Imaging and Analysis of Axial Heterostructured Silicon Nanowires

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Abstract. Silicon nanowires with axially varying $n$- and $p$-doping were grown by the vapor-liquid-solid approach using gold as the catalyst. The microstructures of the axial heterostructured silicon nanowires were studied using electron microscopy techniques. The nanowire sidewalls exhibit periodic nanofaceting, which is dopant-dependent. The nanofaceting occurs during the enhanced sidewall growth that arises when the diborane dopant gas is introduced. It is also found that the silicon nanowire can crystallize in a hexagonal phase, which is thermodynamically unstable in bulk silicon at ambient and may be due to the large surface stress present during the nucleation of SiNWs.

1. Introduction
Semiconductor nanostructures have recently stimulated great interest due to their scientific importance and potential applications as the building blocks for future nanotechnologies as functional devices [1]. For example, silicon nanowires (SiNWs) with axially varying doping to generate junctions could be used as nanoscale field-effect transistors (FET) [2]. Good control of the wire surface and phase purity is an important issue for functional devices based on nanowire structures, because the physical behavior of SiNWs is strongly influenced by their microstructures. Being one of the most powerful tools in nanotechnology, the electron microscope (EM) has played an important role in revealing the microstructures of nanomaterials. In this article, using EM techniques, we characterized the microstructural properties of the axial heterostructured SiNWs synthesized using a vapor-liquid-solid (VLS) method. Here we report the observation of doping-dependent nanofaceting on SiNW surfaces and SiNWs with hexagonal crystalline structure. The possible causes of the observed phenomena are also discussed.

2. Experimental Details
Axial heterostructured SiNWs were synthesized on Si(111) substrates via VLS growth in a FirstNano EasyTube™3000 low pressure chemical vapor deposition (CVD) system with silane as the precursor gas and Au nanoclusters to catalyze the nanowire growth. The growth was carried out at ~600 °C and the SiNWs were either $n$- or $p$-doped by introducing phosphine or diborane gas, respectively. Two different axially doped nanowire heterostructures were prepared: $p$-doped, $n$-doped and intrinsic SiNWs ($p$-$n$-$i$ SiNWs); and intrinsic, $p$-doped, $n$-doped and intrinsic SiNWs ($i$-$p$-$n$-$i$ SiNWs).

After growth, the SiNWs were separated from the growth substrates by sonication in acetone. The suspension was then drop cast onto either a glass substrate or a TEM finder grid with a 20 nm thin holey carbon film, for the Raman spectroscopy and transmission electron microscopy (TEM).
characterization, respectively. TEM and high resolution transmission electron microscopy (HRTEM) imaging was made using JEOL 2000FX and JEOL 4000EX TEMs operating at 200 kV and 400 kV, respectively. Raman spectra of all samples were measured using a JY Horiba Labram Aramis imaging confocal Raman microscope and a coherent 532 nm laser.

3. Results and Discussion

3.1. Doping-dependent nanofaceting on SiNW surfaces

Any dependence of the surface properties of SiNWs on the impurity doping is crucially important to their applications as functional devices. For example, in an FET geometry, it is necessary to achieve a uniform cross section of the gate dielectric and to minimize the carrier scattering at rough interfaces.

In our previous study [3], we observed that the nanowire sidewalls exhibit periodic nanofaceting, which is found to be dopant-dependent, i.e., sidewall facets occur in the boron-doped (p-type) region (Figure 1(a)), while both the phosphorus-doped (n-type) and the intrinsic SiNW regions exhibit smooth surface morphology. HRTEM imaging shows that the nanowires are axially oriented along <111>, and the crystallographic planes on which the nanofaceting occurs are determined to be [111] and [100] (Figure 1(b)). It is shown that the nanofaceting occurs during the enhanced sidewall growth that arises when the diborane dopant gas is introduced [3].

![Figure 1](image.png)

Figure 1 (a) TEM image of the sidewall facets in the B-doped region of an axially doped SiNW, viewed along the <110> direction; and (b) HRTEM image of the facet, inset: Fourier transform of the image.

3.2. SiNWs with hexagonal crystalline structure

The phase purity of SiNWs is important for the physical performance of the SiNW-based devices, since the physical properties of semiconductors are highly sensitive to their crystalline structures. It is known that the stable crystalline form of Si at ambient is a diamond cubic structure (Si I), however, Fontcuberta i Morral et al. [4] demonstrated the formation of hexagonal (sometimes referred to as wurtzite Si, Si IV) SiNWs by a standard CVD approach on oxidized Si substrates. Arbiol et al. [5] reported the switching of the Si structure from diamond to hexagonal along the wire growth direction in SiNWs synthesized via a Cu-catalyzed vapor-solid-solid mechanism. Here we report the observation of hexagonal SiNWs grown from the Au-catalyzed VLS reactions on an oxide-removed Si(111) substrate.

Both diamond cubic and hexagonal Si have a tetrahedral coordination, but the stacking of the tetrahedra is different. Two slightly different Si hexagonal structures have been reported: Si IV_A (a = b = 3.80 Å, c = 6.27 Å, c/a = 1.65) [6] and Si IV_B (a = b = 4.04 Å, c = 6.60 Å, c/a = 1.63) [7].

HRTEM characterization was carried out on the i-p-n-i axial heterostructured SiNWs for the determination of the crystalline structures. Figure 2(a) shows an overview image of a 150° kinked SiNW. Numbers ‘I-III’ in Figure 2(a) are assigned to the different positions on the kink. The corresponding HRTEM images and their Fourier transform are shown in Figure 2(b)-(d). By measuring the interplanar distances and angles, the crystalline structure of the SiNW can be
determined as Si IV B. The wire growth direction is perpendicular to the {10 11} plane before the kink (part III in Figure 2(a)) and perpendicular to the {10 13} plane after the kink (part II in Figure 2(a)). To further confirm the proposed structure, the same SiNW was tilted so that other zone axes were parallel to the incident beam. Figure 2(e)-(f) show the indexed selected area electron diffraction (SAED) patterns for the same specimen region for the [3 2 4 2] and [3 1 2 1] beam direction, respectively.

Figure 2(a) TEM image of a ~150° kink in the axial heterostructured i-p-n-i SiNWs, numbers ‘I-III’ are assigned to label different positions; HRTEM image of (b) part I, (c) part II and (d) part III in (a), insets in (b)-(d) are their corresponding Fourier transform; and indexed SAED patterns for the same kink for the (e) [2 4 2 3] and (f) [1 2 1 3] beam direction. (In (e)-(f), ratios of the spot spacings are shown as well as the angles between the plane normals).

Raman spectroscopy was also employed to characterize the structures of SiNWs. As seen from Figure 3, the first order Raman peak of the bulk Si is at ~520 cm$^{-1}$ with a full-width at half-maximum of ~4 cm$^{-1}$, in good agreement with the literature [8]. To avoid the heating by the excitation laser, the laser power was kept at a relatively low value, where the Raman peak of the diamond cubic SiNWs is also ~520 cm$^{-1}$, suggesting that the samples are at room temperature and the laser heating effect has not yet occurred. At this low laser power, the hexagonal SiNW exhibits a sharp peak centered at 507 cm$^{-1}$, as well as a broad band between 223 and 288 cm$^{-1}$, in excellent agreement with the predicted transverse optical and the 2-fold transverse acoustical modes of hexagonal Si [9, 10].

Both the TEM and Raman analyses confirm that SiNWs with hexagonal crystalline structure can be formed during the Au-catalyzed VLS growth on a Si(111) substrate. This is different from the work done by Fontcuberta i Morral et al. [4], where the hexagonal SiNWs were grown on an oxidized Si substrate with an oxide thickness of 1 µm and the crystallographic alignment with the substrate was lost. It has been suggested previously that the formation of hexagonal crystalline structure in SiNWs can be caused by defects like twins [11] and stacking faults [12], or the phase transformation from
diamond to hexagonal Si under high pressure [10]. Here the defect-induced hexagonal Si formation can be ruled out in this case, as such mechanisms result in the coexistence of both hexagonal and diamond phases, however, only the hexagonal phase is observed from HRTEM observations. Therefore, we suggest that the large surface stress during the nucleation of SiNWs could be a possible cause for the formation of hexagonal SiNWs observed here.

![Raman spectra](image)

Figure 3 Stokes Raman spectra of the Si IV\textsubscript{B} nanowire, bulk Si and Si I nanowire under the same laser power.

4. Conclusions
In summary, we have studied the microstructural properties of axially doped SiNWs using EM techniques. It is found that the diborane dopant gas alters the nanowire growth mechanism and behavior by enhancing the sidewall growth and creating a faceted sidewall surface. SiNWs with hexagonal crystalline structure can be formed during the Au-catalyzed VLS growth on the Si(111) substrate, which can be due to the large surface stress present during the nucleation.

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References
[1] Cui Y, Zhong Z, Wang D, Wang W U and Lieber C M 2003 Nano Lett. 3 149
[2] Gudiksen M S, Lauhon L J, Wang J, Smith D C and Lieber C M 2002 Nature 415 617
[3] Li F, Nellist P D and Cockayne D J H 2009 Appl. Phys. Lett. 94 263111
[4] Fontcuberta i Morral A, Arbiol J, Prades J D, Cirera A and Morante J R 2007 Adv. Mater. 19 1347
[5] Arbiol J, Kalache B, Roca i Cabarrocas P, Morante J R and Fontcuberta i Morral A 2007 Nanotechnology 18 305606
[6] Yeh C, Lu Z W, Froyen S and Zunger A 1992 Phys. Rev. B 46 10086
[7] Jennings H M and Richman M H 1976 Science 193 1242
[8] Richter H, Wang Z P and Ley L 1981 Solid State Commun. 39 625
[9] Gogotsi Y, Baek C and Kirscht F 1999 Semicond. Sci. Technol. 14 936
[10] Kailer A, Gogotsi Y and Nickel K G 1997 J. Appl. Phys. 81 3057
[11] Dahmen U, Hetherington C J Priouz P and Westmacott K H 1989 Scr. Metall. 23 269
[12] Liu X and Wang D 2009 Nano Res. 2 575