

Germanium nanowires: from synthesis, surface chemistry, assembly to devices

Dunwei Wang
Department of Chemistry, Stanford University

In order to continue the ever impressive and successful scaling pace of MOSFETs, tremendous research efforts have been devoted to the search of new materials to complement or replace Si as the Si-based ones are predicted to reach theoretical limits soon. Ge has low band gaps and high carrier mobilities, thus offering appealing potentials as a candidate of choice for future electronics. For the same purpose of discovering new materials, another area of interest is low dimensional nanostructures such as nanowires (NWs), owing to the facile synthesis, high structure perfection and superior properties. In this context, Ge NW has combined advantages and is particularly promising. My thesis focuses on this subject and has advanced in a wide range, from understanding and controlling synthesis and surface chemistry, to highly ordered assembly and devices with excellent performance.

Synthesis of GeNWs.

Single crystalline Ge NW can be readily synthesized with a simple chemical vapor deposition (CVD) method at low temperatures from Au nanocluster seeds, with GeH_4 as the feeding stock. The mechanism follows the widely accepted vapor-liquid-solid (VLS) one, in which reactive Ge species decomposed from GeH_4 diffuse into Au seeds and form alloy; after super saturation, excess precipitate out and prolongate to form single crystalline NW. The NW diameter is defined by the seed size and the length is determined by growth duration. Since GeH_4 decomposes easily and the Ge-Au binary alloy has a low eutectic temperature, an unprecedented low temperature of 275°C is achieved. The key to an optimum growth is balanced Ge feeding and its diffusion in growth seed (Figure 1). Understanding and refining the growth chemistry enable excellent control over the synthesis. For example, 100% yield of Ge NWs relative to the Au seeds is obtained, with one-to-one correspondence of NWs to the seeds. This result leads to deterministic GeNW synthesis by patterning of individual Au nanoclusters. Furthermore, these deterministically

grown NWs can be aligned into quasi-parallel arrays with a simple post-growth fluidic treatment. Optimized NW growth also makes gram-scale synthesis possible by supporting the growth seeds on high surface area material such as silica. Additionally, *in situ* doping during the growth is achieved with co-flows of precursors containing desired dopants, e.g. PH_3 for n-type and B_2H_6 for p-type, and the doping level can be controlled by adjusting the ratios of Ge to dopants.

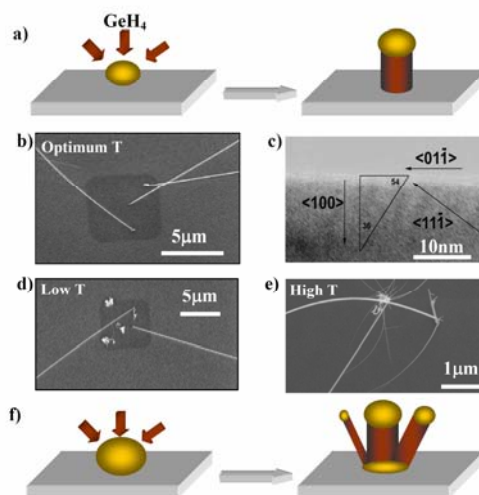


Figure 1. Controlled synthesis of Ge NWs. a) schematic representation of the VLS growth mechanism. Under optimum conditions, i.e. balanced feeding of Ge and its diffusion in Au seeds, one-to-one growth occurs and every Au seed produces one NW, as shown in b). c) These NWs are single crystals as confirmed by high resolution transmission electron microscope (TEM). d) At lower temperatures, under-growth happens as a result of insufficient feeding. Blotches instead of high quality NWs are formed. e) At higher temperatures, over-growth happens, as indicated by the carton in f), i.e. fast feeding of Ge results in more than one NW from a single seed.

Surface chemistry

Nanostructures have considerably higher surface areas than their bulk counterparts, therefore surfaces often play important, sometimes even dominant, roles in the nanostructure properties. For instance, we have calculated quantitatively that existing surface potentials can affect cylindrical semiconductor NWs more significantly than planar ones:

$$\frac{4\pi\epsilon_0\epsilon\phi_0}{2\pi n} = \left(1 - \frac{d}{3R}\right) d^2. \quad (\text{Equation 1})$$

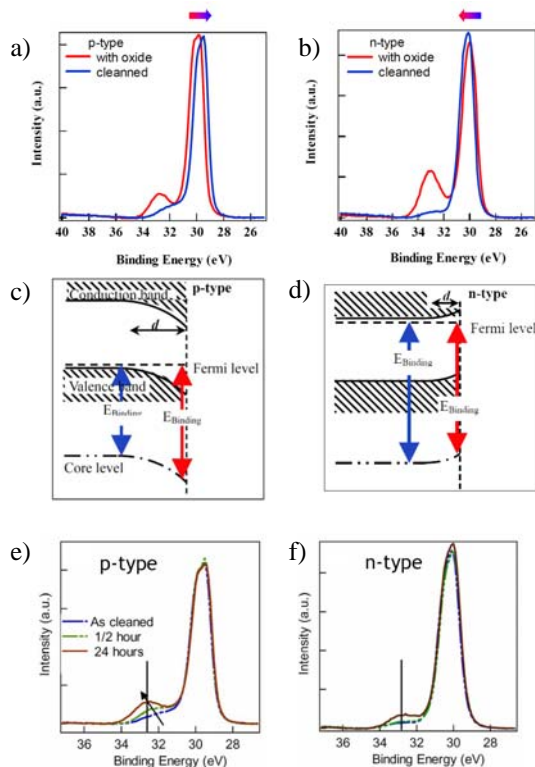


Figure 2. Understanding Ge NW surface chemistry. a) and b) Opposite band-bending caused by existence of surface oxides, and it is qualitatively shown in c) and d) with the band diagrams. e) and f) demonstrate distinct oxidation processes of p and n-type Ge NWs. For p-type, GeO is formed first and gradually converted to GeO₂, whereas GeO₂ is formed directly and quickly on n-type ones without the intermediate GeO step.

In my thesis, the surface chemistry of Ge NWs is studied in a systematic manner and a few novel yet generic findings are unveiled. First, Ge NWs with different doping types exhibit different chemical stabilities. It is evident in our experiments that p-type Ge NWs are more stable in ambient air than n-type ones, due to the Fermi level difference for each doping type. Second, with high resolution x-ray photoelectron spectroscopy (XPS), we have quantified the Fermi level of Ge NWs and mapped out the bending due to surface potentials (Figure 2). The bending trend is identified to be opposite for p and n-type. Third, distinct oxidation routes of Ge NWs with p or n-type doping are uncovered for the first time. In the oxidation process, reactive n-type NWs form GeO₂ directly and quickly while p-type ones form GeO first and then gradually convert to GeO₂. In an effort to block the surface oxidation, we find long chain alkylthiols are effective to passivate Ge NWs. The protection is quantified by comparing the degree of oxidation as a function of time for different alkyl chain length. Other chemistry such as alkalization is compared as well and C₁₂ thiol yields the best resistance to oxidation.

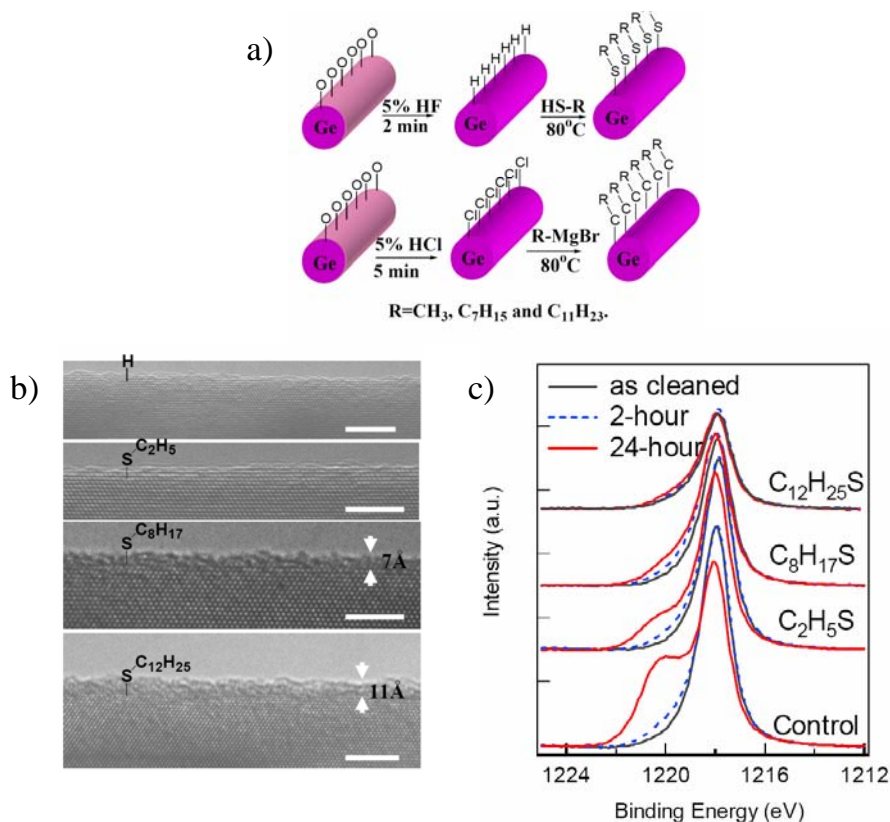


Figure 3. Surface functionalizations. a) Functionalization routes using long chain alkyl thiol (top) and Grignard reactions (bottom). b) High resolution TEM images of Ge NWs coated with different chain-length alkyl thiols. c) Oxide evolution of different protections studied with XPS, clearly demonstrating that long chain alkylthiols provides good protection against oxidation.

Assembly

Successful applications of nanostructures require controlled assembly to afford highly ordered structures at low cost. We have investigated two general assembly techniques for Ge NWs: deterministic synthesis and Langmuir-Blodgett (LB) transfer. As discussed earlier, deterministic synthesis offers ultimate control over NW growth, such as sizes, locations and orientations, etc. It naturally provides a platform for high quality NW assembly and has been successfully demonstrated in our studies. On the other hand, our gram-scale NW synthesis produces high quality bulk quantity materials with uniform properties. We use LB technique as a cost-efficient method to assemble bulk quantity NWs that are functionalized with alkylthiols. This method utilizes the hydrophobicity of the alkyl terminations, which help float NWs on H₂O surface. Upon compression, these free-floating NWs are close-packed into parallel arrays, which can be transferred to various substrates with their order undisturbed. For both deterministic synthesis and LB

assembly, the essential enabling factor is the cleanliness offered by CVD reactions, with which by-products other than high quality NW growth are negligible.

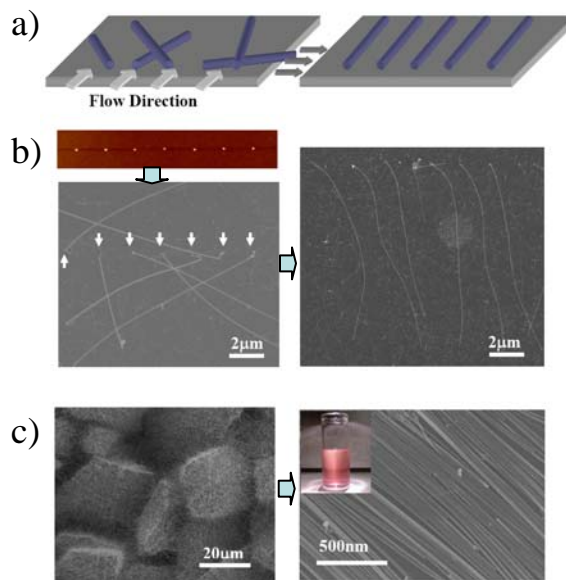


Figure 4. Ge NW Assembly. a) Schematic representation of fluidic alignment of deterministically grown Ge NWs from individually patterned Au nanoseeds. b) Atomic force microscope (AFM) and SEM images of controlled assembly of deterministically grown Ge NWs. Top left panel: AFM image of individually patterned Au nanoseeds (20nm particles, 2μm apart). Bottom left panel: SEM image of Ge NWs grown from these seeds, with the origins of the NWs indicated by white arrows. Right panel: After flow alignment, NWs form quasi-aligned arrays with the origins fixed as pivotal points due to strong interactions with the substrate. c) Gram-scale synthesis of Ge NWs by supporting them with high surface area material (left) and LB assembly after surface functionalizations with long chain alkylthiols (right). Inset in right panel: stable suspension of functionalized Ge NWs in chloroform.

High performance devices

The electrical properties of semiconductor NWs is best manifested in the performance of their field effect transistors (FETs), which also serve as a direct measure of their usefulness as electronic materials. To fabricate Ge NW FETs, we grow doped NWs in a patterned fashion on a heavily doped Si substrate with a SiO₂ capping layer. Afterwards, source (S) and drain (D) contacts are defined and high workfunction metal Pd is deposited as electrodes. In this geometry, the SiO₂ layer works as gate dielectrics and underlying Si is the gate electrode. High hole mobilities $\sim 600\text{cm}^2/\text{V}\cdot\text{s}$ are obtained. The electrical properties are correlated with the surface characteristics to understand the role of surfaces in nanoelectronics. It is revealed that NW FET properties are highly

dependent on the surfaces. As an example, large hysteresis is observed for both p and n-type NW FETs when measured in ambient air as a result of strong H₂O absorption to surface oxides (GeO₂). The hysteresis can be easily removed for p-FETs by eliminating surface oxides whereas it is persistent for n-FETs due to the easy oxidation of n-type Ge NWs. Thus, for NWs, it is of critical importance to control the surfaces, e.g. functionalizations to reduce surface states and protection against oxidation, etc. For such a goal, we have investigated the compatibilities of Ge NW FETs with high dielectric constant (high- κ) materials deposited by atomic layer deposition, or ALD, because it has been shown that ALD high- κ can produce excellent Ge-based MOSFETs. Decent device performance comparable to bottom gated FETs is achieved. We have also characterized Ge NW FETs with surfaces protected by alkylthiols and observed drastic device

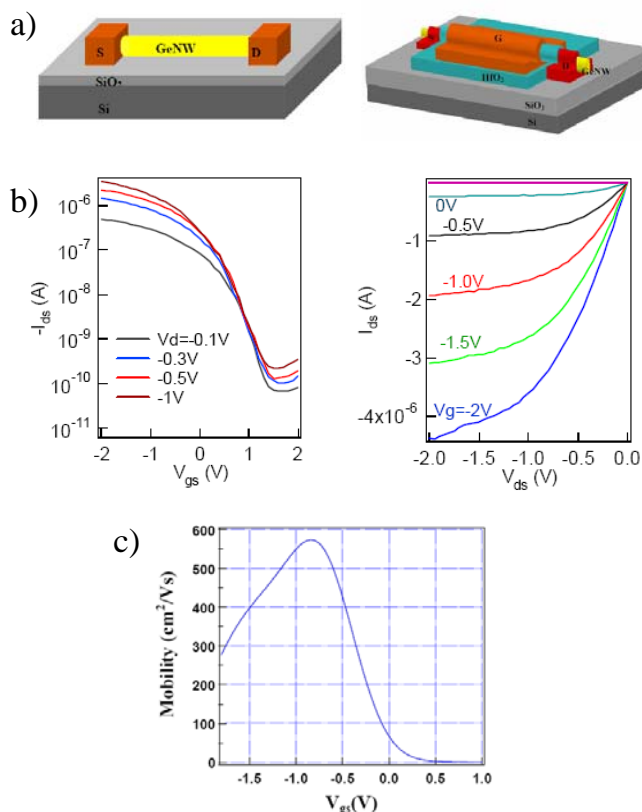


Figure 5. High performance FETs. a) Device structure of bottom-gated (left) and top-gated (right) Ge NW FETs. b) Representative device characteristics of source-drain vs. gate voltage (left) and drain voltage (right). c) Universal mobilities extracted from bottom-gated devices, with the peak value for holes $\sim 600\text{cm}^2/\text{V}\cdot\text{s}$.

improvement in terms of performance and stability in ambient air. Moreover, this surface modification eliminates surface effect on bulk properties of NWs and makes it possible to probe the intrinsic properties of NWs. We have measured band gaps of Ge NWs with different sizes and found that it is similar to bulk Ge for NWs down to ~10nm in diameters. These types of measurements could only be performed with proper surface functionalizations.

In summary, Ge NW has been studied systematically in my thesis, from synthesis and surface chemistry, to controlled assembly and high performance devices. Many of the approaches and results are generic to other types of NWs as well. Doors are opened up to interesting sciences and applications of this novel structure.

Publications during Ph.D. Study:

1. **Dunwei Wang** and Hongjie Dai, Germanium nanowires, from synthesis, surface chemistry, assembly to devices. *Appl. Phys. A*. (invited review), 2006
2. **Dunwei Wang**, Ying-Lan Chang, Zhuang Liu and Hongjie Dai, Oxidation resistant Germanium nanowires: bulk synthesis, long-chain alkanethiols functionalization and Langmuir-Blodgett assembly. *J. Am. Chem. Soc.* 127, 11871-11875, 2005
3. **Dunwei Wang**, Ryan Tu, Li Zhang and Hongjie Dai, One-to-one synthesis of Germanium Nanowires and patterning of individual Gold nanoparticles for aligned nanowire arrays. *Angew. Chem. Int. Ed.* 44, 2925-2929, 2005
4. Randy Grow, Qian Wang, Jien Cao, **Dunwei Wang** and Hongjie Dai, Piezoresistance of carbon nanotubes on deformable thin-film membranes. *Appl. Phys. Lett.* 86, 93104-93106, 2005
5. Jien Cao, Qian Wang, **Dunwei Wang**, Hongjie Dai, Suspended Carbon Nanotube Quantum Wires with Two Gates, *Small*, (inaugural issue) 2005
6. **Dunwei Wang**, Ying-Lan Chang, Qian Wang, Jien Cao, Damon Farmer, Roy Gordon, Hongjie Dai, Chemical and electrical properties of germanium nanowires, *J. Am. Chem. Soc.* 126, 11602-11611, 2004
7. Ali Javey, Jing Guo, Damon B. Farmer, Qian Wang, **Dunwei Wang**, Roy G. Gordon, Mark Lundstrom, and Hongjie Dai, Carbon Nanotube Field-Effect

- Transistors with Integrated Ohmic Contacts and High- κ Gate Dielectrics, *Nano Lett.* 7, 1319-1322, 2004
8. Yiming Li, David Mann, Marco Rolandi, Woong Kim, Ant Ural, Steven Hung, Ali Javey, Jien Cao, **Dunwei Wang**, Erhan Yenilmez, Qian Wang, James F. Gibbons, Yoshio Nishi, and Hongjie Dai, Preferential Growth of Semiconducting Single-Walled Carbon Nanotubes by a Plasma Enhanced CVD Method, *Nano Lett.* 4, 447-450, 2004
 9. **Dunwei Wang**, Qian Wang, Ali Javey, Ryan Tu, Hongjie Dai, Hyounsub Kim, Paul C. McIntyre, Tejas Krishnamohan, Krishna C. Saraswat, Germanium nanowire field-effect transistors with SiO₂ and high- κ HfO₂ gate dielectrics, *Appl. Phys. Lett.* 83, 2432-2434, 2003
 10. Hee Cheul Choi, Summit Kundaria, **Dunwei Wang**, Ali Javey, Qian Wang, Marco Rolandi, and Hongjie Dai, Efficient Formation of Iron Nanoparticle Catalysts on Silicon Oxide by Hydroxylamine for Carbon Nanotube Synthesis and Electronics, *Nano Lett.* 3, 157-161, 2003
 11. Fernando J. Gómez, Robert J. Chen, **Dunwei Wang**, Robert M. Waymouth, Hongjie Dai, Ring opening metathesis polymerization on non-covalently functionalized single-walled carbon nanotubes, *Chem. Comm.* 2, 190-191, 2003
 12. **Dunwei Wang**, Hongjie Dai, Low-temperature synthesis of single-crystal germanium nanowires by chemical vapor deposition, *Angew. Chem. Int. Ed.* 41, 4783-4786, 2002
 13. Hee Cheul Choi, Woong Kim, **Dunwei Wang**, Hongjie Dai, Delivery of catalytic metal species onto surfaces with dendrimer carriers for the synthesis of carbon nanotubes with narrow diameter distribution, *J. Phys. Chem. B*, 106, 12361-12365, 2002
 14. Woong Kim, Hee Cheul Choi, Moongsub Shim, Yiming Li, **Dunwei Wang**, Hongjie Dai, Synthesis of ultralong and high percentage of semiconducting single-walled carbon nanotubes, *Nano Lett.* 2, 703-708, 2002
 15. Yuegang Zhang, Yiming Li, Woong Kim, **Dunwei Wang**, Hongjie Dai, Imaging as-grown single-walled carbon nanotubes originated from isolated catalytic nanoparticles, *Appl. Phys. A Mater. Sci. Process.* 74, 325-328, 2002
 16. Erhan Yenilmez, Qian Wang, Robert J. Chen, **Dunwei Wang**, and Hongjie Dai, Wafer scale production of carbon nanotube scanning probe tips for atomic force microscopy, *Appl. Phys. Lett.* 80, 2225-2227, 2002

17. Robert J. Chen, Yuegang Zhang, **Dunwei Wang**, and Hongjie Dai, Noncovalent sidewall functionalization of single-walled carbon nanotubes for protein immobilization, *J. Am. Chem. Soc.* 123, 3838-3839, 2001
18. Yiming Li, Woong Kim, Yuegang Zhang, Marco Rolandi, **Dunwei Wang**, Hongjie Dai, Growth of single-walled carbon nanotubes from discrete catalytic nanoparticles of various sizes, *J. Phys. Chem. B*, 105, 11424-11431, 2001