Growth and nanoscale reactions of semiconductor nanowires

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Nanowires for nanoscale electronics

Microelectronics to nanoelecronics





A computer chip made of tiny nanowires.

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Nanowire is promising for following Si devices scaling

Drain

Tunnel-FET



From Peter Grünberg Institute Semiconductor Nanoelectronics webpage Quantum computer

gates

Source

nanowire

1µm

Interconnect



Bio-sensor



Patolsky, F. et al. MRS Bulletin 2007, 32, 142.

Cui, Y et al. Science 2001, 291, 2.

Outline

Growth kinetics of Si and GaP nanowires

- □ VLS and VSS growth of nanowires
- □ Heterostructures with abrupt interfaces of Si/Ge
- **G**rowth of Si nanowires and the kinetics in:

ETEM (10⁻⁵ Torr) v.s. UHVTEM (10⁻¹⁰ Torr)

□ III-V (GaP) nanowire growth

Formation of nanowires

Reactions at the catalyst/nanowire interface



VLS growth based on Au is fundamentally unable to form abrupt Si/Ge interfaces...

of Si and Ge in solid catalyst.

AlAu₂ was demonstrated to form abrupt Si/Ge interface but it is air-sensitive...

Use of Ag-based alloy catalyst, AgAu ,to give more flexibility in growth modes

In situ growth setup in TEM

The Hitachi H-9000 UHV-TEM at IBM Watson Center



Objective lens polepiece

□ Flow source gases to carry out CVD while under observation

The real time observation of CVD process in this system allows us to optimize the growth conditions.

Ag-Au alloys for nanowire growth



- From the phase diagrams of Ag with Si, Ge, and Au, it forms eutectics with Si and Ge.
 - Growth T: low enough to avoid
 interdiffusion of Si and Ge during growth
 and high enough to achieve a catalytic
 chemical vapor deposition growth rate that
 is not too slow.
 - Ag is **resistant to oxidation**; Ag-Au alloys are potentially useful for scale-up to standard CVD growth conditions than say $AIAu_2$.



Nucleation of Si from Ag and AgAu

Si



VLS

VSS





Agglomerated Ag on a SiN membrane. At 550 °C and 1x10⁻⁶ Torr disilane.

Nucleation of Si has occurred at the arrowed location



Ag with Au aerosol particles on a SiN membrane. At 580 °C and 5x10⁻⁶ Torr disilane.

VSS and VLS processes are visible in particles of presumably different Ag/Au ratios.

 VSS process from Ag
 VSS nucleation occurs
 hetergeneously at the edge of the particle with the Ag catalyst remains solid before and during nucleation.

VLS and VSS processes from AgAu alloy with different ratios

- Some particles show VLS nucleation while others show VSS due to the variations in composition.
- The growth temperature corresponds to the eutectic temperature of Si with AgAu.

The control of particle composition is critical.

VLS and VSS Si nanowire growth and kinetics from AgAu





VSS growth from Ag_2Au at (a) 512°C and 5x10⁻⁶ Torr disilane and (b) 530°C and 1x10⁻⁵ Torr disilane



VLS growth from AgAu₂ at 556°C and 1x10⁻⁵ Torr disilane



Continued growth by VSS from $AgAu_2$ at 360°C and \Box 1x10⁻⁵ Torr disilane.





- AgAu alloy in both VLS and VSS modes can produce nanowires with well-defined structures.
- VSS growth: the catalysts appear hexagonal and the nanowires grow in [111] with {211} sidewall.
- VLS growth: a hexagonal cross section with {211} sidewalls with sawtooth faceting.
- Catalyst solidification and melting show hysteresis.
- The T variation of growth rate is consistent with an Arrhenius dependence.

Growth of long nanowires by VLS and followed by slow and precise VSS growth of good heterostructures at specific locations.

Hollow point: liquid catalyst Solid point: solid catalyst

Crystallography

AgAu [001]

Si [111]

Si [112]



AgAu (111)

viewing direction

[110]

[121]

[211]

[112]

Si (111)

[111]

[110]

viewing direction

As expected, AgAu catalyst has equilibrium crystal shape. Same as pure Au.

- A regular truncated octahedron on a nanowire with a hexagonal cross section.
- Experimentally the nanowire cross section is a trigonal hexagon, the relative sizes of the AgAu {111} and {001} faces vary; some {001} faces are even absent, and the hexagons are therefore not regular.

Abrupt interface of Si/Ge

After the detailed understanding of the nanowire growth using solid catalyst, we can grow different novel heterostructures



Morphology at different growth conditions



Initial growth in a low pressure MOCVD. $500^{\circ}C$ TMGa = 9.2×10^{-6} Torr PH3 = 1.2×10^{-2} Torr (V/III = 1340) 440°C TMGa = 5×10^{-8} Torr PH3 = 1.0×10^{-5} Torr (V/III = 200) The catalyst during growth contains ~23% Ga. 435° C TMGa = 3.5×10^{-7} Torr PH3 = 1.0×10^{-5} Torr (V/III = 28) The droplet volume is larger and contains ~70% Ga.

GaP nanowire growth



Growth kinetics

Si nanowire growth



GaP nanowire growth at high V/III



GaP nanowire growth at low V/III



Summary

- □ Self assembly nanowire growth: VLS and VSS
- □ Growth of heterostructures with abrupt interfaces
- The aberration corrected ETEM imaging confirms the growth kinetics at atomic scale.
 - a. Step flow kinetics
 - b. Rapid stepwise growth and repeating nucleation
 - c. The presence of small truncation
- The kinetics of III-V nanowire growth by VLS varies with twin formation at specific growth condition but stable growth was found within specific growth region.