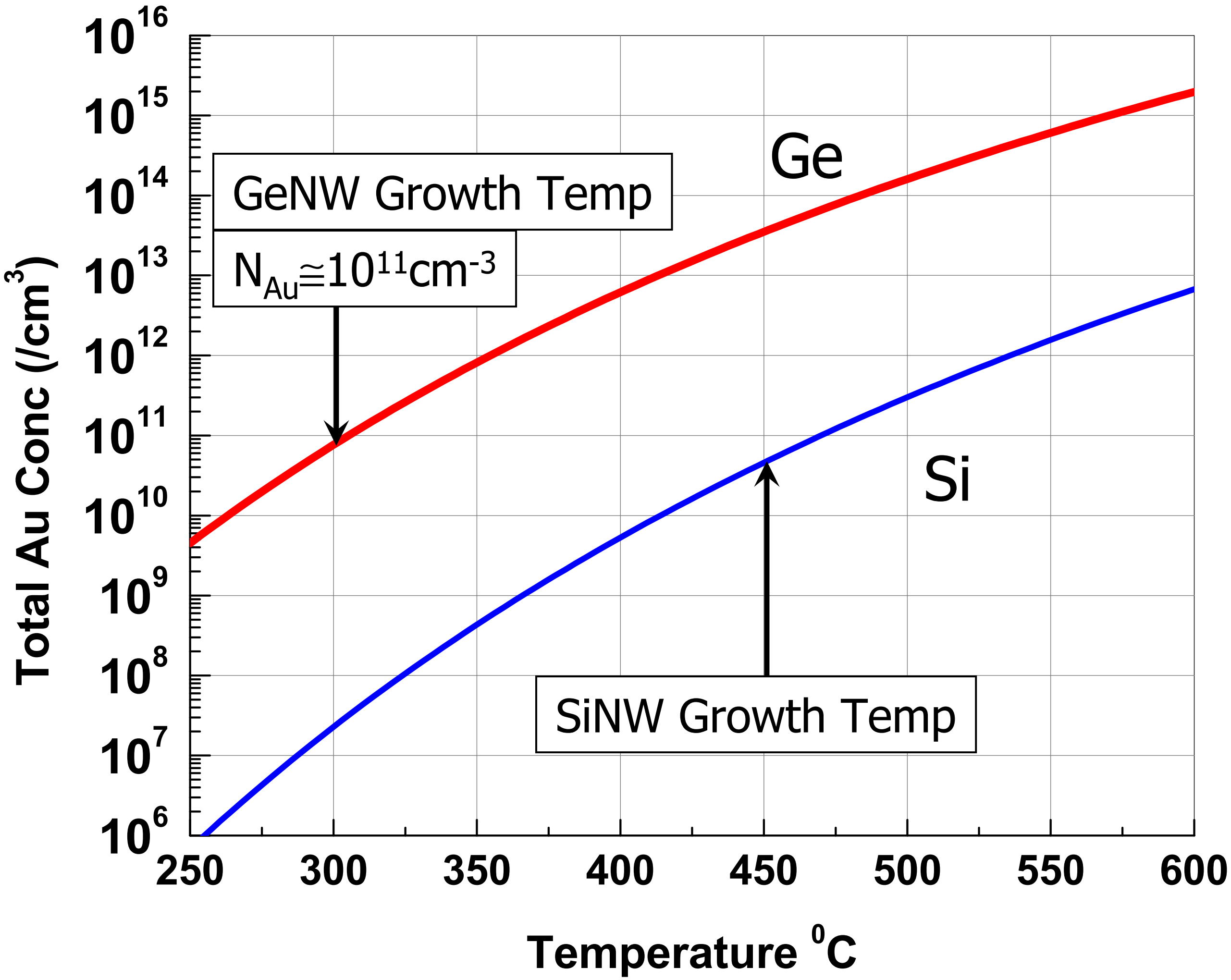
Recombination-Generation Processes in Si



Arrows indicate electron transitions
solid arrows: generation
dotted arrows: recombination

- Gold introduces midgap states into the silicon and germanium bandgaps increasing the rates of electron-hole recombination and thermal generation
- Level closest to midgap is most efficient for recombination-generation processes

Gold Solubility in Si and Ge



- Ge: Bracht, H., Stolwijk, N.A., Mehrer, H.: Phys. Rev. B 43 (1991) 14465.
- Si: Boit, C., Lau, F., Sittig, R.: Appl. Phys. A 50 (1990) 197.

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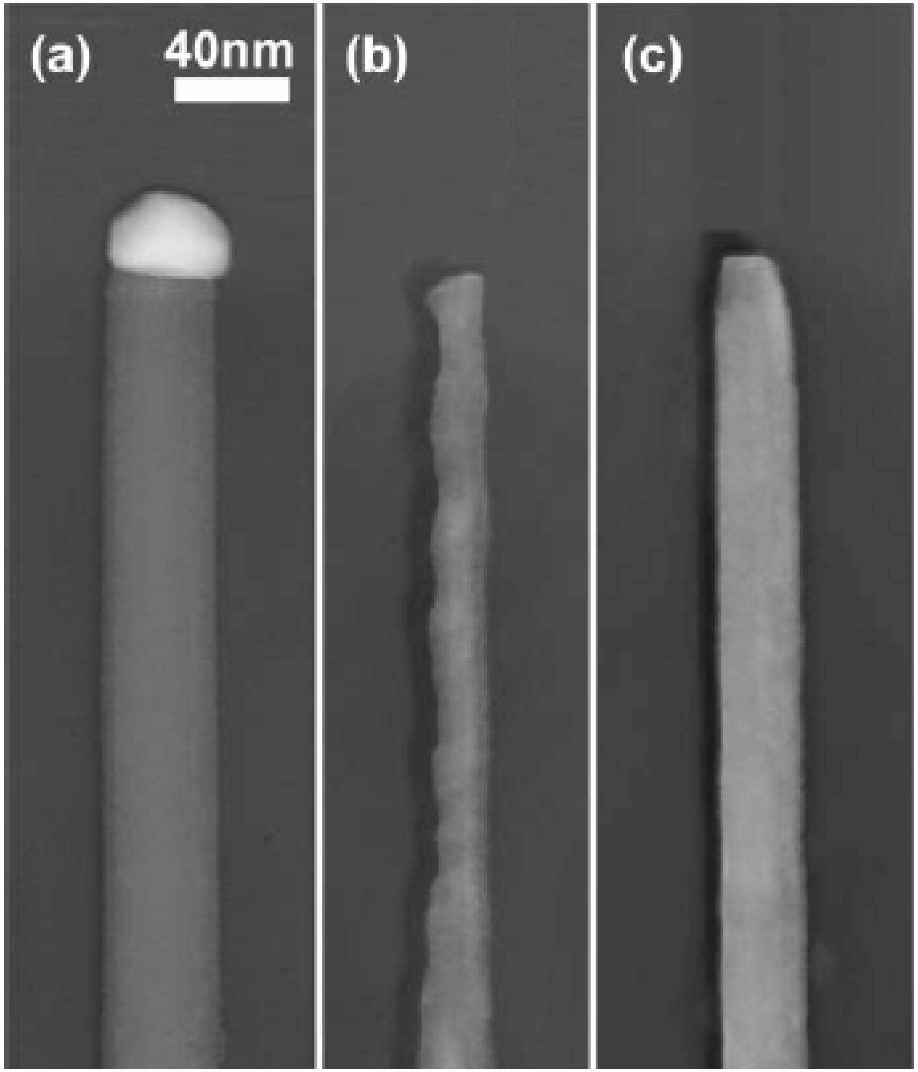
Gold removal from GeNW samples



a) as-grown GeNW

b) gold removed GeNW with triiodide (aq)

c) gold removed GeNW with triiodide-HCl (aq)

Woodruff, J. H.; Ratchford, J. B.; Goldthorpe, I. A.; McIntyre, P. C.; Chidsey, C. E. D.;

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Chemistry of gold removal process

•The overall chemical reaction for the gold removal is expected to be:

$$2\ Au(s) + I_3^-(aq) + I^-(aq) \rightarrow 2\ AuI_2^-(aq)$$

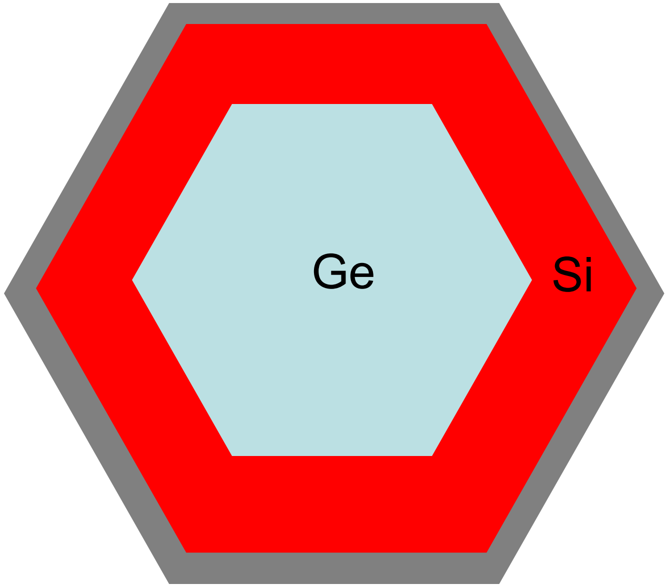
• triiodide etch concentration 1.2% I_2, 30% KI (Transene)

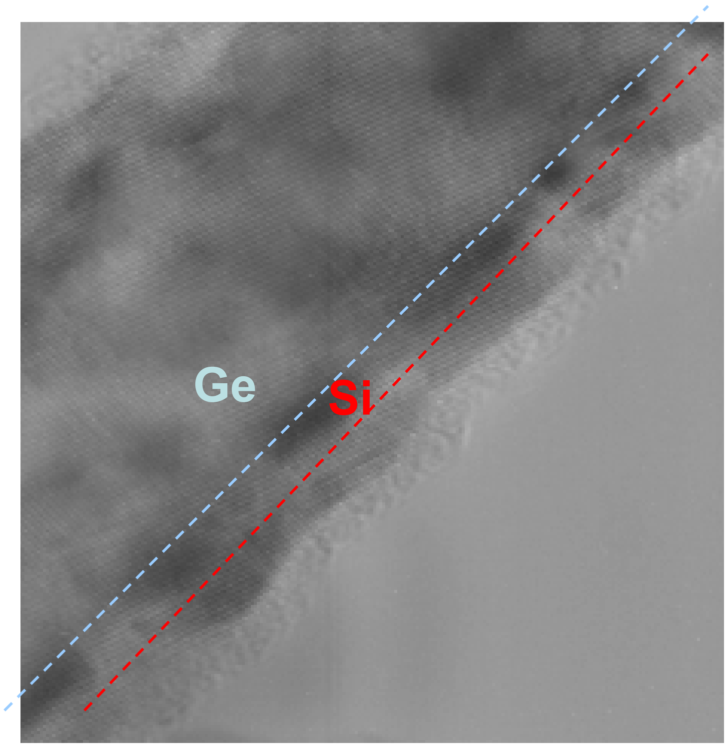
• HCl(aq) prevents GeNW surface oxidation and leaves the GeNW surface Cl terminated

Adhikari, H., McIntyre, P.C., et.al."Photoemission studies of the passivation of germanium nanowires <u>Applied Physics Letters</u> 87(26):263109

Hanrath, T., and B.A. Korgel. "Chemical surface passivation of Ge nanowires "<u>Journal of the American Chemical Society</u> 126(47) 15466-15472

Ge/Si core-shell nanowires

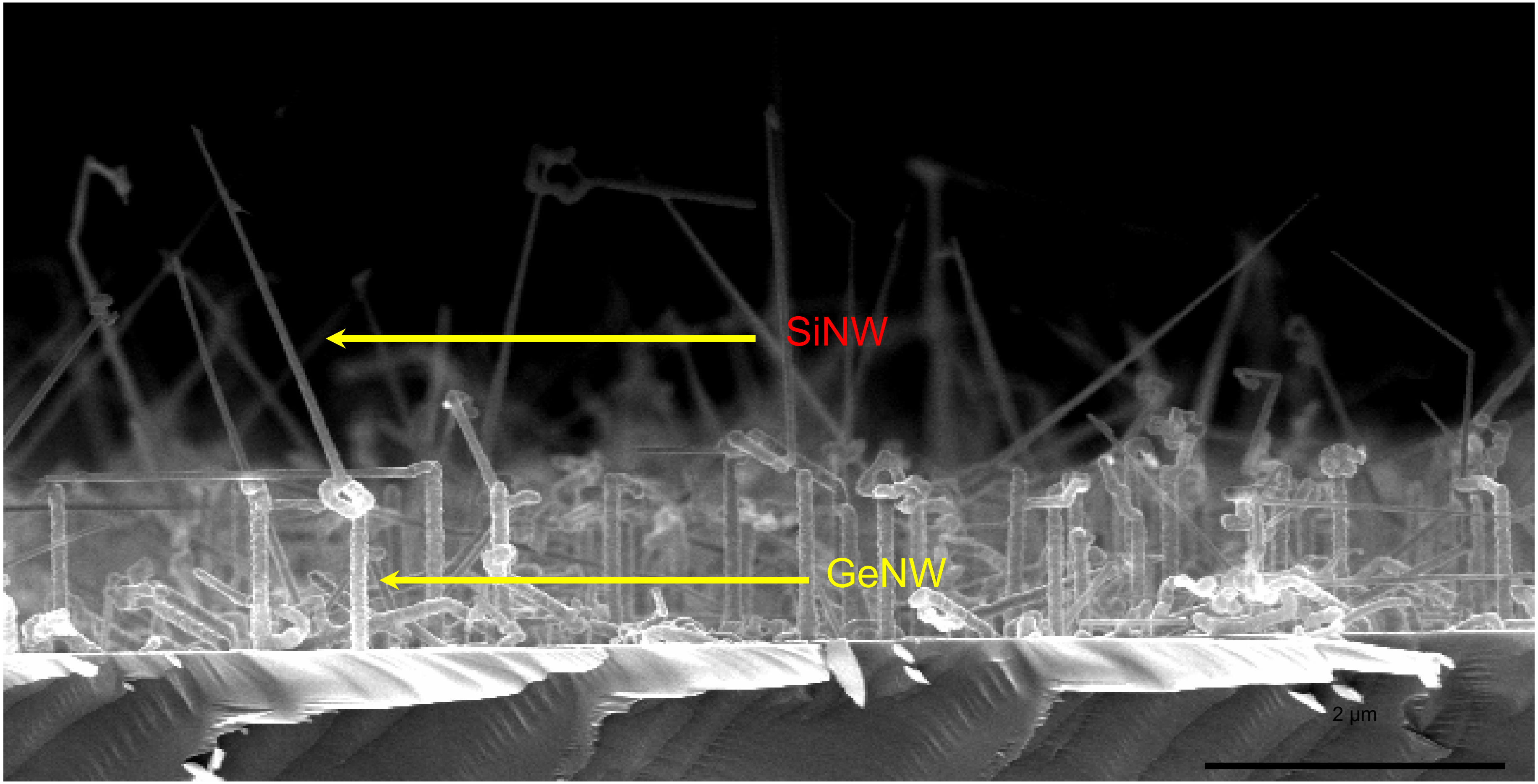




- Ge core because carrier mobilities are higher than in Si, for p-type conduction, and constrains carriers within the Ge core
- Si shell because SiO_2 is a stable, high quality surface passivation

Irene A. Goldthorpe, et. al. "Synthesis of Epitaxially Aligned Ge/Si Core-shell Nanowires" presented 13 Apr. 2007 at MRS Spring Meeting, San Francisco, CA.

Gold tips of GeNWs and residual gold on substrate grow SiNWs



585°C, P_{tot} = 5 Torr (0.35 Torr SiH_4 with H_2 carrier gas)

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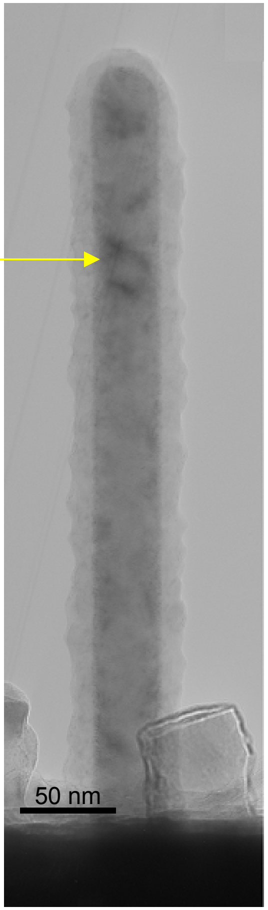
At T > 550˚C for a crystalline Si shell, gold diffuses into nanowire structure

diffused gold



T > 550˚C is need for crystalline Si shell deposition

585°C, P_{tot} = 5 Torr (0.35 Torr SiH_4 with H_2 carrier gas)

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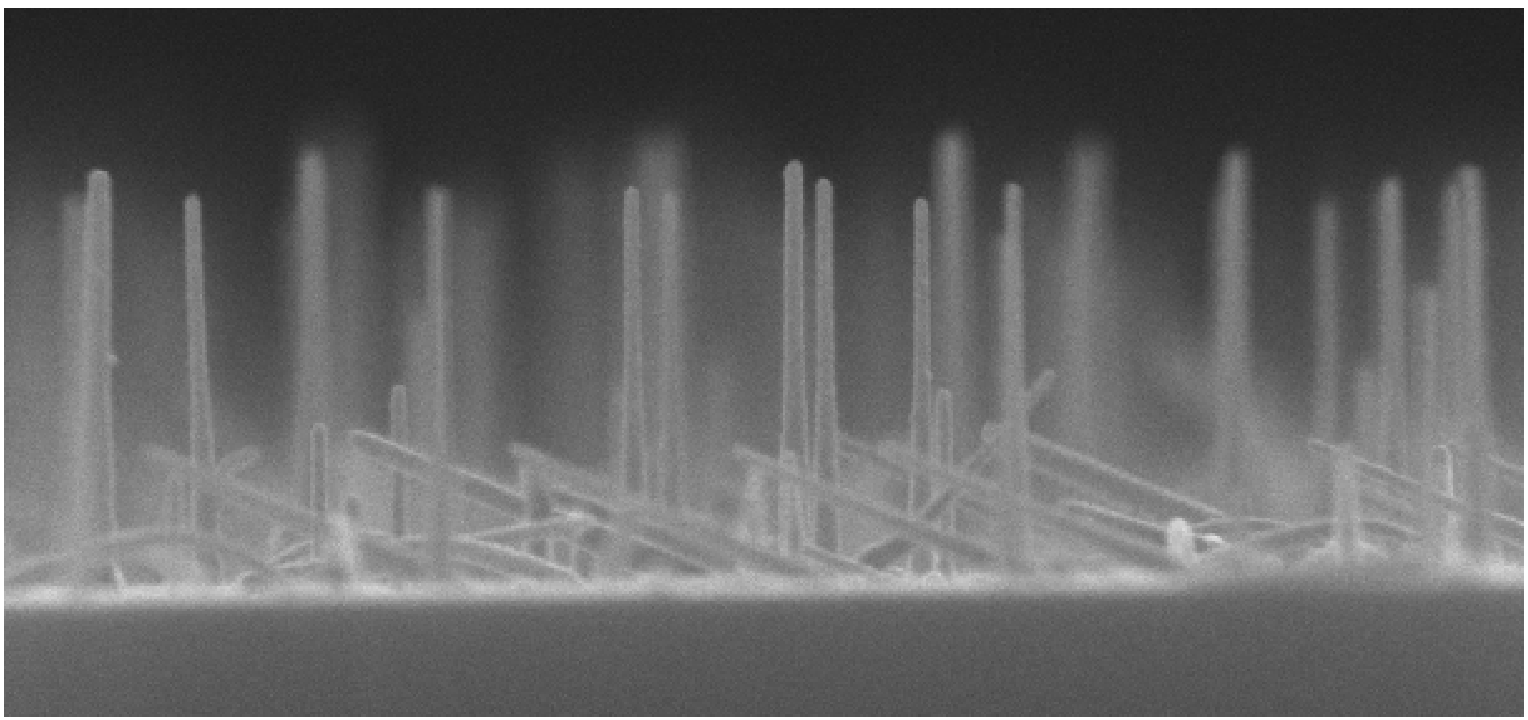
Optimal process for coreshell

1. Untapered GeNW growth from 20 nm catalysts: 370°C/300°C
2. HCl immersion (5 min), triiodide-HCl gold etch (10s), HCl rinse
3. 10 min anneal @ 600°C in H_2
4. Si deposition: 690°C, P_{tot} = 4.5 Torr, P_{SiH4} = 0.11 Torr with H_2 carrier gas, 60s



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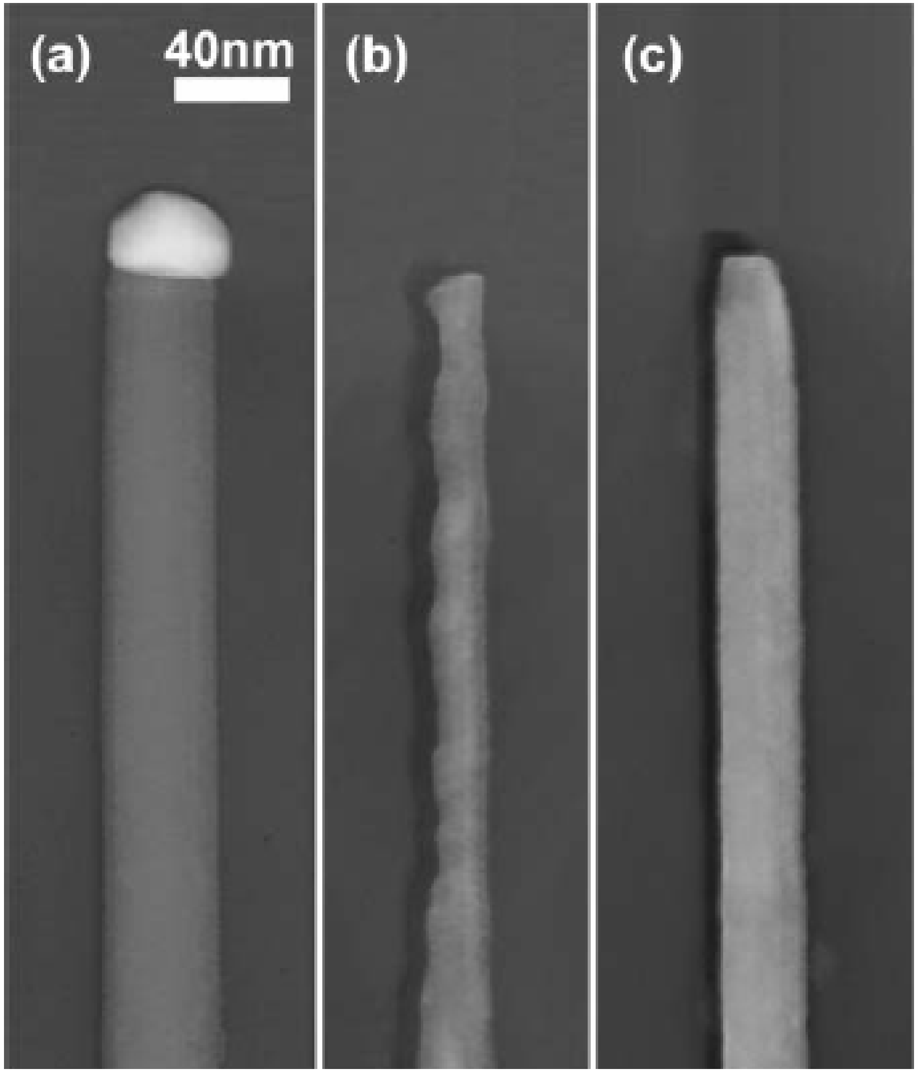

a) as-grown GeNW

b) gold removed GeNW with triiodide (aq)

c) gold removed GeNW with triiodide-HCl (aq)

One needs to characterize the chemical composition of GeNW surfaces for Ge/Si core shell applications

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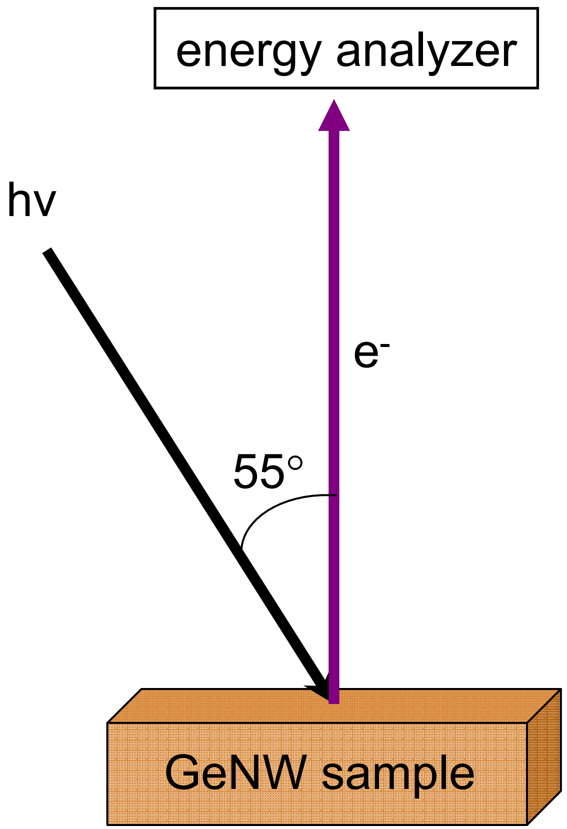
Synchrotron radiation photoemission from GeNW surface

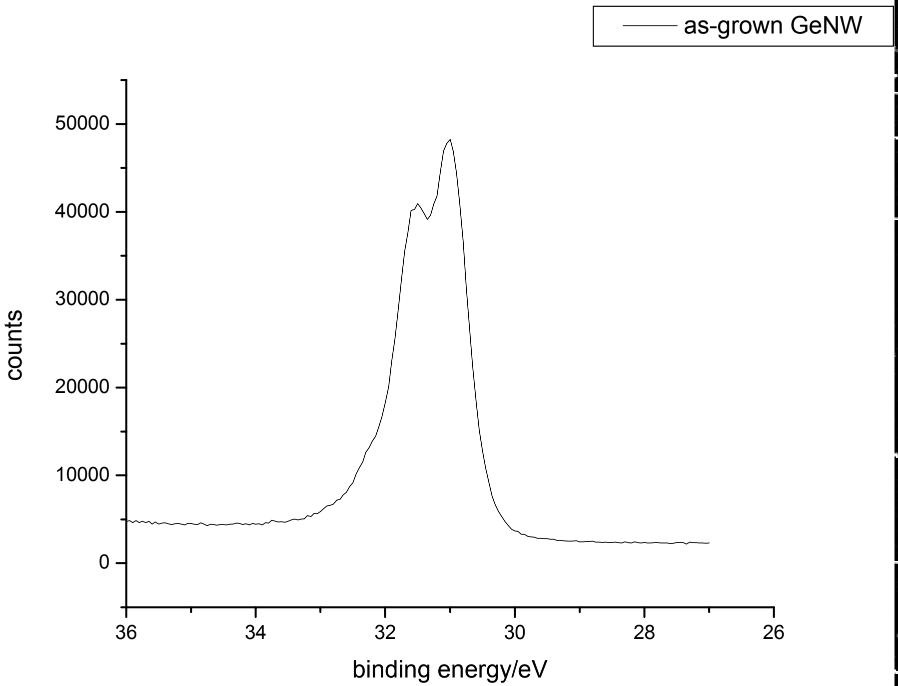


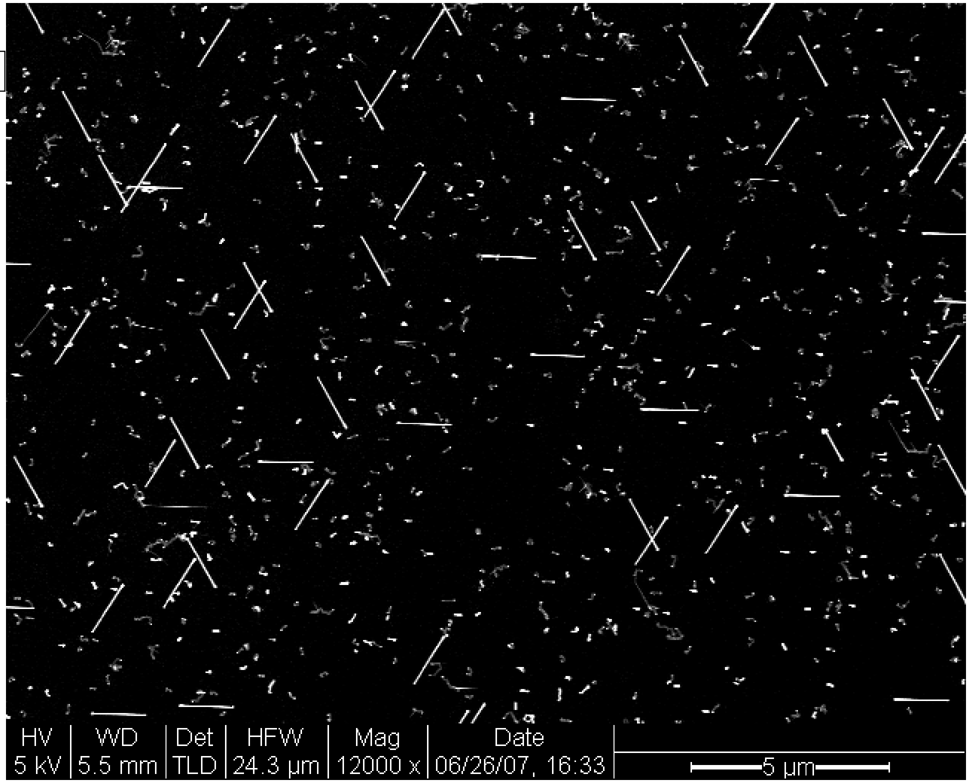
• 10eV to 100eV synchrotron photons were used to study chemical composition of GeNW surfaces

$$E_b = h\nu - E_k - \Phi_a$$

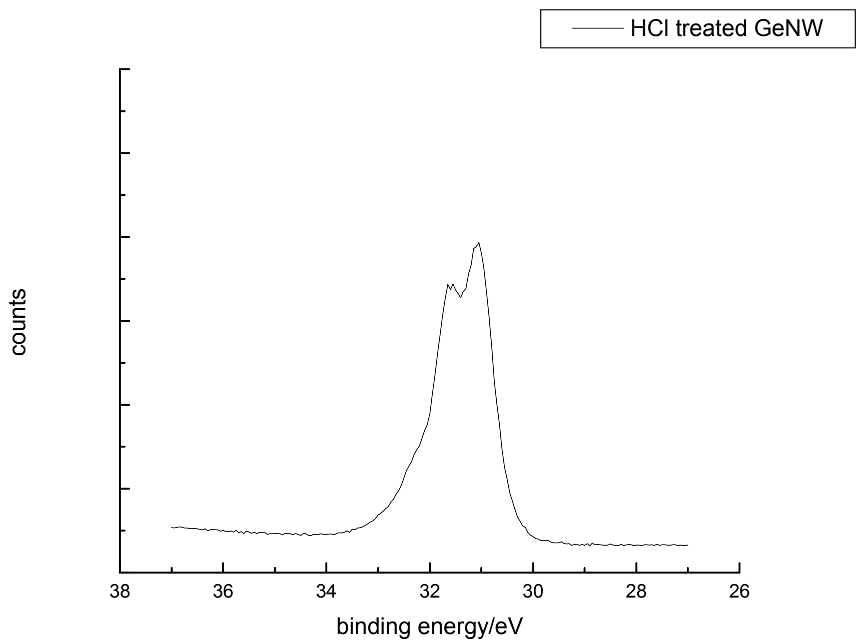
• Ge3d spectrum used to determine any change in the chemical composition of GeNW suface

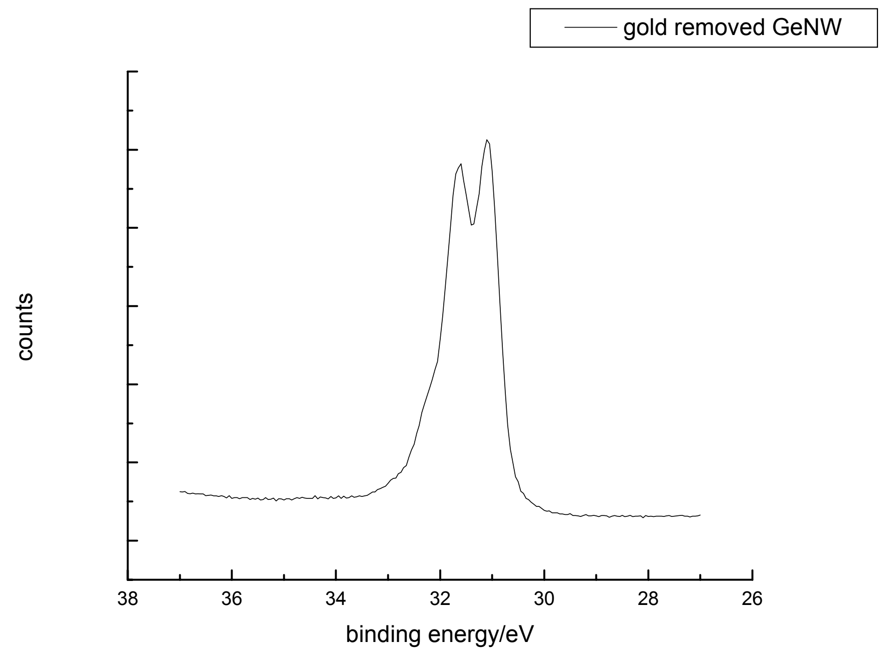
Ge3d spectrum of as-grown GeNW





Ge3d spectrum of HCl treated then triiodide-HCl treated GeNW sample

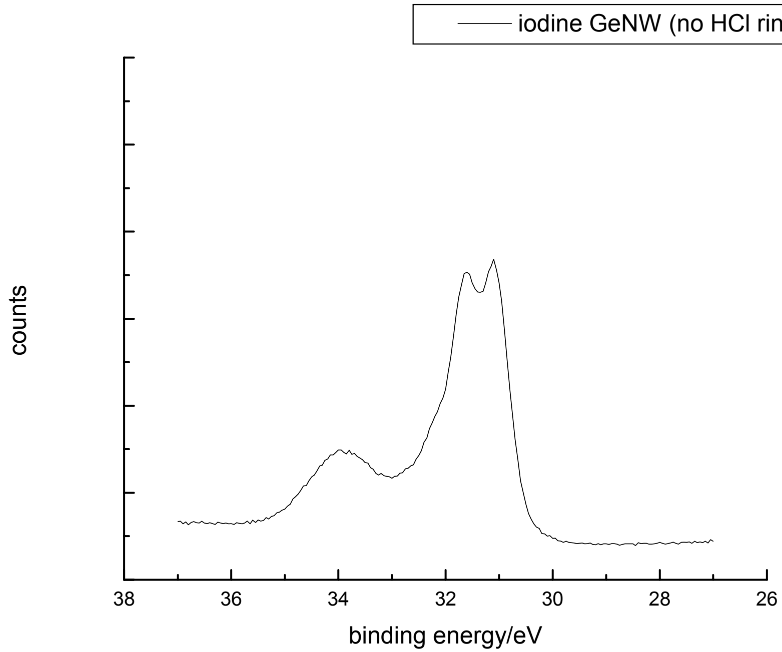


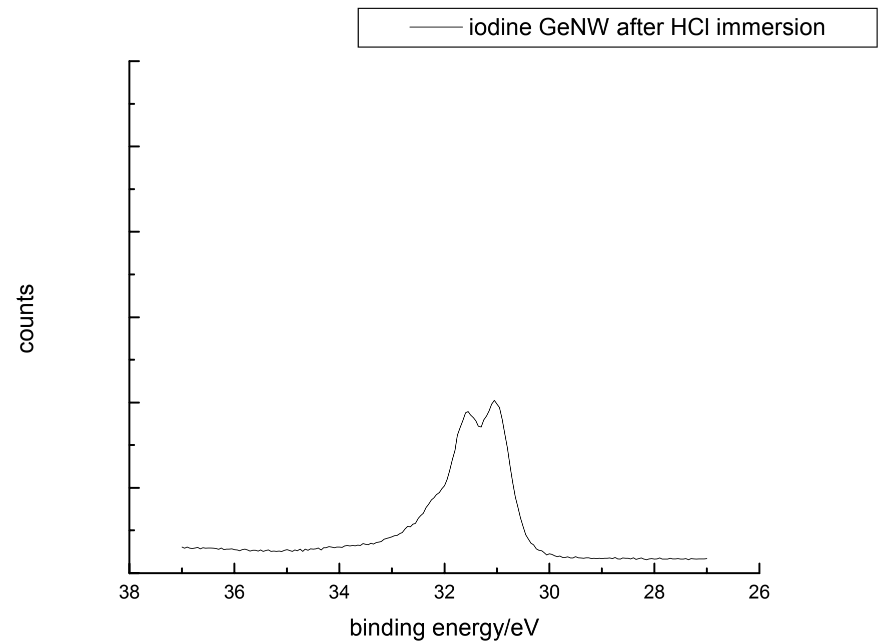


HCl (aq) prevents the oxidation of GeNW surfaces

Adhikari, H., McIntyre, P.C., et.al."Photoemission studies of the passivation of germanium nanowires
Applied Physics Letters 87(26):263109
Hanrath, T., and B.A. Korgel. "Chemical surface passivation of Ge nanowires "Journal of the American Chemical Society 126(47) 15466-15472

Ge3d spectrum of triiodide treated then HCl treated GeNW samples





HCl (aq) renders the GeNW surface Cl terminated

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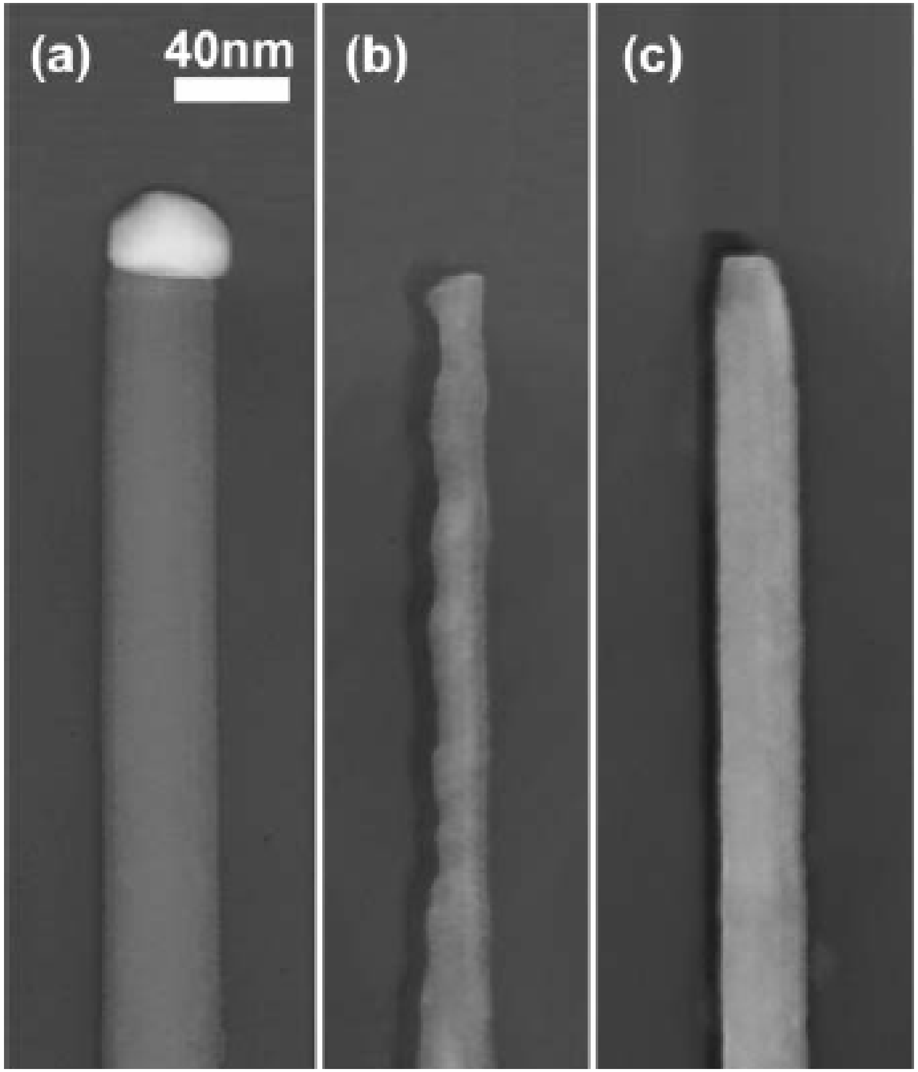

a) as-grown GeNW

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One needs to show that gold atoms have been removed to 1 x 10^{10} atoms/cm^2 (ITRS 2006)

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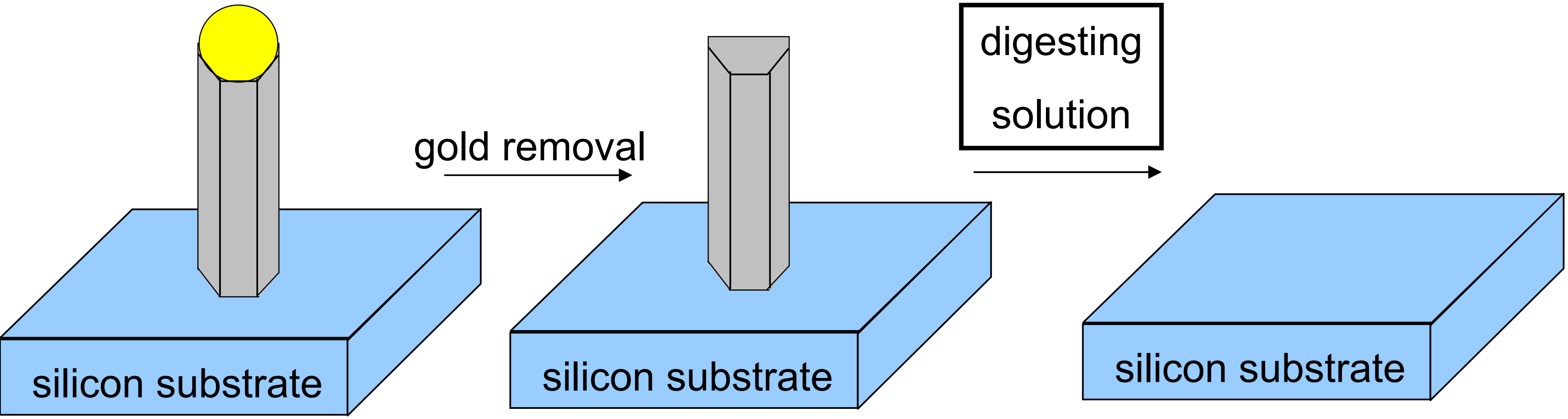
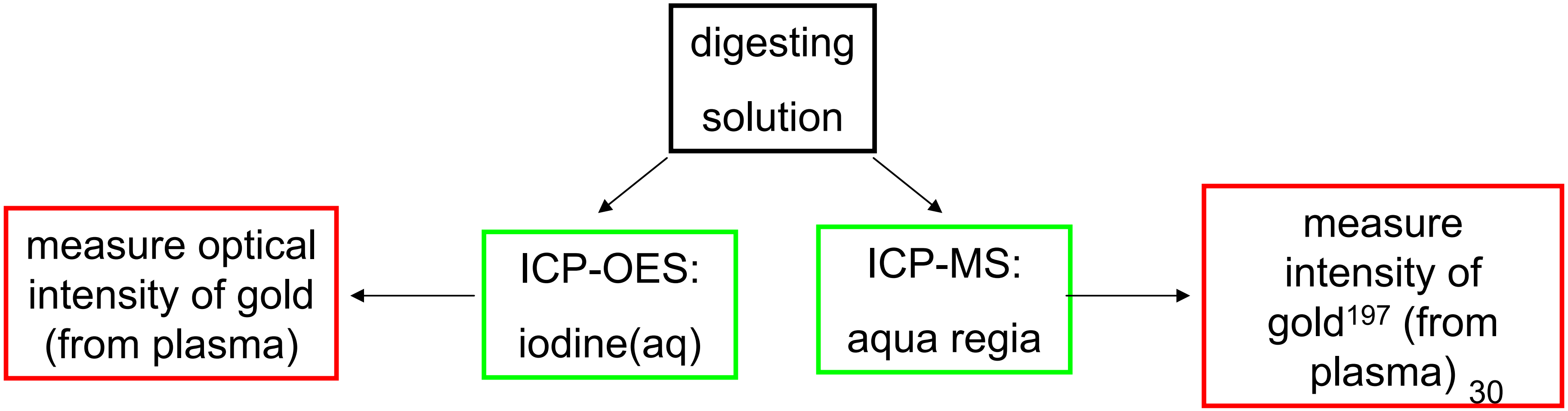
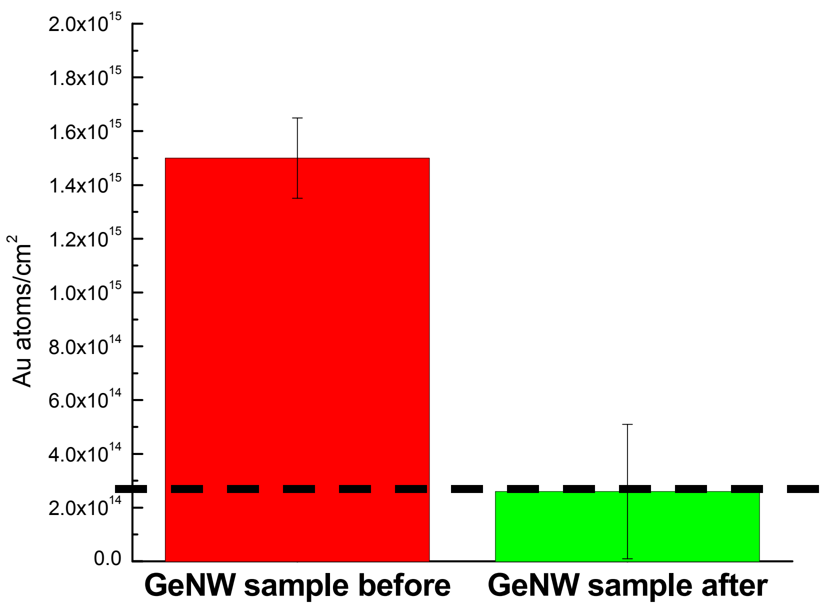
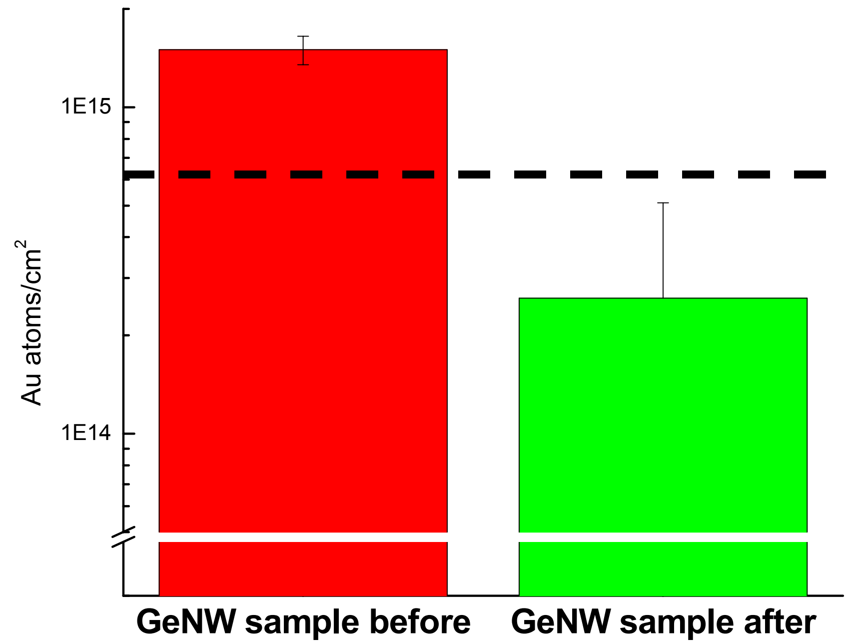
ICP OES and ICP MS method





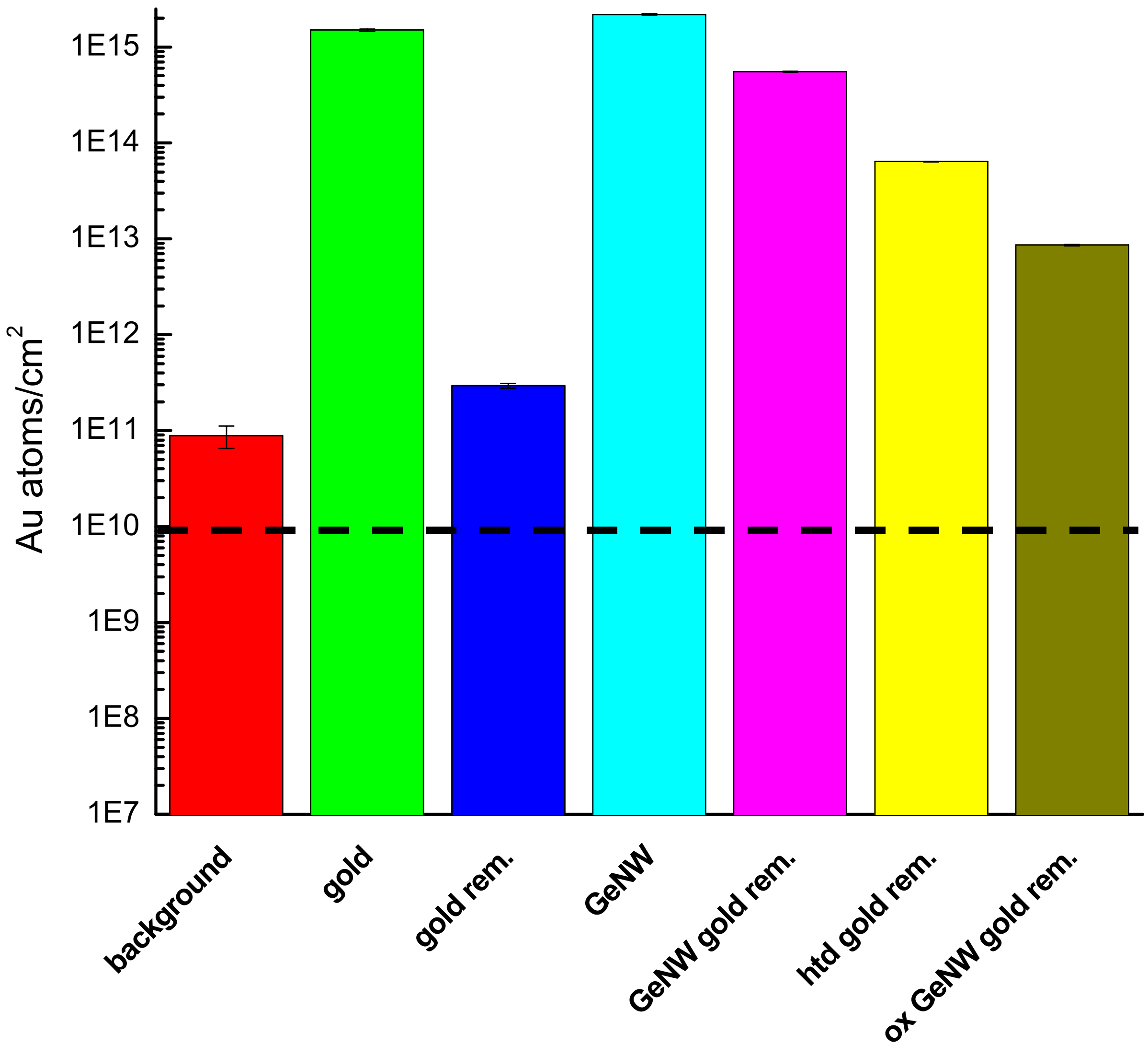
ICP-OES measurement of extent of gold removal





ICP-OES detection limit (– –) too high to measure trace levels of gold

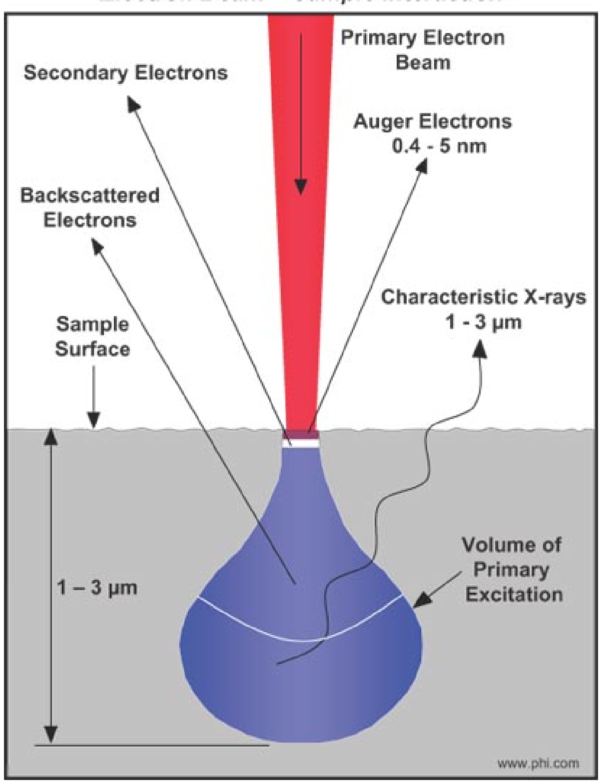
ICP-MS measurement of extent of gold removal

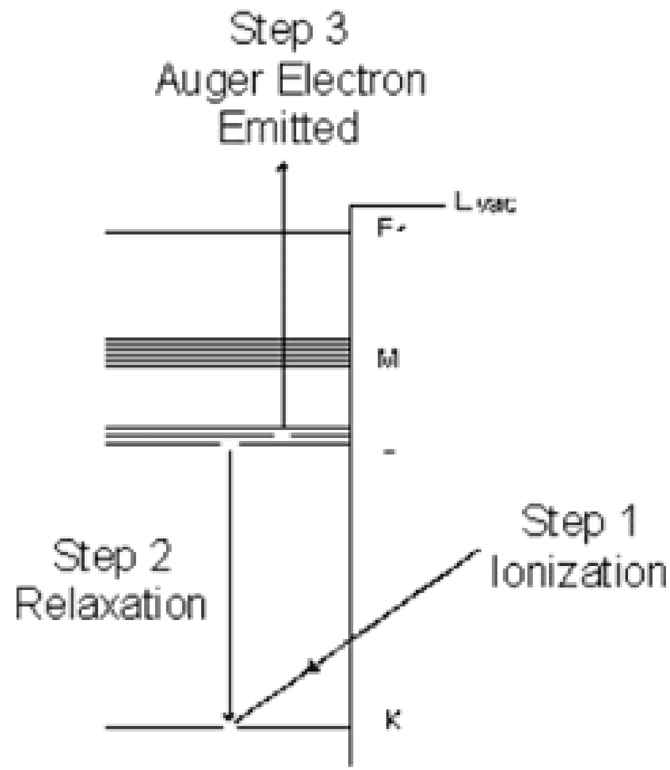


Source of residual gold?

- used Auger electron spectroscopy to perform microanalysis at specific sample features

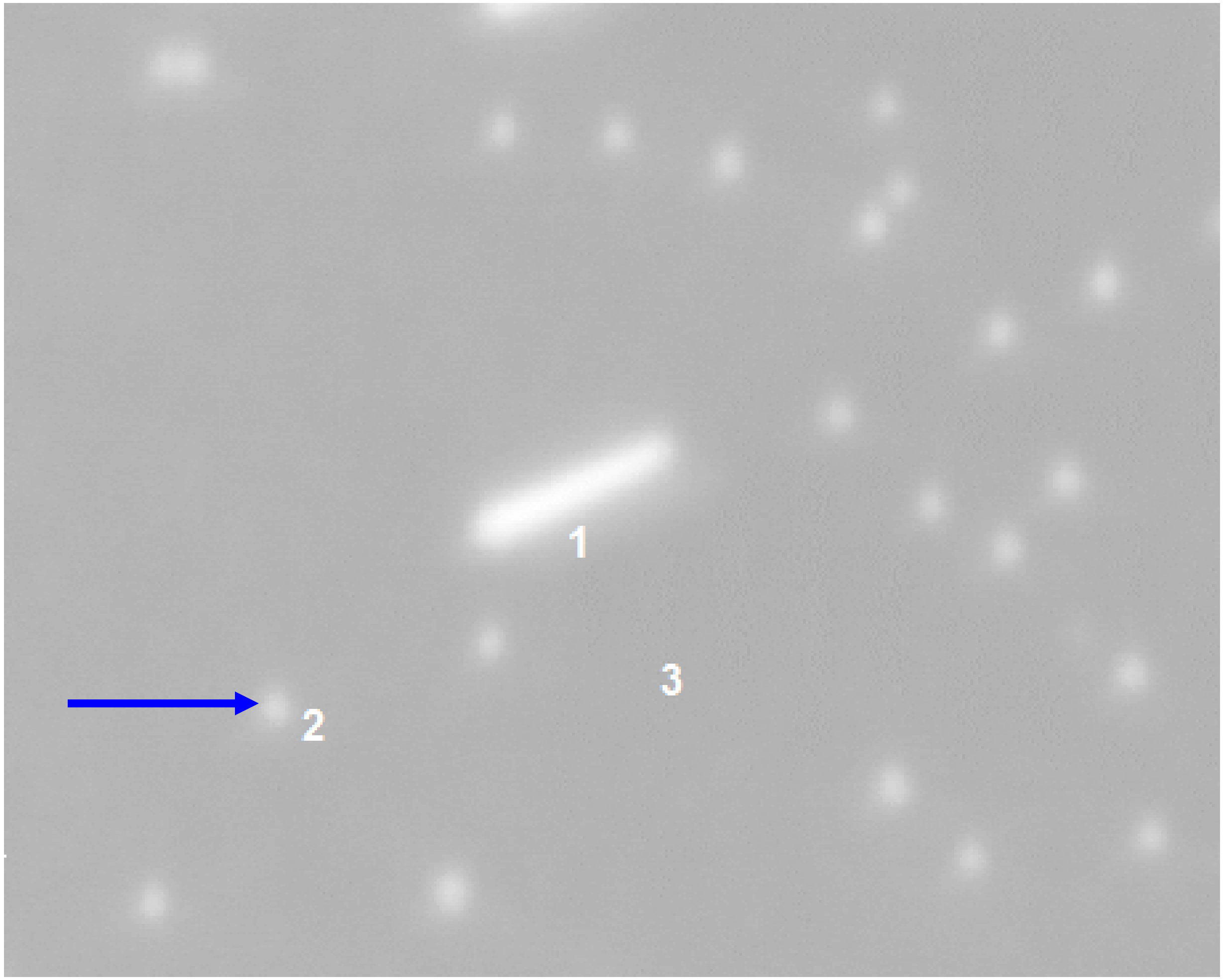
Electron Beam – Sample Interaction



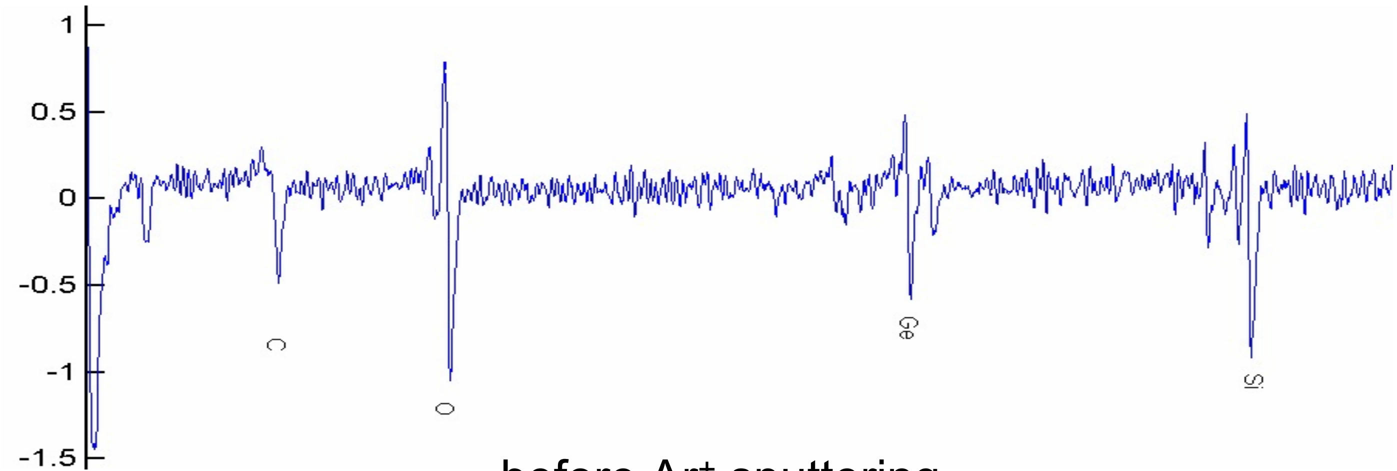


courtesy of Chuck Hitzman, Stanford Nanocharacterization Laboratory

Secondary electron image of gold particles and Ge Wire



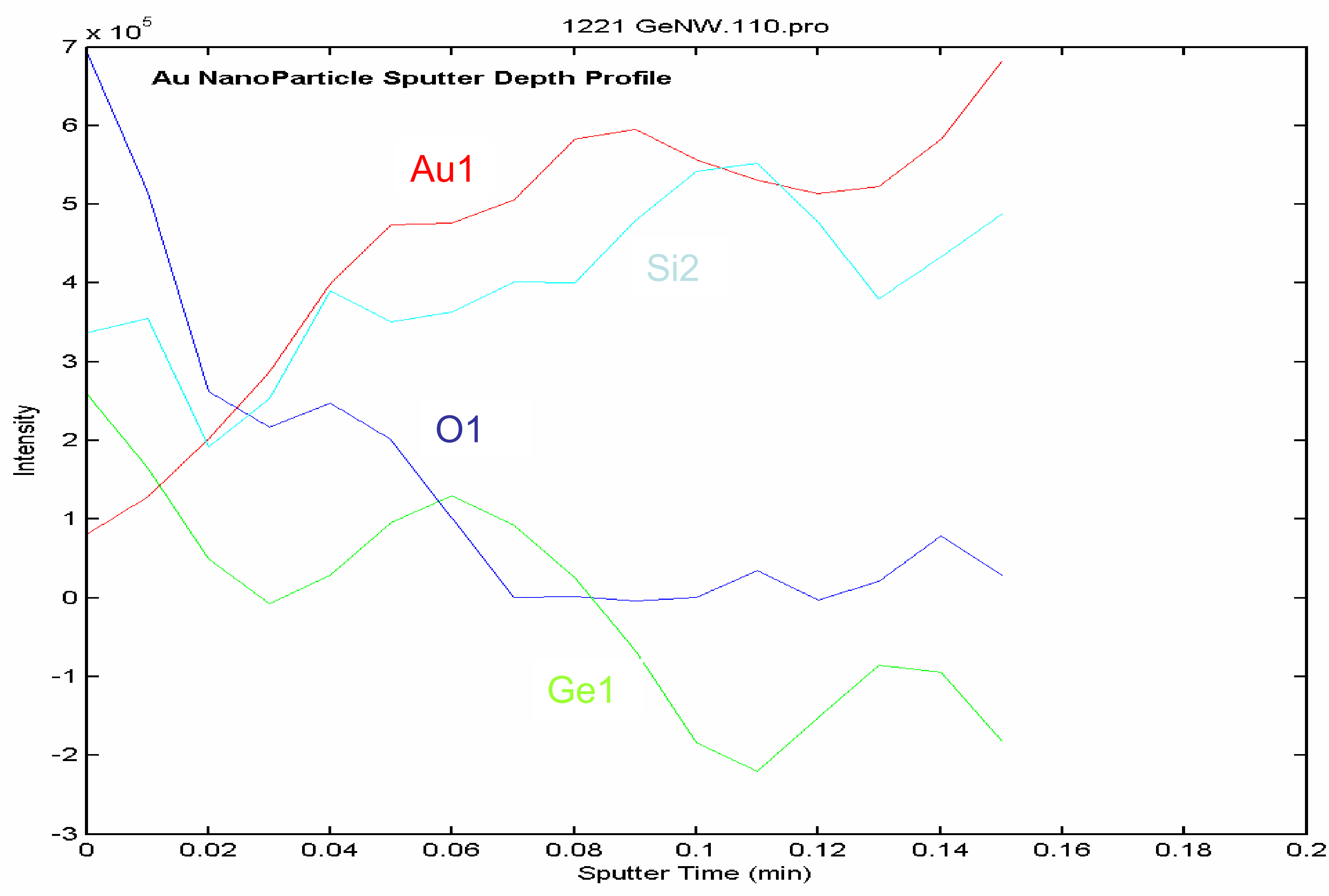
Auger electron spectrum at point 2



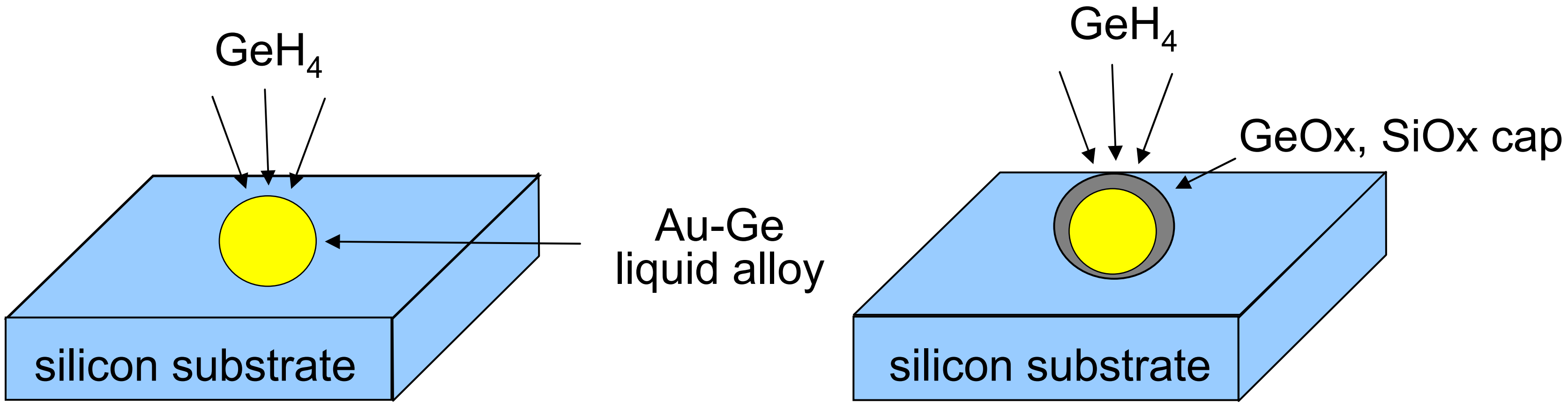
before Ar+ sputtering

after Ar+ sputtering

Sputter Depth Profile of Au nanoParticle



Capped gold nanoparticle reduces yield and effectiveness of gold removal?



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- single crystal growth at lower processing temperature
- unknown semiconductor manufacturing process integration of gold catalyzed GeNWs

Acknowledgements

- Professor Yoshi Nishi
- ICP-MS: Rob Franks, University of California-Santa Cruz Marine Analytical Lab
- AES: Chuck Hitzman, Stanford Nanocharacterization Laboratory
- SRC contract number 2006-VJ-1429 Task 1429.001
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