Spatially Resolved Correlation of Active and Total Doping Concentrations in VLS Grown Nanowires

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Supporting Information

ABSTRACT: Controlling axial and radial dopant profiles in nanowires is of utmost importance for NW-based devices, as the formation of tightly controlled electrical junctions is crucial for optimization of device performance. Recently, inhomogeneous dopant profiles have been observed in vapor−liquid−solid grown nanowires, but the underlying mechanisms that produce these inhomogeneities have not been completely characterized. In this work, P-doping profiles of axially modulation-doped Si nanowires were studied using nanoprobe scanning Auger microscopy and Kelvin probe force microscopy in order to distinguish between vapor−liquid−solid doping and the vapor−solid doping. We find that both mechanisms result in radially inhomogeneous doping, specifically, a lightly doped core surrounded by a heavily doped shell structure. Careful design of dopant modulation enables the contributions of the two mechanisms to be distinguished, revealing a surprisingly strong reservoir effect that significantly broadens the axial doping junctions.

KEYWORDS: Nanowires, VLS, doping, nanoprobe scanning Auger microscopy, Kelvin probe force microscopy

Vapor−liquid−solid (VLS) grown nanowires (NWs) constitute a family of nanostructured materials that enable the exploration of nanoscale phenomena and the development of novel devices. The performance of such devices depends in many instances on the ability to achieve tight control over the density and spatial distribution of active impurity atoms within the NW during its growth and throughout the device fabrication process. Specifically, determination of intentional doping profiles (both axial and radial), probing of unintentional dopant distributions, and characterizing electrical junction regions are key features in chemical and electrical characterization of a NW-based device.

The presently incomplete understanding of the growth and doping mechanisms at the nanoscale regime poses fundamental challenges for the fabrication of well-defined structures with controlled atomic composition. For example, it is not always clear whether dopant incorporation is dominated by the VLS process through the catalyst, by a vapor−solid (VS) process through the wire surface, or by a combination of both. The VLS technique, first described by Wagner and Ellis in 1964, is the most commonly employed method of bottom-up semiconductor NW fabrication of all compositions (groups II−VI, III−V, and IV), enabling versatile fabrication of various structures as homojunctions, heterojunctions, and superlattices. Control of doping employing the catalytic VLS growth mechanism is, therefore, of utmost importance for future nanoscale applications.

In many NW systems, the majority carrier type is controlled by intentional doping, which is commonly achieved by adding a gas-phase doping precursor to the growth system.
example, the addition of a phosphine ($\text{PH}_3$) precursor to the growth system produces an n-type silicon NW (SiNW), while the addition of diborane ($\text{B}_2\text{H}_6$) or trimethylborane (TMB) will produce a p-type SiNW.\textsuperscript{9,26–30} In 2009, Schmid et al. showed, using four-probe measurements, that the maximum attainable doping concentration using a $\text{PH}_3$ precursor is $1.5 \times 10^{20}$ cm$^{-3}$.\textsuperscript{31} However, phosphorus impurities tend to accumulate at the surface, forming a thin layer of highly doped silicon.\textsuperscript{32,33} This tendency, together with the pentavalent nature of P, causes a termination of Si(001) surface dangling bonds, thus decreasing the growth rate of the NWs and also of the fraction of electrically active dopants due to dielectric mismatch resulting in an increase of their ionization energy.\textsuperscript{5,17} Hence, an additional effort is required to distinguish between the chemical and the active dopant concentrations.

In 2009, Koren et al. showed, employing Kelvin probe force microscopy (KPFM), that in situ P doping of Si results in a nonuniform distribution of electrically active dopants along the growth axis,\textsuperscript{19} which has been attributed to the exposure of the SiNW surface to $\text{PH}_3$ throughout the growth.\textsuperscript{9,17,19,34–36} Similar results were reported by Perea et al. employing atom probe tomography (ATP) to study P incorporation into GeNWs.\textsuperscript{37} The VS mechanism, also referred to as surface deposition, generates a dopant-rich area at the base of the NW with a gradual decrease in dopant concentration toward the wire tip. This structure is a result of the fact that the wire base is exposed to the precursor atmosphere for a longer time than the tip. Moreover, since the material deposited at the surface is richer in dopants as compared to the material deposited through the catalyst for hydride growth chemistries, in situ doping usually results in a pseudocore–shell structure with a few nanometer-thick, heavily doped shell covering a lightly doped core.\textsuperscript{18,37,38} Recently, Connell et al. used atom probe tomography to show that for both B-doped SiNWs and P-doped GeNWs, the dopants incorporated through the liquid catalyst are not uniformly distributed, with up to 100-fold enhancements in concentration near the VLS tri-junction.\textsuperscript{39}

Here, we demonstrate the effects of the two different dopant incorporation mechanisms on both chemical and active dopant profiles considering both unintentional radial inhomogeneities and intentional axial junctions. The chemical composition and electronic properties of modulation doped wires and the junctions thus formed are correlated by combining nanoprobe scanning Auger microscopy (np-SAM), current–voltage measurements, and KPFM measurements of segmentally P-doped SiNWs (Figure 1a).\textsuperscript{40,41} The jointly active VLS and VS incorporation mechanisms lead to notable differences in properties between an $i$–$n$ junction (i.e., a junction where the $i$ region is grown first) and an $n$–$i$ junction (where the intrinsic region is grown after the doped region). Spatially resolved electrical characterization provides evidence of significant dopant incorporation into a nominally intrinsic segment through the so-called “reservoir effect”\textsuperscript{17,42–47} which has been previously demonstrated for NWs heterostructures and uniformly grown NWs. The combined physical and electronic characterization presented here provides new insights into how to engineer the properties of semiconductor nanowires and dopant junctions.

The segmented SiNWs produced for this study were grown in a hot-wall low-pressure chemical vapor deposition (LPCVD) setup. The 80 nm Au nanoparticles (AuNPs) were used as catalysts, high-purity SiH$_4$ as the precursor gas, He as the carrier gas, and $\text{PH}_3$ (1000 ppm in H$_2$ carrier) served as the n-doping precursor gas. Growth conditions were chosen to be comparable to those conventionally used for both intrinsic and highly P-doped SiNWs growth\textsuperscript{17,18,36} while enabling taper-free growth for a relatively long growth period.

The NWs used in this study are nominally 80 nm in diameter and $\sim$20 $\mu$m long with no observable tapering (see SEM image in Figure 1b and topographic AFM image in Figure 3b) and composed of three distinct segments shown in Figure 1a: the first segment, 4–5 $\mu$m in length, was grown without phosphine; the second segment, 10 $\mu$m in length, was grown at a phosphine-to-silane precursor ratio of 1:500; and the last segment, 5 $\mu$m in length, was grown without phosphine. The segmented structure was achieved by independently scaling the growth times of both intrinsic and highly doped SiNWs grown under the same conditions: $P = 20$ torr, $T = 460$ °C, and He, SiH$_4$, and $\text{PH}_3$ (200 ppm in He) flow rates of 30, 2, and 20 SCCM, respectively. A detailed description of the basic growth

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**Figure 1.** (a) Schematic illustration of the segmented wire growth and predicted dopant profile. Step 1: growth of the 1st, 5 $\mu$m long, intrinsic segment. Step 2: growth of highly P-doped (1/500), 10 $\mu$m, segment on top of the intrinsic segment as well as the VS growth of a heavily doped shell around both segments. Step 3: growth of the 3rd, 5 $\mu$m long, intrinsic segment in which the catalyst is the only dopant source. (b) SEM image of a 20 $\mu$m long, 80 nm diameter, segmented SiNW with no observable morphological signs of the different growth conditions of the three segments.
procedure was previously reported. The segmented SiNWs contain two junctions (transitions between segments). Approaching the first junction from the bottom of Figure 1a, the intrinsic core region is covered by a phosphorus-rich surface layer that was deposited from the vapor (VS doping) during the second (middle) segment growth, while the second n-type segment was doped via both VLS and VS dopant incorporation mechanisms. The second junction is formed between the phosphorus-doped second (central) segment and the third (top) segment, which was grown without phosphine. As we will show, this unintentionally doped segment contains dopants that are incorporated solely from the catalyst reservoir. Figure 1a illustrates schematically the segmented SiNW’s configuration.

The NWs were mechanically transferred onto a highly oriented pyrolytic graphite (HOPG) film supported by conductive copper tape (to avoid charging effects) for npSAM measurements. The use of HOPG reduced the Auger spectral background, thus lowering the P detectability limit. The Auger data were acquired by a Physical Electronics PHI 700Xi scanning Auger equipped with a Schottky field emission electron gun and a coaxial cylindrical mirror analyzer (CMA) featuring a probe diameter down to ~6 nm. The Auger data for elemental identification and for calculations of surface atomic concentrations were obtained using the \( \frac{dN(E)}{dE} \) peak to peak heights of the P LMM and Si KLL spectra and PHI supplied sensitivity factors. The P detectability limit was determined by the signal-to-noise limit of the observable Auger P LMM peak and was found to be 1/6000 (8 \( \times \) 10\(^{-3}\)) for the HOPG substrate. Depth profiling was performed by argon ion sputtering and calibrated employing atomic force microscopy (AFM). (See Supporting Information for the Auger technique technical details and data analysis.)

Single NW devices, used for KPFM measurements, were fabricated by electron beam lithography and nickel evaporation to form symmetric contacts. The wafer on which the NWs were dispersed forms the backgate terminal and was grounded throughout the measurements. Prior to the electrode evaporation step, the contact area was treated with a 24 s oxygen plasma to remove residual photoresist and organic contamination, and with a 3 s wet etch in buffered hydrofluoric acid to remove the native oxide layer.

Current–voltage measurements were conducted using a semiconductor parameter analyzer (Agilent B1500A). The KPFM measurements were conducted using a Dimension 3100 AFM system (Bruker AXS) and an Au-coated tip in a controlled nitrogen environment glovebox (less than 5 ppm \( \text{H}_2\text{O} \)). Measurements were performed in the "lift mode", where the topography is first scanned in the "tapping mode". Next, the tip is raised to a constant 8 nm height above the topography trajectory and the CPD is measured.

The limited characteristic depth from which Auger electrons are emitted (escape depth) is the basis for the surface sensitivity of Auger electron spectroscopy (AES). A sampling depth \( d \) of 2.6 nm is used in this study, ensuring that measured surface concentration is independent of the concentration measured after ~3 nm of material is removed by chemical etching [see Supporting Information for further details]. We have previously shown how sequential etching is useful for radial dopant profiling. It should be noted that np-SAM measures the total dopant concentration, whereas KPFM is sensitive to the carriers generated by active dopants. Thus the combination of these two techniques is particularly useful.

Figure 2 shows the axial dependence of the surface P distribution along segmented NWs versus the distance from the catalyst averaged over three NWs (green points), one of which was remeasured (red points) after 3 nm etching with an Ar ion gun. The first (nominally undoped) segment has a surface P concentration of about 0.65% throughout its whole 5 \( \mu \text{m} \) length, which is attributed to surface deposition of P during growth of the second (highly doped) segment. Segment 2 exhibits decreasing P surface doping from 0.65% (3.25 \( \times \) 10\(^{19}\) cm\(^{-3}\)) to slightly less than 0.1% (5 \( \times \) 10\(^{19}\) cm\(^{-3}\)) toward the tip due to the accumulation of P on the surface during its growth. np-SAM measurements of P-doped NWs grown under similar conditions as the second segments yielded a similar decrease of the P surface concentration along the NW. The final 5 \( \mu \text{m} \) segment exhibits a lower surface P concentration of about 0.1%. The detection of P in this third segment, despite the fact that no PH\(_3\) was flowing during its growth, indicates that residual P in the catalyst serves as the doping source. The last 200 nm of the third segment (in close vicinity of the Au tip) shows a rapid increase in P concentration reaching up to 4% ~25 nm from the Au tip. The rather high P concentration in the vicinity of the Au tip also implies that traces of P remaining in the Au catalyst were expelled during cooling below the eutectic temperature.

Etching 3 nm of the NW surface, thus removing the VS surface-doped layer, drastically changes the axial P concentration profile (Figure 2, red points). The first (VS doped) segment showed no detectable P concentration. In contrast, a measurable P concentration of about 0.1% was obtained for the second segment, which is attributed to incorporation from the catalyst into the NW core. The initial gradual increase, if considered statistically significant, may be due to a buildup up of P in the catalyst upon initial exposure to phosphine. The third segment, which was doped by the residual P in the catalyst, did not exhibit any P doping above the detectability limit of 8 \( \times \) 10\(^{18}\) cm\(^{-3}\) following the surface etching.

The contributions of different dopant incorporation mechanisms to the surface dopant concentration can be identified by comparing the distinct doping profiles in each
of the three segments. By integrating the P concentration throughout the third segment, including the region of high P concentration in the vicinity of the tip, the (previously unknown) P concentration in the liquid catalyst ($C_P$) during growth of the last segment is determined to be in the range of $1\text{–}10$ atom %. In the absence of a flux of P across the vapor–liquid interface, $C_P$ must decrease throughout the third segment. However, the rate of decrease is not resolved by the np-SAM measurement as the dopant concentration lies at or below the detectability limit. The nearly constant near-surface dopant concentration throughout most of segment 3 is consistent with a very small distribution coefficient, leading to a very diffuse junction when considering primarily near surface (but not fully active) dopants. Comparison of the dopant profiles in the last two segments obtained after the 3 nm etch shows a much higher P incorporation into the NW core in the second segment (approx. $7 \times 10^{19}$ cm$^{-3}$) than in the third segment, which was below the detectability limit of $8 \times 10^{18}$ cm$^{-3}$. We are therefore unable to determine the precise abruptness of the axial junction within the core. We note however that reduction in P concentration below the detection limit upon etching segment 3 suggests that most of the P was incorporated near the VLS trijunction, in agreement with recent APT observations.

Previous analyses of modulation-doped structures including intrinsic-highly P-doped segments in SiNWs in ref 31 and axial p–n junctions in ref 48 appear to show transitions that are more abrupt than those measured here, but the prior measurements are sensitive only to active dopant concentration. The surface dopants, to which the np-SAM measurement is especially sensitive, are not expected to be fully active.

Under certain conditions, the properties of the electrical junction may be dominated by axial concentration variations within the core, rather than within the shell. We investigate this possibility in some detail in the next section, but it is clear from the discussion above that one should consider both the radial and axial dopant distribution in order to accurately describe the behavior of a nominally axial junction.

With the np-SAM results in mind, the NWs should show electrical characteristics similar to those of a single n$^−$–n diode with a graded junction. Because of the heavily doped surface layer surrounding the interface between the first and the second segments, both sides of this junction are expected to be degenerately doped. A sizable depletion region is therefore likely to form only in the second junction between the heavily doped second segment and the lightly doped third segment. Figure 3a shows a typical current–voltage ($I$–$V$) curve of a segmented SiNW device.

Several deviations from the ideal diode characteristics are observed in Figure 3a. First, the slope of the forward bias is significantly lower than that expected for an ideal diode. Such a phenomenon can be modeled by two resistors in series: (1) the internal resistance of the NW and (2) an ohmic contact resistance. Second, an offset bias is clearly seen in the graph. This offset bias is usually attributed to the built-in potential across the junction ($V_{bi}$); however, an accurate determination of the built-in potential from the $I$–$V$ curve is impossible as the diode resistance in the offset region changes drastically over a small bias interval. Third, a “knee” in the reverse current, typically indicative of a generation–recombination current, is indicated at bias values lower than $-0.5$ V. An equivalent circuit diagram accounting for these deviations from ideality is shown in the inset of Figure 3a.

Figure 3 shows topography (b) and CPD (c) images of a segmented SiNW. The base of the NW is on the left side and the Au catalyst is on the right side. Both terminals of the device were grounded, as was the bottom gate terminal. The two line profiles shown in Figure 3d are line scans of the two surface measurements at the center of the wire, respectively. An abrupt change in the surface potential is observed at a distance of 15 $\mu$m, which is the expected location for the junction between the second and the third segments.

A typical series of CPD line-profiles taken at different reverse-biases from a single NW junction is shown in Figure 4a. The measurement was performed by applying negative biases to the top (catalyst side) electrode, which is connected to the third segment of the wire, while keeping the bottom (n$^+$) electrode grounded. The bias applied to the top electrode was varied between 0 and $-2$ V with 0.25 V steps, which is a reverse biasing of the n$^-$–n junction. The junction-potential drop
under reverse bias, shown in Figure 4a, follows the expected $V_{bi} + V_R$ behavior of a typical diode, where $V_R$ is the applied reverse bias. The figure demonstrates a considerable nonlinear voltage drop on the n-side of the wire with a built-in potential of $V_{bi} = 0.15 \, V$.

The cylindrical $n^+--n$ NW system cannot be modeled using a simple analytical expression. A two-dimensional model was therefore implemented using Sentaurus TCAD Device Simulator (Synopsis Inc.). The program numerically solves the Poisson equation coupled to the electron and hole continuity equation to simulate the electrical behavior of a single isolated semiconductor device, or several devices combined in a circuit. Using the one-dimensional built-in voltage for an $n^+--n$ junction

$$V_{bi} = \frac{k_B T}{q} \ln \left( \frac{n^+}{n} \right)$$

and using the measured $V_{bi}$ of 0.15 $V$, the ratio between the electron densities in the second and third segments, $n^+/n$, is calculated to be 312.5. Initially, the device was modeled using an $n^+--n$ diode model (Figure 4b). The model is of a semiconductor NW composed of two 10 $\mu$m long and 80 nm wide segments with different P doping concentrations, placed over a 200 nm oxide layer and a thick silicon substrate, representing the complete device geometry. The calculation was repeated several times using different doping profiles, ranging from $n^+ = 10^{20} \, cm^{-3}$ to $n^+ = 10^{17} \, cm^{-3}$. The $n$ concentration was changed accordingly to keep the $n^+/n$ ratio constant at 312.5, the value that was extracted from the $n^+--n$ diode equation. The results of this calculation with the highest and lowest concentrations used are shown in Figure 4c,d, respectively, overlaid with the experimental surface potential profiles. Figure 4 shows that these simulations do not reproduce the measured potential profiles under reverse bias. Also, the simulated voltage drop over the $n$ segment is approximately linear, whereas the measured curves show a significant nonlinear behavior. The measurements show that the band bending changes from that of a heavily doped wire at a small reverse bias to that of an intrinsic wire for larger values of reverse bias, suggesting that a thin doped layer dominates the device behavior under low bias but becomes fully depleted under higher bias.

To improve the agreement with the measurements, a modified model, shown in Figure 5a, was employed. This model includes a core-shell structure in the $n$ segment with a P-doped shell of thickness $t$ and an intrinsic core. The
simulation parameters \(n^+\), \(n\), and \(t\) were optimized to fit the measured results and were found to be \(n^+ = 5 \times 10^{18} \text{ cm}^{-3}\), \(n = 7 \times 10^{16} \text{ cm}^{-3}\) in the shell and \(10^{14} \text{ cm}^{-3}\) in the core. The shell thickness was found to be 10 nm. The optimized results of the modified model, overlaying the measured results, are shown in Figure 5b. The simulations show that the electrostatic characteristic of the junction is drastically altered. A recent study of ultrashallow doped p–n junction by Popadic et al. showed that in such depletable junctions, the current–voltage characteristics approach those of Schottky junctions, with significantly larger reverse (leakage) currents and ideality factors.

This correlated study has two main advantages. First, validation of the lightly doped core–heavily doped shell structure of the VLS-doped third segment was achieved independently by both npSAM and KPFM. These findings are consistent with a recent report that VLS doping is with signifi-

...properties and heterostructures with better definition of the dopant incorporation mechanisms, will be useful for the design and fabrication of many device structures, including doped semiconductor NWs with better control over their electrical properties and heterostructures with better-defined junctions.

**REFERENCES**
