



DIGITAL ACCESS TO  
SCHOLARSHIP AT HARVARD  
DASH.HARVARD.EDU



HARVARD LIBRARY  
Office for Scholarly Communication

# Diameter-dependent dopant location in silicon and germanium nanowires

The Harvard community has made this  
article openly available. [Please share](#) how  
this access benefits you. Your story matters

|                   |  |
|-------------------|--|
| Citation          | Xie, P., Y. Hu, Y. Fang, J. Huang, and C. M. Lieber. 2009. "Diameter-Dependent Dopant Location in Silicon and Germanium Nanowires." Proceedings of the National Academy of Sciences 106 (36) (August 24): 15254–15258. doi:10.1073/pnas.0906943106.  |
| Published Version | 10.1073/pnas.0906943106  |
| Citable link      | <a href="http://nrs.harvard.edu/urn-3:HUL.InstRepos:34737212">http://nrs.harvard.edu/urn-3:HUL.InstRepos:34737212</a>  |
| Terms of Use      | This article was downloaded from Harvard University's DASH repository, and is made available under the terms and conditions applicable to Open Access Policy Articles, as set forth at <a href="http://nrs.harvard.edu/urn-3:HUL.InstRepos:dash.current.terms-of-use#OAP">http://nrs.harvard.edu/urn-3:HUL.InstRepos:dash.current.terms-of-use#OAP</a> |

## **Diameter-Dependent Dopant Location in Silicon and Germanium Nanowires**

Ping Xie<sup>1</sup>, Yongjie Hu<sup>1</sup>, Ying Fang<sup>1,2</sup>, Jinlin Huang<sup>1</sup> and Charles M. Lieber<sup>1,3\*</sup>

---

<sup>1</sup>Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA 02138, USA; <sup>2</sup>National Center for Nanoscience and Technology China, Beijing 100190, PRC; <sup>3</sup>School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA.

\*To whom correspondence should be addressed. E-mail: [cml@cmliris.harvard.edu](mailto:cml@cmliris.harvard.edu)

## **Abstract**

We report studies defining the diameter-dependent location of electrically-active dopants in Si and Ge nanowires (NWs) prepared by nanocluster catalyzed vapor-liquid-solid (VLS) growth. The location of active dopants was assessed from electrical transport measurements before and after removal of controlled thicknesses of material from NW surfaces by low-temperature chemical oxidation and etching. These measurements show a well-defined transition from bulk-like to surface doping as the diameter is decreased below 22-25 nm for n- and p-type Si NWs. Similar diameter-dependent results were also observed for n-type Ge NWs, suggesting that surface dopant segregation may be general for NWs synthesized by the VLS approach. Natural surface doping of small diameter semiconductor NWs is distinct from many top-down fabricated NWs, explains enhanced transport properties of these NWs and could yield robust properties in ultra-small devices often dominated by random dopant fluctuations.

The incorporation of electrically-active dopants in semiconductor materials has been central to development of electronic and optoelectronic devices (1, 2). Dopants can be introduced in well-defined concentrations during the growth of bulk crystal (1), yet in synthesized nanoscale structures such as nanoparticles and NWs, the incorporation of dopants during growth may be affected by kinetic and thermodynamic factors associated with finite size (3-9). Difficulties in incorporating dopants into nanoparticles have been attributed to surface energetics within the context of the kinetics for colloidal growth (3, 4) and thermodynamic factors during high-temperature growth (5). In the case of synthesized semiconductor nanowires, there is considerable evidence from electrical transport measurements that active dopants can be incorporated during growth (6-9). However, details of the distribution of dopants within these nanostructures and size-dependent doping, which are critical to the fundamental understanding of their behavior, modeling, and applications of nanoelectronic devices based on NWs, remain poorly understood.

Synthesized silicon NWs (SiNWs) represent an extensively studied doped NW structure (6, 7, 9), and also can be compared directly to lithographically-defined nanoscale silicon devices that are the standard of the semiconductor industry (10). Previous investigations have shown that basic p- and n-channel field-effect transistors (7, 9) as well as more complex axial and radial modulation doped structures including p/n diodes (11, 12) could be realized. However, measurements in smaller diameter p-Si NWs have yielded room-temperature hole-mobilities (7) and low-temperature transport behavior (13) consistent with clean, intrinsic material and not that expected for a nanostructure with the same effective dopant concentration homogeneously

distributed within the NWs.

These latter results suggest that dopants may be inhomogeneously distributed in the radial direction, and moreover, that the distribution may depend on NW diameter. Theoretical studies suggest a tendency towards surface doping in molecular diameter p- and n-Si NWs (*14, 15*) that are considerably smaller than structures used to fabricate most reported NW devices. Direct experimental determination of dopant location in NWs is challenging, although there has been recent progress (*16-18*). For example, high-resolution secondary ion mass spectroscopy was used to probe for gold-impurities in micron diameter Si wires with a depth resolution ca. 20 nm (*16*), and local electrode atom probe has been used to investigate the distribution of Au atoms in Si NWs with nanometer resolution (*17*). The vertical geometry needed for these latter measurements may, however, place limitations on growth conditions that yield NWs suitable for analysis. In addition, Raman scattering studies of 80-100 nm diameter Si NWs have indicated that active boron dopants are located only at the surface with higher concentrations remote to the active growth tip, suggesting that dopant incorporation occurs by homogeneous surface deposition during axial NW elongation (*18, 19*).

Here we characterize the distribution of electrically-active n- and p-type dopants as function of diameter in Si and Ge NWs synthesized by the nanocluster catalyzed VLS approach (*6-9*). Our method (Fig. 1) is based on one or more cycles of controlled nanometer-scale low-temperature NW surface oxidation and selective surface oxide etching, followed by electrical transport measurements made with NWs configured as field-effect transistors (FETs). Low (< 100 °C) temperature oxidation and etching precludes thermal diffusion or segregation of

dopants following NW synthesis (1, 19). This approach can distinguish uniform dopant incorporation versus surface segregation of dopant since an oxidation/etch cycle will yield a relatively small change in FET properties for uniformly doped NW, while removal of surface dopant, which leaves a nominally intrinsic (undoped) NW, will manifest a large change in device threshold voltage.

The growth conditions for doped Si and Ge NWs were optimized to achieve axial nanocluster-catalyzed growth without competing homogeneous decomposition and surface over coating as described previously (11, 20). Experimentally, these conditions were confirmed from scanning electron and transmission electron microscopy images, which exhibit uniform diameter and crystalline structure extending to the outer surface (11). In contrast, tapered nanowire structures (18, 19), which are formed by surface over-coating during axial elongation, were not investigated since dopant incorporation by homogenous surface deposition is distinct process and could lead to an unintentional enhancement of dopant at the NW surface. We do note that controlled homogenous deposition of radial shells (21) is an effective synthetic approach for creating doped NW structures, including those with electrically-active junctions (12).

Atomic force microscopy (AFM) data recorded from a phosphorus-doped (n-type) Si NW before and after 1-cycle of chemical oxidation and etching (Fig. 2A) (20) show a 3.0 nm reduction in height. The large apparent change in width (Fig. 2A) is due to tip-induced broadening (22) and changes in the AFM tip before and after the oxidation/etching process. Analysis of cross-sectional data recorded from a sampling of 7 n-type SiNWs yields average  $\pm$  1SD reduction of  $3.8 \pm 0.9$  nm of SiO<sub>2</sub>, which corresponds to removal of ca. 3 - 4 atomic layers

of Si during the native oxide etch and single oxidation/etch cycle.

We have characterized the electrical properties of 15 – 70 nm diameter n-type Si NWs following the single oxidation/etch cycle in a field effect transistor (FET) configuration. These data (Figs. 2B,C) exhibit two distinct classes of behavior depending on NW diameter. Current ( $I$ ) versus gate-voltage ( $V_g$ ) for devices with larger, ca. >25 nm diameter NWs all exhibit relatively high conductances and none of these FETs can be depleted within the  $\pm 10$  V accessible  $V_g$  window. In contrast, devices with smaller, ca. < 22 nm diameter NWs (Figs. 2C,E) exhibit dramatic change after a single oxidation/etch cycle: the NW FETs show well-defined threshold voltage ( $V_{th}$ ) with  $V_{th} > 0$  on average and an on current typically 10-100 times lower than larger diameter NWs.

Comparison of n-Si devices fabricated from control NWs (20) and those following a single oxidation/etch cycle further highlight these diameter-dependent differences. Specifically,  $I$ - $V_g$  data from devices fabricated with  $\sim 32$  nm diameter control NW and one following a single oxidation/etch cycle (Fig. 2D) are similar except for the reduction ca. 2x reduction in conductance. The  $I$ - $V_g$  curve calculated from the control NW data assuming a uniform dopant distribution and decrease in channel cross-section due to oxidation/etch (20) does, however, yield a larger conductance than observed experimentally. This calculation indicates that the surface dopant concentration is enriched in the larger diameter n-Si NWs, although the NW FETs still behave as a heavily-doped depletion mode devices after removal of this surface layer. In contrast,  $I$ - $V_g$  data recorded from devices with  $\sim 22$  nm diameter single oxidation/etch and control NWs (Fig. 2E) highlight a well-defined positive  $V_{th}$  and much lower on current after a single

oxidation/etch cycle.

A summary of data recorded from 42 distinct n-type Si NW FET devices (Fig. 2F) illustrates clearly these two distinct classes and shows that the behavior for NWs with diameters  $>$  or  $<$   $\sim 23$  nm is robust. Specifically, these data show that  $V_{th}$  changes sharply from beyond the measurement limit ( $-10$  V) to a positive value around 23 nm diameter. In addition, control NW devices with diameters as small as 18 nm (red squares, Fig. 2F), which have not undergone an oxidation/etch cycle, exhibit characteristics similar to heavily doped n-type devices and the larger diameter NWs. This shows that the substantial change in transport properties can be associated with removal of the surface layer in the small diameter NWs. We attribute these results primarily to diameter-dependent dopant incorporation during growth, and discuss this versus other mechanisms below after presenting additional data for other NW systems.

We have also characterized the diameter-dependent behavior of p-type Si and n-type Ge NWs. Results from as-grown and oxidized/etched boron doped p-type Si NWs show comparable behavior as a function of diameter as n-Si NWs. For example,  $I-V_g$  data from  $\sim 25$  nm diameter as-grown and etched NWs (Fig. 3A) are similar except for the reduction ca. 2x reduction in conductance for the etched NW. The calculated  $I-V_g$  curve for the etched NW based on the as-grown data (20) shows a larger conductance than observed experimentally, which is consistent with higher concentration of dopant at the surface. The transport behavior of larger diameter etched p-Si NW FETs is, however, consistent with heavily-doped depletion mode devices (i.e., no  $V_{th}$  within  $V_g \pm 10$  V window) after removal of the surface layer. Representative  $I-V_g$  data recorded from devices with  $\sim 22$  nm diameter (Fig. 2B) exhibit distinctly different characteristics



after the oxidation/etch cycle with a well-defined  $V_{th}$  and order of magnitude lower on current. The reproducibility of these results and clear transition between large and small diameter NWs can be seen in the plot of data from 33 p-Si NW devices (Fig. 3C), where a well-defined  $V_{th}$  is observed in devices with diameters  $<23$  nm after etching. As-grown, control NW devices with diameters as small as 15 nm exhibit characteristics similar to heavily doped n-type devices and the larger diameter p-Si NWs, and thus demonstrate that the transition can be associated with removal of the surface layer in the small diameter p-Si NWs.

The generality of these results was further assessed through studies of n-type Ge NWs. Ge represents an attractive experimental system since water soluble  $GeO_2$  can be readily removed *in-situ* without degrading the device contacts (20), thus allowing for direct comparison of the same NW device before and after oxidation/etching. We were careful to optimize Ge NW synthesis for the diameters investigated to realize axial growth without radial overcoating to avoid complications from the latter in the analysis of dopant incorporation. A typical large, 40 nm diameter NW (Fig. 3D) exhibited a  $2\times$  decrease in channel conductance with little change in  $V_{th}$  after etching. The drop in conductance is, however, greater than expected for a reduction in cross-section and indicates that dopant concentration is higher at the surface of the Ge NWs. In contrast, a representative small, 22 nm diameter NW (Fig. 3E) showed a  $>20$ -fold drop in conductance and a  $\sim 3$  V shift in  $V_{th}$  after etching. A summary of data from 5 devices (Fig. 3F) shows a transition in  $V_{th}$  at ca. 25-30 nm, although the relatively small number of devices makes this cross-over diameter less certain than for n- and p-Si NWs. In addition, we have compared the resistance ratio (after/before etching) at  $V_g = 0$  since the measurements were made on the

same devices. These data (Fig. 3F) also show clearly the distinct behaviors between large vs. small diameter Ge NWs.

Our investigations of n-Si, p-Si and n-Ge NWs show that there is a distinct diameter-dependent transition in electrical transport behavior following removal of the surface region of NWs by low-temperature oxidation and etching. In small diameter NWs, removal of the surface layer yields device characteristics without carriers at  $V_g = 0$  V, while large diameter NWs exhibit properties of heavily doped material. Over the entire range of diameters studied, 15 - 70 nm, all NWs showed characteristics of heavily doped semiconductor before oxidation and etching. Hence, the substantial change in transport properties can be associated with removal of the surface layer in the small diameter NWs. These diameter dependent results could arise from several factors, including (i) diameter-dependent dopant incorporation during growth, (ii) dielectric confinement (23) and (iii) surface depletion (24, 25), although results indicate that (i) is the dominant factor. The dielectric confinement model predicts that dopant ionization energy will be larger than room-temperature thermal energy in NWs with diameters  $< 10$  nm, which more than a factor two smaller than transition diameter defined in these studies. Studies of surface depletion (24), which arises from carrier trapping at the Si/SiO<sub>x</sub> (or Ge/GeO<sub>x</sub>) interface, suggest a gradual diameter dependent change in  $V_{th}$  in contrast to our observations (20). Importantly, the effects due to both dielectric confinement and surface depletion are determined only by the final diameter of the NW FETs, unless there is diameter dependent dopant incorporation. Hence, the absence of a transition in control NWs over the entire range of diameters strongly indicates the existence of diameter dependent dopant incorporation.

To address further the diameter-dependent dopant distribution and these models we have also carried out measurements on n-Si NWs after multiple oxidation/etch cycles. Representative I- $V_g$  curves recorded from NWs with as-grown diameters slightly larger than and ca. the same as the transition point following four cycles of oxidation and etching (Fig. 4A) show several important features. The NW with as-grown diameter at the transition point of 24 nm exhibits, as expected, switch to enhancement mode after the 4 oxidation/etching cycles, where the final diameter is 19.4 nm. The NW device with as-grown diameter of 27.4 nm, which is several nm larger than the observed transition diameter, and final diameter after 4 oxidation/etch cycles of 22.6 nm, which is  $\leq$  transition diameter, could not be turned off and exhibited a relatively large current over the entire  $V_g$  window. This behavior is consistent with a heavily doped FET even after etching to below the transition diameter. Importantly, these data confirm that the major contribution to the diameter-dependent transition is not associated with surface depletion or dielectric confinement, which would manifest itself independent of initial starting diameter, but rather is due to diameter-dependent dopant incorporation.

These multi-cycle oxidation/etch data together with the results presented earlier for Si and Ge NWs are summarized schematically in Fig. 4B. During nanocluster-catalyzed VLS growth of small diameter Si and Ge NWs, the active dopants segregate in the  $\sim$ 1-2 nm surface region while the remaining bulk of the NW is effectively free of active dopants. During the corresponding growth of larger diameter NWs, there is an enrichment of dopants in the surface region but the bulk of the NW also contains dopants. Several models for dopant surface segregation in nanostructures have been proposed (5, 14, 15, 26). First, “self-purification” driven

dopant surface segregation has been reported in nanoparticles during nucleation (5) or annealing (26). This model cannot explain the present results because (i) nucleation occurs only at the initial stage of NW elongation and (ii) NW growth temperatures are far below those where dopant diffusion would be significant (1). Second, the energy for a dopant may be lower at the surface versus bulk due to lattice relaxation, although calculations suggest that this energy difference should only become important in the molecular size limit (14, 15). Third, surface reconstruction could also lower the energy of dopant at the surface versus bulk, and notably, calculations suggest that the energy scale ( $> 100$  meV) is compatible with segregation at growth temperatures (15). Qualitatively, this mechanism could yield a diameter dependent transition in dopant incorporation: When the NW diameter is small all dopants can be accommodated at the reconstructed surface with an intrinsic core, but as the surface to volume ratio decreases all dopants cannot be accommodated at the surface and there is a transition to bulk doped material.

Last, there are important implications of the observed diameter-dependent dopant incorporation independent of the specific mechanism. First, our results can explain the enhanced electrical performance of small diameter Si NWs in which low-temperature studies (13) showed clean structures on length scales up to at least 400 nm and more than an order of magnitude longer than top-down fabricated NW structures (27). The uniform transport properties in chemically-synthesized small-diameter NWs can now be attributed to the preferential segregation of dopant at the surface, which minimizes potential fluctuations due to ionized dopant impurities. Second, the surface segregation of dopant in small diameter NWs is an ideal realization of delta doping (28), which is proposed to overcome the critical problem of random

dopant fluctuations in aggressively scaled top-down fabricated metal-oxide-silicon field effect transistors (MOSFETs). The natural spatial separation of dopants in a cylindrical surface layer of small-diameter NWs is an ideal doping geometry and could open up opportunities for exploring high-mobility, scaled NW FETs as well as low-temperature studies of one-dimensional electron and hole gases.

## References and Notes

1. S. M. Sze, *Semiconductor Devices Physics and Technology* (Wiley, New York, ed. 2, 2002), chap. 2, 10 and 13.
2. J. Singh, *Semiconductor Optoelectronics Physics and Technology* (McGraw-Hill, New York, 1995), chap 3.
3. S. C. Erwin *et al.*, *Nature* **436**, 91 (2005).
4. G. M. Dalpian, J. R. Chelikowsky, *Phys. Rev. Lett.* **96**, 226802 (2006).
5. X. Feng *et al.*, *Science* **312**, 1504 (2006).
6. Y. Cui, X. Duan, J. Hu, C. M. Lieber, *J. Phys. Chem. B* **104**, 5213 (2000).
7. Y. Cui, Z. Zhong, D. Wang, W. U. Wang, C. M. Lieber, *Nano Lett.* **3**, 149 (2003).
8. D. Wang, H. Dai, *Appl. Phys. A* **85**, 217 (2006).
9. G. Zheng, W. Lu, S. Jin, C. M. Lieber, *Adv. Mater.* **16**, 1890 (2004).
10. D. Wang, B. Sheriff, J. R. Heath, *Small* **2**, 1153 (2006).
11. C. Yang, Z. Zhong, C. M. Lieber, *Science* **310**, 1304 (2005).
12. B. Tian *et al.*, *Nature* **449**, 885 (2007).
13. Z. Zhong, Y. Fang, W. Lu, C. M. Lieber, *Nano Lett.* **5**, 1143 (2005).
14. H. Peelaers, B. Partoens, F. M. Peeters, *Nano Lett.* **6**, 2781 (2006).
15. M. V. Fernández-Serra, Ch. Adessi, X. Blase, *Phys. Rev. Lett.* **96** 166805 (2006).
16. M. C. Putnam *et al.*, *Nano Lett.* **8**, 3109 (2008).
17. J. E. Allen *et al.*, *Nature Nanotech.* **3**, 168 (2008).
18. G. Imamura *et al.*, *Nano Lett.* **8**, 2620 (2008).

19. T. Kawashima *et al.*, *J. Phys. Chem. C* **111**, 15160 (2007).
20. Materials and methods are available as supporting material on Science Online.
21. L.J. Lauhon, M.S. Gudiksen, D. Wang, C. M. Lieber, *Nature* **420**, 57 (2002).
22. S. S. Wong *et al.*, *Appl. Phys. Lett.* **73**, 3465 (1998).
23. M. Diarra, Y. M. Niquet, C. Delerue, C. G. Allan, *Phys. Rev. B* **75** 045301 (2007).
24. V. Schmidt, S. Senz, U. Gösele, *Appl. Phys. A* **86**, 187 (2006).
25. K. Seo, S Sharma, A. A. Yasserli, D. R. Stewart, T. I. Kamins, *Electrochem. and Solid-State Lett.* **9**, G69 (2006).
26. S. Oswald *et al.*, *Anal. Bioanal. Chem.* **378**, 411 (2004)
27. T. Mizuno, J. Okamura, A. Toriumi, *IEEE Trans. Electron Devices* **41**, 2216 (1994).
28. We thank L. J. Lauhon, Q. Quan, Q. Xiong and B. Tian for discussion. C.M.L. acknowledges the Air Force Office of Scientific Research, a contract from MITRE Corporation, and Samsung Electronics for support of this work.

## Figure Captions

**Figure 1.** Overview of experimental method. Left (right) column shows sequence of steps used to investigate dopant location in surface (bulk) doped nanowires, including (i) controlled oxidation of the nanowire surface, (ii) etching to remove the surface oxide, and (iii) device fabrication. Pink shaded areas indicate regions where dopant is located.

**Figure 2.** Diameter-dependent transport behavior of n-type Si NWs. (A) Averaged cross-sectional height profiles determined from AFM images before (red) and after (blue) oxidation and etching of a NW. (Inset) the topographical AFM image, the yellow rectangle indicates the  $\sim 500\text{nm} \times 1000\text{nm}$  averaging area. (B) and (C) Series of  $I$ - $V_g$  curves at  $V_{sd} = 1\text{V}$  measured from NWs after oxidation and etching with different as-grown diameters.  $I$ - $V_g$  curves at  $V_{sd} = 1\text{V}$  measured from large (D) and small (E) diameter control NWs (red) and NWs after (solid blue) oxidation and etching. The blue dashed line in (D) is the  $I$ - $V_g$  curve calculated from the control NW (red line) after a single oxidation/etching cycle based on a uniform bulk doping model (20). The diameters labeled in (B) – (E) for blue curves are as-grown diameters before the oxidation and etching process; the diameters for red curves correspond to diameter of the control NW. (F) Diameter dependence of threshold voltage. Blue (red) squares represent data from NWs after oxidation and etching (control NWs). The blue (pink) shaded areas highlight diameters of NWs that do (do not) exhibit clear depletion behavior following a single oxidation/etch cycle.

**Figure 3.** Diameter-dependent transport behavior of p-type Si and n-type Ge NWs. (A),(B)  $I$ - $V_g$  curves at  $V_{sd} = 1\text{V}$  measured from as grown p-Si NWs (red) and NWs after a single oxidation/etch cycle (solid blue). (C) Diameter dependence of threshold voltage for p-Si NWs.



Blue and red squares represent data from p-Si NWs after oxidation/etch cycle and as-grown NWs, respectively. The blue (pink) shaded areas highlight diameters of NWs that do (do not) exhibit clear depletion behavior after a single oxidation/etch cycle. **(D)**, **(E)**  $I$ - $V_g$  curves at  $V_{sd} = 1\text{V}$  for same n-GeNWs before (red) and after (solid blue) etching. Blue dashed lines in **(A)** and **(D)** are  $I$ - $V_g$  curves calculated from the control (red lines) based on the uniform bulk doping model (20). **(F)** Diameter dependence of  $V_{th}$  and resistance ratio for n-Ge NWs. The blue (pink) shaded areas highlight diameters of n-Ge NWs that do (do not) exhibit large threshold voltage shift and resistance ratio following removal of a thin surface layer. All diameters labeled in this figure are as-grown diameters.

**Figure 4.** Diameter dependent dopant distribution. **(A)** Comparison of  $I$ - $V_g$  curves at  $V_{sd} = 1\text{V}$  between different diameter NWs after four cycles of oxidation and etching.  $D$  ( $D_0$ ) is the diameter after (before) oxidation and etching. **(B)** Schematic of dopant distribution. Pink and dark pink shaded parts together represent heavily doped regions, with darkness of the pink color indicating the relative dopant concentration (darker = higher), and blue corresponds to intrinsic region.

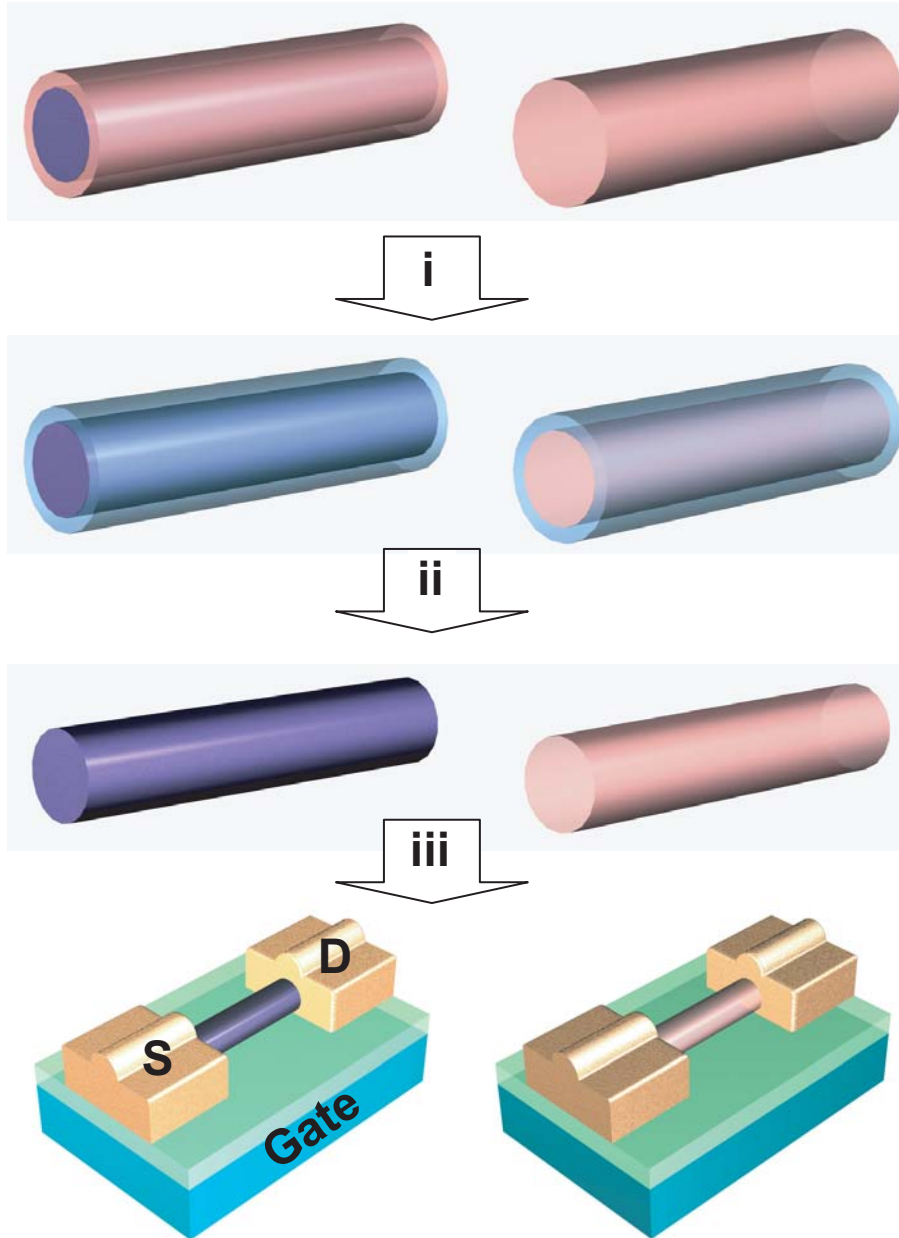


Figure 1

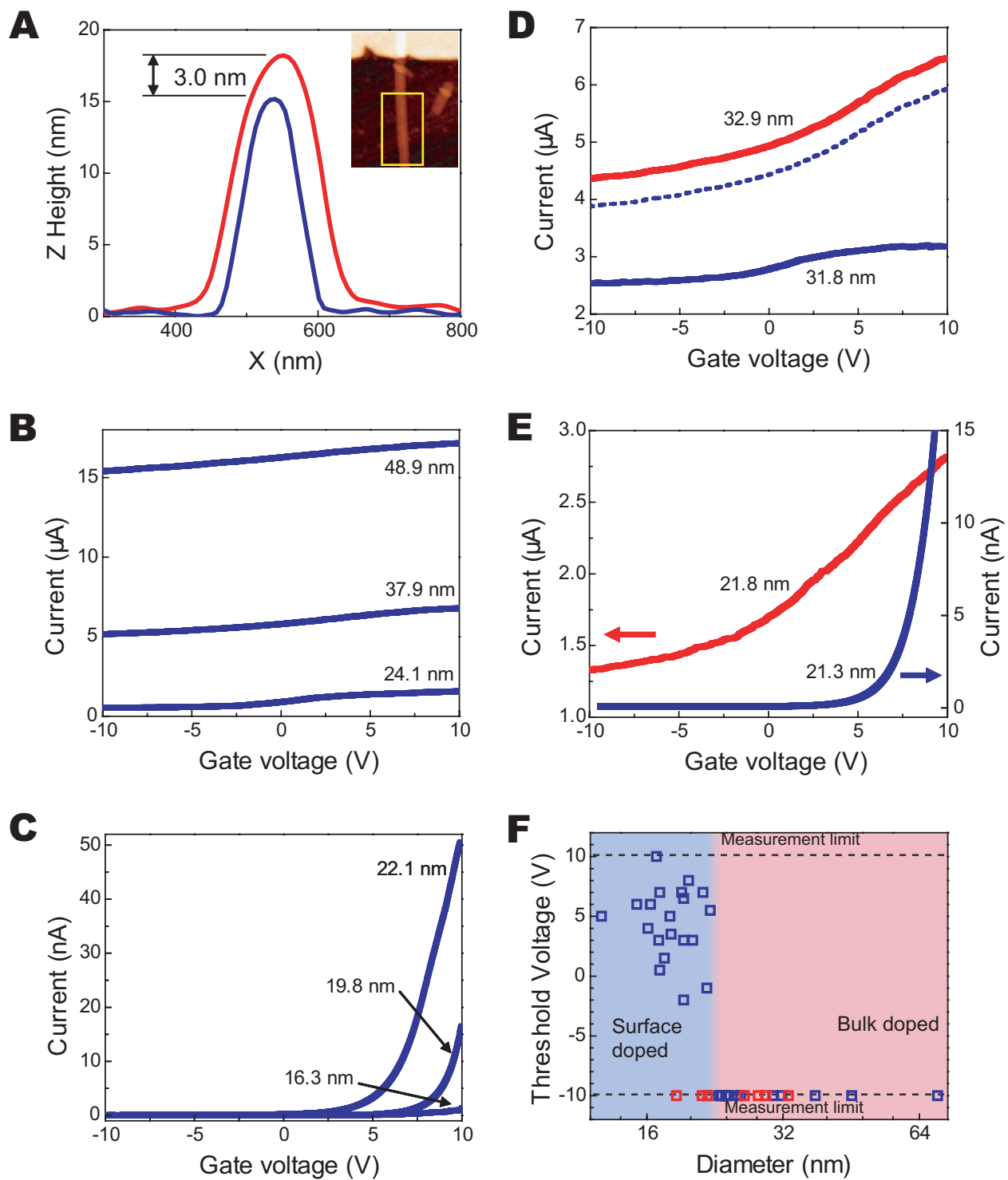


Figure 2

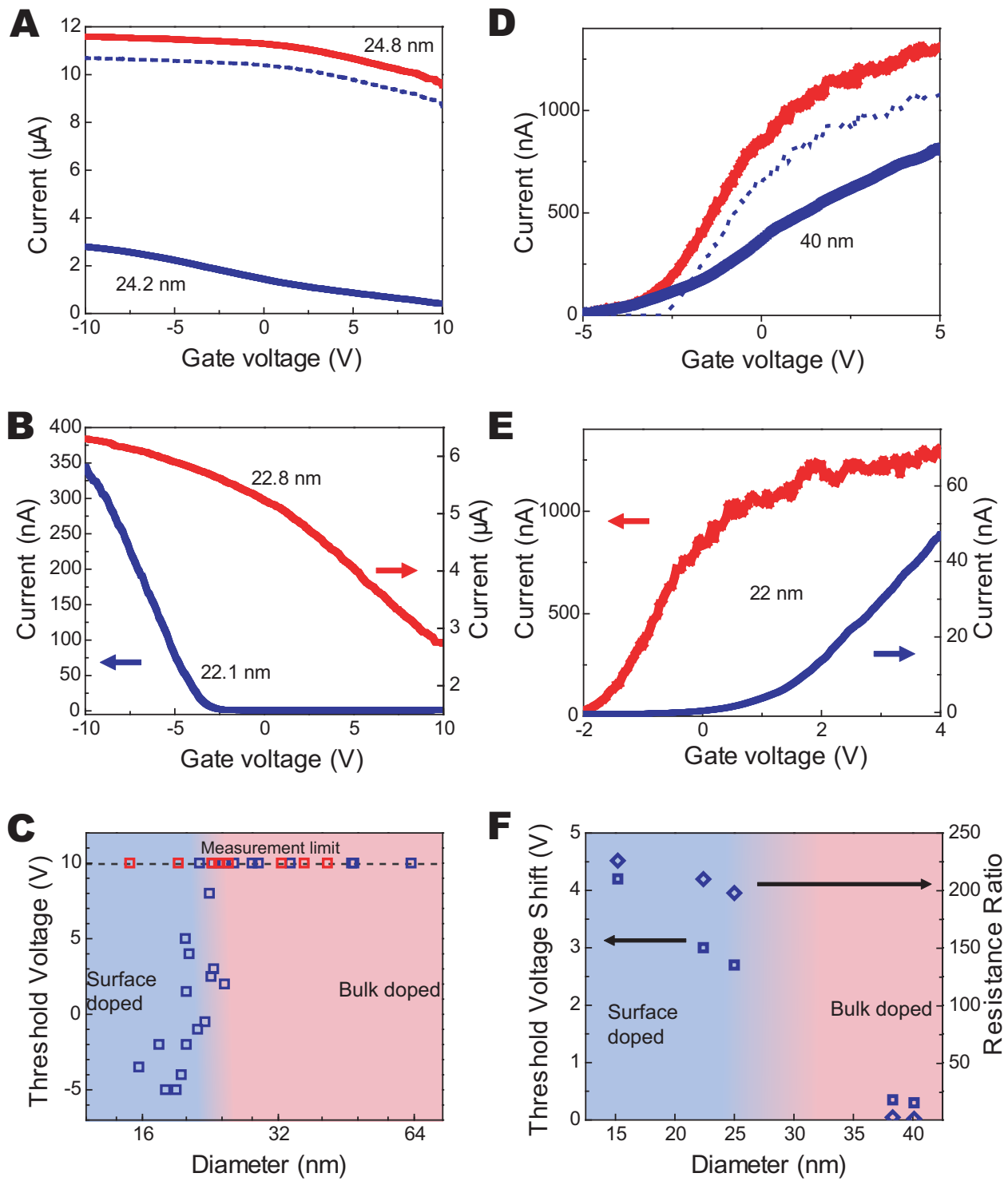


Figure 3

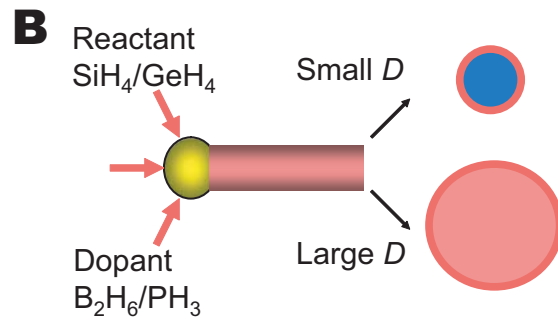
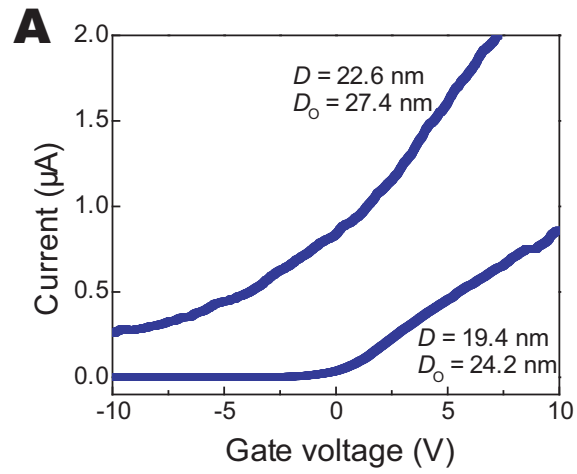


Figure 4

## Supporting Online Material for

### **Diameter-Dependent Dopant Location in Silicon and Germanium Nanowires**

Ping Xie, Yongjie Hu, Ying Fang, Jinlin Huang and Charles M. Lieber \*

\*To whom correspondence should be addressed. E-mail: [cml@cmliris.harvard.edu](mailto:cml@cmliris.harvard.edu)

#### **This PDF file includes:**

Materials and Methods

References

## **Materials and methods**

### **Nanowire synthesis**

NWs were synthesized by gold nanocluster catalyzed chemical vapor deposition as described previously (*S1*, *S2*). The n-type Silicon NWs (SiNWs) are synthesized at 435°C at 30 Torr pressure with 3 standard cubic centimeters per minute (sccm) silane as Si source, phosphine (0.1% in H<sub>2</sub>) as n-type dopant source and 60 sccm H<sub>2</sub> as carrier gas. The flow rate of phosphine varies from 3 sccm to 10 sccm to achieve feed-in ratio from 1000:1 to 300:1 (Si:P) and the growth time is 60 minutes. p-type SiNWs are synthesized at 440°C at 30 Torr with 2.5 sccm silane, 4.1 sccm to 12.5 sccm 100ppm diborane in He (Si:B = 3000:1 – 1000:1) and 10 sccm Ar, and the growth time is 30 minutes. n-type Germanium NWs (GeNWs) are synthesized at 280°C at 400 Torr with 10 sccm 10% GeH<sub>4</sub>, 10 sccm 0.1% PH<sub>3</sub> and 200 sccm H<sub>2</sub> (Si:P = 100:1), the growth time is 30 minutes. Growth conditions were optimized to minimize the overcoating due to the non-catalytical decomposition of precursors. Transmission electron microscopy (TEM) images demonstrated that the synthesized NWs used in these studies had uniform diameters, thus verifying the absence of homogeneous radial deposition during axial nanowire elongation as described previously (*S3*).

### **NW surface oxidation and etching**

The n-type Si NW growth wafer was first etched with 1% HF for 1 min. to remove the native oxide layer. Subsequent cycles of chemical oxidation/etching were carried out: oxidation in boiling 1:1:6 HCl:H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>O solution 20 minutes (*S4*), and then etching with 1% HF for 1 min. When multiple cycles of oxidation/etching were used to reduce the diameter, each subsequent cycle was carried out immediately following the 1% HF etch step to avoid formation of new native oxide. Control samples for n-type Si NWs were prepared by 1% HF etching (1 min) immediately following growth. The first cycle for p-type SiNWs consisted of native oxide growth for 24 h in a cleanroom followed by 1% HF etching for 1 min. The control sample for the p-type Si consisted of as-grown NWs with native oxide. Since both oxidation and etching reactions for Si are self-limiting (*S4*, *S5*), the thickness of the removed surface layer is uniform.

The n-type Ge NWs were oxidized and etched in a continuous process using 0.02% H<sub>2</sub>O<sub>2</sub> solution; a single step involved etching for 5 seconds followed by rinse with deionized H<sub>2</sub>O.

### **NW diameter characterization**

NW diameters were measured by atomic force microscopy (AFM). To measure the diameter change after oxide removal for the same Si NW, the NW was fixed at one end by a Cr/Au pad defined by electron beam lithography (EBL) on a ZrO<sub>2</sub>/Si substrate. Because Cr/Au and ZrO<sub>2</sub> are stable in both 1:1:6 HCl:H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>O and 1% HF solution, the same NW can be located after etching and there will be no artifacts contributing to diameter change from etched substrate. AFM images were recorded before and immediately after the 1% HF etch step. The NW diameter was determined from the height change in the cross-sectional profile averaged over ~1 μm along the NW axis. AFM data for Ge NWs were obtained directly from working devices before and immediately after etching since the source/drain contacts were stable to the Ge etching solution.

The measured diameter changes associated with native oxide removal in n-type and p-type Si NWs were  $1.8 \pm 0.8$  and  $2.2 \pm 1.2$  nm, respectively, corresponding to the removed surface Si thickness of 0.4 and 0.5 nm respectively (radius change, converted by factor 0.44, SiO<sub>2</sub> to Si) (*S6*). The diameter change due to removal of chemical oxide on Si NWs was  $2.3 \pm 0.4$  nm (0.5 nm Si thickness) and H<sub>2</sub>O<sub>2</sub> etching of Ge NWs was  $2.5 \pm 1.3$  nm. The values were based on averages over 7, 7 and 6 independent NWs for the cases of n-Si, p-Si and n-Ge, respectively. The native and chemical oxide thicknesses determined from our measurements on SiNWs were comparable to those values obtained from studies of planar Si wafers (*S4, S7*).

### **Device fabrication and measurements**

NW suspensions in isopropanol were deposited on 60 nm ZrO<sub>2</sub> coated degeneratively doped silicon wafer (<100> orientation, 0.005 Ω-cm, Silicon Valley Microelectronics Inc., San Jose, CA). Contact electrodes are defined by e-beam lithography and metal evaporation (Ni for SiNWs and Ti for GeNWs). Devices are annealed in forming gas (380 °C 2 min. for Ni-Si and 330 °C 30



sec for Ti-Ge) before measurement to reduce both contact resistance (*S8*) and interfacial trap states (*S6*). All electrical measurement is performed in Desert probe station at room temperature,  $10^{-5}$  torr base pressure. I- $V_g$  curve was recorded at 1V source drain voltage.  $\pm 10V$  measurement limit of gate voltage is set by the maximum voltage  $ZrO_2$  film can hold ( $<1$  nA leakage).

### Surface depletion

Surface depletion is a general phenomenon expected in planar (*S6*) and NW (*S9*) devices due to states at the Si/SiO<sub>x</sub> interface which trap carriers. The thickness of the surface depletion layer is governed by the interface trap density and dopant/carrier concentration (*S6*, *S9*). In our experiments, the dopant concentration estimated from I- $V_g$  data is from  $0.5 - 1.7 \times 10^{20}/\text{cm}^3$  for large diameter Si NWs after one oxidation/etching cycle, and yields – even for a very high interface trap density  $2 \times 10^{12}/\text{eV}/\text{cm}^2$  (*S10*) – a depletion thickness less than  $<1$  nm (*S9*). The lack of a threshold voltage transition in the control NWs (without etching) down to a diameter of 15-18 nm is consistent with this analysis. A larger depletion could occur after the first oxidation/etching cycle if the dopant concentration is much lower, although this would simply yield a monotonic shift of threshold voltage with decreasing diameter in contrast to the sharp transition we observe. We thus conclude that surface depletion cannot yield the observed sharp transition at a diameter of ca. 23 nm.

### Diameter dependent device response

Assuming a uniform dopant distribution and unchanged mobility after oxidation/etching for large diameter NWs, the I- $V_g$  curve after oxidation and etching can be estimated from the control group NW I- $V_g$  data through the geometrical reduction of the cross-sectional area and gate capacitance as:

$$I(V_g) = I_0(0) \left(\frac{D}{D_0}\right)^2 + (I_0(V_g) - I_0(0)) \frac{C_{gate}}{C_{0,gate}} \quad (1)$$

where  $C_{gate} = 2\pi\epsilon\epsilon_0 L / \cosh^{-1}(2h/D)$  (*11*), and  $D$ ,  $C_{gate}$  and  $L$  are the diameter, gate capacitance and channel length of NW respectively and  $h$  is the thickness of gate dielectric. Because the doping

concentration for our large diameter NW is relatively high, the effects of contact resistance, surface depletion and electron affinity differences can be ignored. Equation-1 is also applicable to estimating I-V<sub>g</sub> curves after several oxidation/etch cycles as long as these assumptions are valid.

## References

- S1. G. Zheng, W. Lu, S. Jin, C. M. Lieber, *Adv. Mater.* **16**, 1890 (2004).
- S2. Y. Cui, Z. Zhong, D. Wang, W. U. Wang, C. M. Lieber, *Nano Lett.* **3**, 149 (2003).
- S3. C. Yang, Z. Zhong, C. M. Lieber, *Science* **310**, 1304 (2005).
- S4. W. Kern, Ed., *Handbook of Semiconductor Wafer Cleaning Technology: Science, Technology, and Applications* (Noyes Publications, Westwood, New Jersey, 1993), chap. 1.
- S5. K. R. Williams, K. Gupta, M. Wasilik, *J. Microelectromech. Syst.* **12**, 761 (2003).
- S6. S. Wolf, R. N. Tauber, *Silicon Processes for the VLSI Era* (Lattice Press, Sunset Beach, California, 1986), vol. 1, chap.7.
- S7. Y. Morita, K. Miki, H. Tokumoto, *Appl. Phys. Lett.* **59**, 1347 (1991).
- S8. Y. Wu, J. Xiang, C. Yang, W. Lu, C. M. Lieber, *Nature* **430**, 61 (2004).
- S9. V. Schmidt, S. Senz, U. Gösele, *Appl. Phys. A* **86**, 187 (2006).
- S10. K. Seo, S Sharma, A. A. Yasseri, D. R. Stewart, T. I. Kamins, *Electrochem. and Solid-State Lett.* **9**, G69 (2006).
- S11. W. Lu, J. Xiang, B. P. Timko, Y. Wu, C. M. Lieber, *PNAS* **102**, 10046 (2005).