Effect of HCl on the doping and shape control of Silicon nanowires

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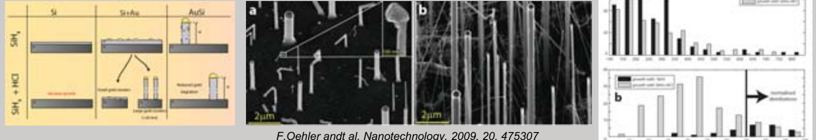
In the case of silicon nanowires (SiNWs), the Chemical Vapor Deposition (CVD) technique has shown interesting results, mostly using gold as the liquid catalyst. However the wire surface is often polluted by gold clusters, metallic impurities that diffuse from the main catalyst. The wire surface also presents uncontrolled facets which are potential scattering centers for the carriers in the FET channel. The presence of HCl during the growth induces a surface chlorination of the NWs. We have shown that the chlorination takes places on the sidewalls of the wire. On this surface it changes both the lateral growth speed and the gold migration. Nanowires grown using HCl then present a lower gold cluster density. The Silicon NWs are doped during the growth by adding Phosphine or Diborane. We show here the effect of HCl on the shape and the doping of the SiNWs.

The growth of the NWs is realized by VLS method with gold catalyst on a CVD reactor:
EasyTube3000 First Nano, a Division of CVD Equipment Corporation

The doped rate is control by a double diluted system in our reactor

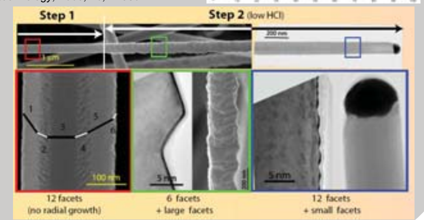
Effect of HCl on Si NWs growth

- The gold diffusion on the SiNWs sidewalls is blocked by adding HCl during the growth.
- HCl modifies the diameter distribution of the SiNWs



F.Oehler andt al, Nanotechnology, 2009, 20, 475307

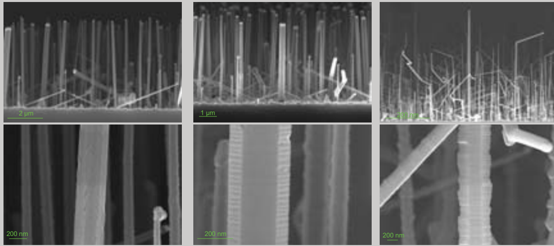
In presence of HCl the 2D growth on the NWs sidewalls is inhibited by the surface chlorination and the lack of gold who is a catalyst for the 2D growth. Then the faceting is changed with HCl.



F. Oehler and al, Nano Lett. 2010, 10, 2335–2341

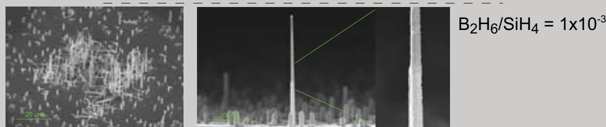
Si NWs doped without HCl

P doped by adding B_2H_6 during the growth



$B_2H_6/SiH_4 = 2{,}4x10^{-5}$ $B_2H_6/SiH_4 = 1{,}6x10^{-4}$ $B_2H_6/SiH_4 = 1x10^{-3}$

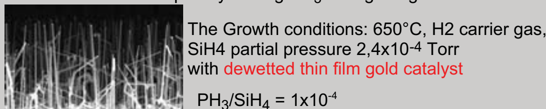
The Growth conditions: 650°C, H2 carrier gas, SiH4 partial pressure $2{,}4x10^{-4}$ Torr with dewetted thin film gold catalyst



$B_2H_6/SiH_4 = 1x10^{-3}$

The Growth conditions: 650°C, H2 carrier gas, SiH4 partial pressure $2{,}4x10^{-4}$ Torr with 100 nm gold colloids catalyst

N doped by adding PH_3 during the growth



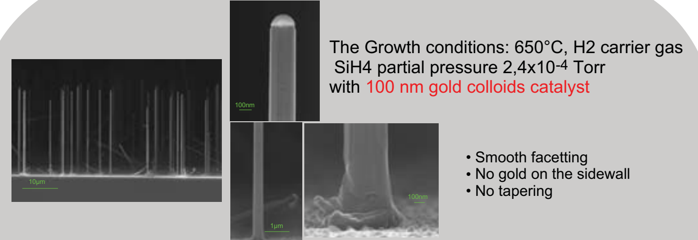
The Growth conditions: 650°C, H2 carrier gas, SiH4 partial pressure $2{,}4x10^{-4}$ Torr with dewetted thin film gold catalyst

$PH_3/SiH_4 = 1x10^{-4}$

The 2D growth and the faceting of the NWs increase with the ratio dopant/Si

Si NWs doped with HCl

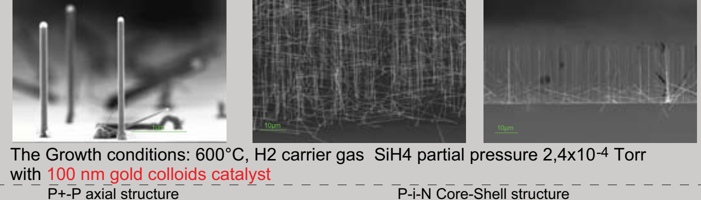
P doped by adding B_2H_6 and HCl during the growth



The Growth conditions: 650°C, H2 carrier gas SiH4 partial pressure $2{,}4x10^{-4}$ Torr with 100 nm gold colloids catalyst

- Smooth facetting
- No gold on the sidewall
- No tapering

N doped by adding PH_3 and HCl during the growth



The Growth conditions: 600°C, H2 carrier gas SiH4 partial pressure $2{,}4x10^{-4}$ Torr with 100 nm gold colloids catalyst

P+-P axial structure — P-i-N Core-Shell structure

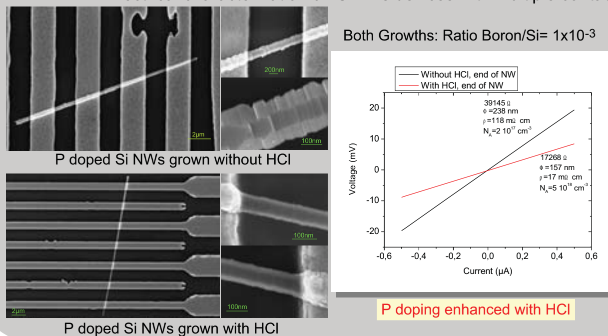
P
P+
I-N Shell
P core

Core growth with HCl and the shell i-N without HCl

The growth with HCl reduces the faceting of the NWs and the 2D growth on the Nws sidewalls: allows making abrupt junction in axial configuration and smooth interface in Core-Shell structure

Electrical characterization

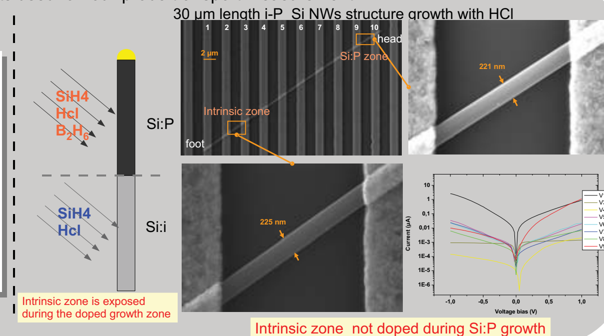
Electrical characterization on SiNWs devices with multiple contacts used for four-probe transport measurement.



P doped Si NWs grown without HCl

P doped Si NWs grown with HCl

P doping enhanced with HCl



Intrinsic zone is exposed during the doped growth zone

Intrinsic zone not doped during Si:P growth

With Hcl

- **Growth:**
  - 2D growth highly reduced
  - Sidewall gold diffusion blocked
- **Morphology:**
  - Tapering highly reduced
- **Electrical properties:**
  - Enhancement of the doping level
  - Nanowires doping is not done trough the sidewalls

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