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***In-situ* chemical doping of silicon nanowires by
supercritical-fluid synthesis**

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***In-situ* chemical doping of silicon nanowires by
supercritical-fluid synthesis**

by

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Por mi familia

Acknowledgments

“En fin voy a comenzar \ a ver si puedo o no
puedo. \ A ver si puedo trobar \ o a medio
verso me quedo \ sin poderlo declarar.”

— Anonymous
Folk poetry of Veracruz, México

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***In-situ* chemical doping of silicon nanowires by supercritical-fluid synthesis**

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Supervisor: Brian A. Korgel

Silicon nanowires show promise as components in electronic devices and integrated circuits. The ability to chemically dope nanowires is desirable in order to enable further technological development of this material. In this study, phosphorus-doped (P-doped) silicon nanowires were synthesized *in situ* by the supercritical fluid-liquid-solid (SFLS) growth mechanism through addition of diphenylphosphine (DPP) or tris(trimethylsilyl)phosphine ($\text{P}(\text{SiMe}_3)_3$) as phosphorus dopants. Conduction electrons from P donor states in crystalline Si have been observed in the *in-situ* -doped nanowires by detection of a resonance peak at $g = 1.998$ via electron paramagnetic resonance spectroscopy (EPR) at 4.2 K. Elemental analysis via inductively coupled plasma-atomic emission spectroscopy (ICP-AES) has shown that the amount of P in *in-situ* -doped nanowires is commensurate with the dose of P precursor, and by appropriate dosing, the doping level can be modulated between 10^{17} and 10^{19} P atoms cm^{-3} without an intolerable degradation in nanowire quality or yield. Field-effect

transistors (FETs) were fabricated from the undoped and doped nanowires. An n-channel, field-effect response was in general not clearly observed in FETs fabricated using the *in-situ* doped nanowires, though in some cases unipolar p-type and ambipolar behavior were observed with strong hysteresis regardless of the direction of the gate-voltage sweep. The poor performance of the tested devices might be attributed to the use of Au seeds, which introduce mid-gap trap states in Si, and to the presence of surface defects that can scatter charge carriers.

In addition, ion implantation of silicon nanowires was performed, as an alternative to *in-situ* doping of P. The nanowires were subjected to ion implantation at targeted dopant concentrations similar to those of *in-situ* doping. FET transfer characteristics of these implantated nanowires were determined for as-received nanowires as well as post-implantation annealed nanowires. FET characterization was inconclusive, and EPR studies did not reveal a clear sign of conduction electrons from P. However, compelling changes in the surface states of the nanowires were revealed. In particular, for annealed nanowires, paramagnetic states associated with oxide defects in silicon were observed. Nevertheless, high-resolution transmission electron microscopy did not reveal widespread amorphization of silicon nanowires after ion implantation, as might be expected in bulk silicon. These results suggest that ion implantation of silicon nanowires has a strong effect on surface states, while leaving the crystalline core of the nanowires relatively intact.

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Chapter 1

Introduction

“If I have seen further, it is by standing on the shoulders of giants.”

— Sir Isaac Newton, 1676

1.1 Introduction

The genesis of this research can be found in the collaborative work undertaken by Dr. Korgel and his industry colleagues to search for an alternative to amorphous silicon as the channel material of thin-film transistors (TFTs), the tiny switches that are at the heart of each pixel in a liquid crystal display (LCD). The goal of this research was to modify the growth conditions of solution-grown silicon nanowires in order to incorporate a dopant that would provide the necessary charge carrier concentrations, with adequate mobilities, and device currents and ON/OFF ratios, as measured in field-effect transistors, — which might enable their use in TFTs in LCD technology, given that further developments in the production of TFTs based on amorphous silicon could not yield ever fast switch rates.

In addition, with an eye towards future processing advancements that would enable large-area solution-based processing of substrates for display technologies, silicon nanowires synthesized by the supercritical-liquid-solid (SFLS) method were seen

as a good candidate for development. However, it would be necessary to develop synthesis methods whereby silicon nanowires could be deterministically and reproducibly doped with, for example, a phosphorus impurity at an appropriate level, in order to increase the concentration of charge carriers and confer tunable conductivity.

Many methods were attempted to dope silicon nanowires, and some of those methods are described herein. Diffusion doping by means of a phosphorus-doped silicate glass was attempted but was unsuccessful and resulted in defect-ridden nanowires. Diffusion of a molecular monolayer containing a phosphorus dopant, in the form of trioctylphosphine, for example, suffered from many problems results to the nanowire surface properties, especially for nanowires synthesized from monophenylsilane.

In the end, *in-situ* doping of silicon nanowires by incorporation of an impurity concentration of an organophosphorus precursor, was the only method that proved successful in incorporating P donor states in silicon, as evidenced by electron spin resonance studies.

The elaboration of rudimentary field-effect transistor devices by dip processing, was used as a test to determine whether *in-situ* doped silicon nanowires displayed characteristic n-type behavior. Solution-based processing was used as a facile method for rapidly confecting the devices.

Finally, ion implantation was performed as another means of doping. These studies did not yield success in terms of demonstrating the feasibility of n-type doping of nanowires by ion implantation. Rather, the observations gleaned from these studies reveal, in part, the evolution of surface properties vis-à-vis transistor char-

acteristics and paramagnetic defects of nanowires subjected to ion implantation and post-implantation annealing, and are suggestive of subtle alterations to the nanowire surfaces, with possible impacts on device performance.

It is a rare opportunity for a researcher to strike out in search of a technological advancement that has the potential to change such a ubiquitous technology. In the course of this research, many new insights were gained into the synthesis space within which the nanowire system could be modified. In the future, this research may serve as a launching pad for further studies of *in-situ* doping and of nanowire surface effects.

1.2 Organization of the Thesis

This section outlines the organization of the work contained within this thesis.

Chapter 2 is entitled “*In-situ* chemical doping of silicon nanowires”. In this chapter, the growth method is described in order to provide the reader with background and understand the context within which the studies were conducted. The synthesis and *in-situ* doping procedures are described. A discussion of electron paramagnetic resonance spectroscopy is provided in order to familiarize the reader with this specialized technique. Microscopy data show the morphology of nanowires subjected to *in-situ* doping. Spin resonance spectra reveal the incorporation of P donor states in silicon by detection of conduction electrons.

Chapter 3 is entitled “Nanowire Field-effect Transistors”. In this chapter, studies of the transistors made from *in-situ* doped nanowires are presented. The method of nanowire FET confection is described. The transfer curves are presented

for a number of devices made from nanowires synthesized from two different silicon precursors and doped with two different phosphorus precursors, as well as optical micrographs of the devices themselves. FET characteristics in general did not display clear hallmark of n-type behavior.

Chapter 4 is entitled “Ion Implantation of Si nanowires’: EPR and FET studies”. In this chapter, the details of ion implantation of silicon nanowire mats synthesized from trisilane and monophenylsilane are presented. FET studies were conducted and revealed a wide range of performance characteristics. In many cases, these effects can only be explained by inference based on the processing carried out on the nanowires. EPR studies revealed large intensity peaks related to oxide defects and surface dangling bonds in silicon, but no evidence of P donor states was observed. Insights into the evolution of surface defects can be inferred from the data.

Chapter 5 summarizes the research carried out and provides conclusions and insights for future work.

Chapter 2

In-situ phosphorus doping of silicon nanowires

“La vie n’est facile pour aucun de nous. Mais quoi, il faut avoir de la persévérance, et surtout de la confiance en soi. Il faut croire que l’on est doué pour quelque chose, et que, cette chose, il faut l’atteindre coûte que coûte.”

— Marie Curie

2.1 Introduction

Silicon nanowires (SiNWs) are promising candidate materials for nanostructured electronic and electro-optical devices, given that the solid-state physics based on silicon semiconductor devices is well-understood and certain applications that do not require ever-higher transistor densities continue to be restricted by the processing constraints entailed by monolithic single-crystal Si microchip fabrication [1–17]. Flexible devices that conform to irregular surface geometries could be one potential application of SiNWs.

The incorporation of silicon nanowires (SiNWs) as active components in nanoscale devices will be predicated in part upon a deterministic control of charge-carrier concentration and mobility, among other considerations. To this end, impurity doping of SiNWs with phosphorus and boron has been demonstrated [?, 17–23], and some

studies have shown the attendant changes in electronic transport properties and in carrier type with doping, e.g., via measurements conducted on nanowire field-effect transistors (NWFETs) [8, 9, 17, 23, 24] or through two- and four-terminal electrical measurements on single NWs [?, 18, 23]. Although some studies have shown that switching behavior in rudimentary nanowire devices can be achieved with undoped nanowires, the ability to dope nanowires in a controlled manner enables an additional processing functionality via methods that are amenable to the current technique of supercritical fluid-liquid-solid (SFLS) synthesis.

While prior work has dealt with doping of nanowires synthesized by chemical vapor deposition (CVD) or by laser ablation methods [14, ?, 19, 25] by the vapor-liquid-solid (VLS) mechanism, a doping method was developed *de novo* based upon nanocrystal-seeded SFLS synthesis [26–29] for *in-situ* phosphorus doping of SiNWs. The SFLS growth method is attractive for its ability to produce single-crystal nanowires of uniform diameters in batch quantities of 30–50 mg and for its adaptability to industrial scale-up for production of commercially relevant quantities of high-quality nanowires. This method consists of introducing a mixture of a high boiling-point organic solvent, metal nanocrystals, and an organosilane precursor in a reactor at elevated temperatures and pressures. *In-situ* doping is accomplished by simply adding an organophosphorus precursor, in this case diphenylphosphine (DPP), at a concentration commensurate with the targeted level of doping. This synthesis method has been developed over the past 15 years in the Korgel group and has served to produce large batch quantities as high as 1 g for applications ranging from thin-film photovoltaics to Li-ion batteries.

2.1.1 Supercritical synthesis

Traditionally, synthesis of Si nanowires has been carried out in the gas phase (vapor-liquid-solid, VLS synthesis) by means of chemical vapor deposition (CVD) [15, 16, 30, ?]. This method of synthesis, while it is widely utilized and well-understood, relies on relatively expensive laboratory equipment, highly toxic precursors that are of high cost, constant monitoring of the process conditions to ensure proper synthesis, high equipment-maintenance costs, and highly trained staff and specialized facilities to ensure the safety of workers, given the toxic nature of the precursor gases [26–28]. In addition, CVD synthesis is relatively slow and produces sub-mg quantities in a typical batch process. Nanocrystal-seeded SFLS synthesis allows for the crystallization of Si in solution with high throughput that results in large batch quantities. Thermolytic decomposition of an organosilane precursor coupled with nanocrystal-mediated growth is a robust system for generation of tens-of-mg quantities of highly uniform, monocrystalline, high-aspect ratio Si nanowires.

Why supercritical fluids? Let us consider the phase behavior of a unary system for a typical substance, such as water, carbon dioxide or even an organic solvent, such as benzene or toluene. Ordinarily, any sufficiently large change in pressure or temperature (while holding other variables of state constant) results in the system crossing a line of two-phase equilibrium and thus leads to a change of thermodynamic phase, *i.e.*, a first-order phase transition such as melting or boiling. However, above a critical temperature and critical pressure in the vicinity of the single-phase liquid or single-phase gas regimes, the system exhibits no discernable phase transition but

rather enters a regime in which the diffusivity resembles that of the gas phase but the density is more akin to that of the liquid. This regime is what is referred to as the supercritical fluid — the substance can undergo effusion, such as gas-like transport through a porous solid, while at the same time it can dissolve another material or suspend colloidal solids as if a liquid [31]. These properties of a supercritical fluid — in particular the gas-like diffusivity and liquid-like solubility — are what make it ideal for solution-based synthesis of colloidal nanomaterials, such as nanoparticles, nanorods, and nanowires.

In the case of silicon nanowires, at the elevated pressure (c. 50 atm) and temperature (c. 400°C - 500°C) within the SFLS reactor, the organosilicon precursor can breakdown to generate the desired silicon atoms and diffuse into the Au nanocrystal seeds, which form liquid droplets thanks to the eutectic system. These single-phase liquid alloy droplets then become supersaturated with the metalloid, which increasingly becomes enriched with the solute atom as more precursor is feed into the reactor. Once the system crosses the silicon liquidus phase boundary, solid silicon precipitates from the liquid droplet because the melting point of silicon (1414°C) is so much higher than the temperature of the supercritical fluid, and the nanowire grows from the seed, given stable conditions of precursor decomposition and diffusion of silicon into the seed [26–28, 31–34].

Typical VLS growth relies on gaseous precursors, such as a mixture of SiH_4 and H_2 , which, as mentioned has its disadvantages. Solution-based methods are attractive because more stable precursors can be used, such as monophenylsilane — which can be safely stored in the liquid state at ambient temperatures and pressures

for relatively long periods of time without degradation. However, a precursor such as monophenylsilane is far less volatile and reactive than its VLS counterpart, silane. As a result, different reaction pathways must be taken in order to take advantage of the Au-Si eutectic. Ambient pressure solvents, such as toluene, benzene, or hexane, at temperatures and pressures above their thermodynamic critical point are ideal for such an application [26–28, 31–34].

Colloidal synthesis of Si nanomaterials was for many years considered a challenge, and until recently very little was understood about the chemistry of organosilane precursors. Studies from the Korgel group dating back to 2000 [31–38] have shown that the SFLS synthesis scheme relies on two systems or processes that occur concomitantly and in conjunction to produce high-quality Si nanowires in large quantities, — the Au-Si binary eutectic system and the disproportionation of aryl silane precursors to form silane, which subsequently decomposes to Si atoms that crystallize into nanowires via Au nanocrystal seeds. Decomposition of the precursors leads to sufficiently high conversion of Si to warrant the use of organosilane precursors over other potential Si precursors that have been more widely studied but whose decomposition kinetics is not suitable for seeded growth in solvent at relatively low reaction temperatures [28]. The Si precursor of choice used in studies of *in-situ* doping was monophenylsilane (MPS). Size selection of the Au nanocrystal seeds allows for control of the Si nanowire diameter. Careful control of the reaction temperature and pressure within the SFLS reactor ensures stable decomposition of the MPS, which is the key factor affecting the crystallinity, length, and absence of defects in the synthesized nanowires. Similarly, germanium nanowires can be synthesized via the

SFLS method, using Au nanocrystal seeds and organogermane precursor, though the studies described herein did not deal with *in-situ* doping of germanium nanowires.

2.1.2 Doping

Intrinsic silicon behaves more like an insulator in many ways than like a conductor. It is an indirect bandgap semiconductor, and the energy of the bandgap is 1.11 eV. To be useful as in semiconductor devices, silicon must have some appreciable concentration of mobile charge carriers[39–41]. Intrinsic silicon has a carrier concentration at room temperature (c. 300 K) of approximately $1.08 \times 10^{10} \text{ cm}^{-3}$ [42, 43]. These carriers are a result of thermal excitation, as described by the **Fermi-Dirac distribution**¹. Equation 2.1 gives the average number of electrons in state i as a function of the absolute temperature T , of the energy of the i^{th} state ϵ_i , and of the chemical potential of the electron μ , where k is Boltzmann’s constant.

$$\bar{n}_i = \frac{1}{e^{(\epsilon_i - \mu)/kT} + 1} \quad (2.1)$$

In order for dopant atoms to yield large changes in the mobile charge carrier concentration in silicon, they must be incorporated as substitutional impurities in the diamond-cubic crystal structure of silicon, i.e., in the case of phosphorus, a phosphorus dopant atom must replace or substitute a silicon atom and take up the same tetrahedral coordination of a silicon site in the diamond cubic crystal structure by forming four bonds with each of one of its four nearest neighbor atoms. Because phosphorus has one more valence electron than silicon, there is one electron state

¹i.e., the statistical distribution of indistinguishable particles of half-integer spin (fermions) over states of certain energies

that is donated for each phosphorus atom that is incorporated as a substitutional impurity. These donor states can be spatially localized but are also subject to the same thermal excitation that gives intrinsic silicon a certain number of charge carriers in its conduction band at finite temperatures. However, these donor states are present near the edge of the conduction band in silicon. The presence of donor states also has the effect of shifting the energy of the Fermi level (i.e., the chemical potential of the electrons). This shift for n-type doping is given by:

$$E_F = E_C - kT \ln \frac{N_C}{N_D}, \quad (2.2)$$

where E_F is the Fermi energy (located at midgap for intrinsic silicon), E_C is the energy of the conduction band edge, N_C is the concentration of intrinsic charge carriers in the conduction band, and N_D is the concentration of donors. Phosphorus donor states are located approximately 45 meV below the conduction band minimum. Thermal energy kT at 300 K is equal to 25.85 meV. Thus, for $N_D = 10^{17} \text{ cm}^{-3}$, the Fermi energy E_F would be located within the conduction band of silicon at an energy of approximately 415 meV above the conduction band minimum.

Because the atomic density of silicon is $5 \times 10^{22} \text{ atoms cm}^{-3}$, phosphorus doping concentrations of $n = 10^{17}$ to $n = 10^{19}$ translate to Si:P mole ratios of 10^5 to 10^3 . These concentrations are easily achieved via *in-situ* doping by introducing impurity concentrations of a phosphorus precursor, such as DPP or tris(trimethylsilyl)phosphine, $\text{P}(\text{SiMe}_3)_3$, into the reaction mixture. In this way, the phosphorus precursor will decompose in the conditions of the reactor concomitantly with the silicon precursor, and both will diffuse into the Au seed and be incorporated into the nanowires.

Lastly, *in-situ* doping has been demonstrated in CVD-grown nanowires [44–49]. These methods suffer from the same disadvantages (primarily high cost) of CVD, as well as potential segregation of the dopant to the nanowire surfaces, which could affect the properties of the dopant and thus the donor states.

2.2 Electron Paramagnetic Resonance Spectroscopy (EPR)

2.2.1 Electron spin

Historical overview Physics predicts that electrons and atomic nuclei possess an intrinsic angular momentum that is called spin. Conceptually, spin was first described by Wolfgang Pauli, albeit partially. Famously in 1922, Otto Stern (at the time, an assistant to Max Born) and Walther Gerlach working at the University of Frankfurt, conducted their famous experiment in which a beam of silver ions was passed through an inhomogeneous magnetic field toward a target. Due to the quantization of electron spin, the ions were deflected towards either the north pole of the magnet or the south pole but never in between, because the magnetic component of the spin can only take on a value of either $1/2$ or $-1/2$. The interpretation at the time was that the directional angular momentum was quantized, which corroborated the then-reigning theory of Niels Bohr and Arnold Sommerfeld. Later in 1925, though, George Uhlenbeck and Samuel Goudsmit in Leiden explicitly described a theory in which the electron possesses an intrinsic angular momentum, which they called “spin”. [50–52]

In addition to electron spin, atomic nuclei also possess spin, and the use of nuclear spin has become a powerful analytical tool in medicine and in the chemical sci-

ences. Nuclear magnetic resonance spectroscopy permits the inspection of molecules and compounds by absorption of electromagnetic radiation in an applied magnetic field [50–54].

In a similar way, electron spin resonance can be used as an analytical tool to interrogate molecules, surfaces, nanomaterials, and bulk materials, so long as they possess paramagnetic electron states, *i.e.*, unpaired electrons².

The system that is explored in this study is P-doped Si nanowires, in which phosphorus is incorporated as a substitutional point defect in the silicon diamond-cubic crystal structure, thereby donating a valence electron, and it is the electron spin of this phosphorus-donor state that is paramagnetic, which can be detected via resonance.

EPR principles Because of the charge of the electron, its spin together with its orbital angular momentum give rise to a magnetic moment³. In the absence of a strong applied magnetic field, the spin states are degenerate. However, in an external applied magnetic field, the magnetic moment of the electron becomes aligned with the magnetic field, and a splitting of the degeneracy occurs, leading to a difference in energy between the parallel, spin-down state ($m_s = -1/2$, of lower energy) and the anti-parallel, spin-up state ($m_s = 1/2$). This phenomenon is known as the **Zeeman effect**, and it is possible to exploit this effect for analytical purposes.

²As the reader might imagine, stable systems of unpaired electrons are, for reasons of chemistry, much less common than their nuclear cousin, and so EPR tends to be a highly specialized technique is most widely used to detect and quantify the presence of free radicals.

³Every electron, in essence, is a tiny, quantum-mechanical magnet.

As expressed in Equation 2.3, the difference in energy, $\Delta E = E_{1/2} - E_{-1/2}$ between the two states $m_s = -1/2$ and $m_s = 1/2$ is directly proportional to the strength of the external applied magnetic B_0 , and the relationship takes as a scaling factor the *g-factor*⁴ of the electron, g_e .

$$\Delta E = g_e \mu_B B_0 \quad (2.3)$$

As is often the case, unpaired electrons in the external applied magnetic field can absorb (or emit) energy by absorption (or emission) of a photon of the appropriate energy, $h\nu$. This photon energy then yields the resonance condition, $h\nu = \Delta E$. The so-called fundamental equation of EPR is given below in Equation 2.4, where μ_B is the Bohr magneton and h is Planck's constant.

$$h\nu = g_e \mu_B B_0 \quad (2.4)$$

It will be intuitively obvious to the reader that this fundamental equation admits of an ample range of frequencies ν of electromagnetic radiation — that serves to excite the transition between spin states — and of magnetic field strengths B_0 [53, 54].

The distribution of the two quantum mechanical spin states are random in nature, but because the electron spin system obeys Maxwell-Boltzmann statistics, the lower-energy parallel states are slightly more probable and therefore slightly greater in number than the high-energy antiparallel states at any finite temperature at thermal

⁴Similar in nature to the Landé g-factor or the spectroscopic splitting factor, the g-factor can be thought of as a dimensionless version of the gyromagnetic ratio that associates the magnetic moment of the electron, its angular momentum quantum number, and the Bohr magneton.

equilibrium. The spin populations are given by Equation 2.5.

$$\frac{n_{\uparrow}}{n_{\downarrow}} = e^{-\frac{\Delta E}{kT}} \quad (2.5)$$

In general, thermal energy tends to drive the system to thermal equilibrium, and the spin populations are to a large extent equal in number, differing by only approximately 0.08% [54]. Thus, for a temperature of 300 K and $\nu = 9.5$ GHz, substituting $h\nu$ for ΔE , we see that the above ratio is $\frac{n_{\uparrow}}{n_{\downarrow}} = 0.9985$, a difference of only 0.15%.

In addition, absorption of microwave energy heats up the sample, and it is the tendency of the system to deëxcite by dissipation of thermal energy to the environment in which the spins are present⁵. This spin-relaxation behavior, which possesses a characteristic decay time, τ , also leads to broadening of the absorption signal, as the spins interact with the lattice by thermal vibrations that induce a field within the system and lead to the line width that is observed in the spectrum. For most systems, this broadening is mostly due to spin-lattice relaxation, but in other systems, especially those of high spin concentration, the interaction of spins with other spins leads to another phenomenon known as spin-spin relaxation[53, 54].

Therefore, one of the strengths of EPR is its sensitivity in detecting small spin concentrations at relatively low microwave power (~ 1 mW), which is one way in which the technique differs strongly from NMR. In addition, phase-sensitive detection via magnetic field modulation allows for the reduction of noise, which is extremely advantageous for systems of low spin concentration. Because of phase-sensitive detection

⁵This environment is termed the “lattice” regardless of the physical nature of the system in question

and field modulation, the EPR signal is output as the first derivative of absorption [53, 54].

Modern continuous-wave EPR spectrometers, however, commonly operate over only one specific frequency band, the X-band — with frequencies ranging from 9,000 MHz to 10,000 MHz⁶. X-band frequencies are in the microwave range, and so it is common to speak of microwave frequency in EPR experiments, as the resonant cavity and waveguides of the spectrometer is specifically tailored to maximize the sensitivity to and resonance of microwaves.

Moreover, the resonant properties of a system with paramagnetic electron states can be observed either by varying the magnetic field strength while keeping the microwave excitation frequency constant (so-called “constant wave” operation) or by varying the microwave excitation frequency while holding the magnetic field strength constant (“constant field” operation). For practical reasons of signal acquisition and detection sensitivity, it is most common to operate the EPR spectrometer in “constant-wave” mode⁷.

EPR has long been used to study donor states in silicon [55–60]. In order for dopant atoms to yield large changes in the carrier concentration in silicon, the dopant atoms must be incorporated as substitutional impurities in the silicon crystal

⁶It is rather less common to operate the EPR spectrometer in the Q-band at frequencies of c. 35 GHz. In the EPR facility at the University of Texas at Austin, the Bruker spectrometer is configured to operate at either the X band or the Q band.

⁷Even more specialized techniques exist in which the microwave excitation is pulsed — in order to observe, e.g., spin resonances that are transitory and have interesting spin-relaxation properties, as well as the ENDOR technique that applies a radiofrequency excitation to excite nuclear spins and observe hyperfine splitting due to the interaction electron spins and nuclear spins.

structure, i.e., in the case of phosphorus, a phosphorus dopant atom must replace or substitute a silicon atom and take up the same coordination of a silicon site in the diamond-cubic crystal structure and form four bonds with each of its four nearest neighbor atoms. Because phosphorus has one more valence electron than silicon, there is one unpaired electron that is donated for each phosphorus atom that is incorporated as a substitutional impurity.

2.2.2 Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES)

Inductively coupled plasma - atomic emission spectroscopy is an analytical technique that is used in the detection and quantification of trace chemical elements [61–64]. An argon plasma is generated by radio-frequency induction [65], thereby producing a plume at temperatures ranging from 6,000 to 10,000 K, and into which a solution of analytes is injected. The plasma excites electrons in the atoms of the analyte out of their ground states, and upon deexcitation, photons are emitted, and reach a detector to produce a signature that uniquely identifies the atoms in the analyte. In this way, chemical identification of trace elements down to parts-per-billion concentrations can be achieved from relatively small sample sizes. An elemental standard at known concentration is typically used for instrument calibration.

2.3 Experimental Details

2.3.1 *In-situ* doping

2.3.1.1 Materials

All reagents used in the procedures described here were utilized as received without further purification. Anhydrous toluene (99.8%), chloroform (CHCl_3 , 99.8%), diphenyl phosphine (98%), ethanol (99.9%), dodecanethiol ($\geq 98\%$), tetrachloroaurate trihydrate ($\geq 99\%$), sodium borohydride ($\geq 98\%$), and tetraoctylammonium bromide (98%) were purchased from Sigma-Aldrich. Monophenylsilane ($> 95\%$) was purchased from Gelest (Morrisville, PA). Trisilane (99.99%) was purchased from Voltaix (Branchburg, NJ). Hydrochloric acid (25% v/v), nitric acid (70%, 15.8 N, Certified ACS Plus), and sodium hydroxide (pellets, Certified ACS, $\geq 97.0\%$) were purchased from Fisher Chemical, and hydrofluoric acid (48 - 51% v/v) was purchased from EMD Chemical. Si and P elemental standards ($10 \mu\text{g mL}^{-1}$) were purchased from Inorganic Ventures (Christiansburg, VA). Liquid helium (Industrial Grade, 99.999% purity, 60 L cryogenic liquid shipped in a 304 stainless-steel dewar) was purchased from Praxair (Praxair Distribution, Inc., Austin, TX). Reactor parts were purchased from High Pressure Equipment Co. (Erie, PA).

2.3.1.2 NWs synthesized from MPS

The SFLS synthesis of Au-seeded SiNWs from MPS using procedures published in the literature [66]. The reactor apparatus equipped with a high-pressure liquid chromatography (HPLC) pump system was built in house and kept in a chemical fume hood. A schematic of the apparatus can be found in works cited in the

bibliography [31, 66].

In a typical synthesis reaction, a 28-mL reactant solution was prepared containing anhydrous toluene (ACS grade, Sigma-Aldrich, 99.8%), 40 mg L⁻¹ of dodecanethiol-capped Au nanocrystals (averaging 2 nm in diameter, prepared according to the method enunciated by Brust et al. [67]), and 135 mM MPS (Gelest, > 95%), inside a nitrogen- or argon-filled glovebox. This solution was placed into a stainless steel injection cylinder that was sealed inside the glovebox before being brought into the ambient.

For *in-situ* P doping using DPP, DPP (Aldrich, 98%) was added as a P precursor at Si:P mole ratios ranging from 10⁵ to 10³, which would correspond to doping concentrations of $n = 10^{17}$ to 10¹⁹. For example, to obtain a Si:P mole ratio of 10⁵, 1.35 μ M DPP was added to the reactant solution. To obtain a highly dilute solution of DPP, a one-step serial dilution was performed by using a micropipetter to add approximately 7 μ L of DPP to a glass vial containing 5 mL of anhydrous toluene (inside a nitrogen-filled glovebox). This solution was mixed by manual agitation, and a 5- μ L aliquot was added to the reactant solution using a micropipetter.

A 10-mL tubular titanium reactor was heated to 490°C in a heating block⁸. The injection cylinder containing the reactant solution was then connected to the

⁸The reactor was heated by means of a ceramic heating block equipped with ceramic rods heated by the Joule effect. The geometry of the heating block was that of a rectangular box with upper and lower sections and an interior geometry shaped like a cylindrical tube cut in half along the longitudinal axis such that the tubular reactor could be accommodated between the upper and lower sections, with satisfactory contact between the heated elements of the block and the reactor. The desired reaction temperatures were reached and maintained by means of a temperature-control unit equipped with a thermocouple and powered by a variable autotransformer (Variac).

reactor system. The headspace of the injection cylinder was eliminated first by flowing a small amount of the reactant solution thru the secondary outlet of a six-way valve. Once a good seal between all connections was established and each line was cleared of potential air bubbles, the reactor was filled with anhydrous toluene at a volumetric flow rate of approximately 1 mL min^{-1} to a pressure of 1,100 psi (8.27 MPa). Then, the reactor inlet line was closed. The six-way valve was switched to feed the injection cylinder, which was pressurized to 1,200 psi (7.58 MPa), and the outlet valve of the injection cylinder was opened. Then, the six-way valve was then switched to connect the injection cylinder outlet line to the reactor inlet line. The toluene feed from the HPLC pump was momentarily paused with all valves open except for the reactor inlet, to ensure proper seals throughout the system. Then, the toluene feed was restarted. At this point, the volumetric flow rate of the HPLC pump was reduced to 0.5 mL min^{-1} , the reactor inlet valve was opened, and the pressure was allowed to increase to 1,400 psi (9.65 MPa) with the reactor outlet closed. Once a pressure of 1,450 psi (10 MPa) was reached, the reactor outlet valve was opened. A chronometer was set for a reaction time of 40 minutes, and the pressure throughout the system was maintained at $1,500 \pm 50 \text{ psi}$ ($10.34 \pm 0.34 \text{ MPa}$) by means of a manually-operated millimeter valve. A glass vial was connected to the exit line by means of a septum stopper in order to collect the effluent from the reactor. At the conclusion of 40 minutes, the synthesis reaction was terminated, the reactor was sealed, the HPLC pump was shut off, the variac power was also terminated, and the upper portion of the heating block was removed to expose the reactor, and the reactor was allowed to cool isochorically in the ambient of the fume hood. Once cool to the touch, the reactor was

unsealed under a chemical fume hood. The nanowires were extracted manually using a glass pipette and dispersed in toluene or CHCl_3 . Then, the collected nanowires were ablated three times via centrifugation (Eppendorf centrifuge, model 5804R) at 5,000 rpm in a mixture of toluene, chloroform, and hexane (2:1:1) to remove unreacted precursors. A similar procedure was carried out using tris(trimethylsilyl)phosphine ($\text{P}(\text{SiMe}_3)_3$, Sigma-Aldrich, 95%) instead of DPP as the P dopant for *in-situ* doping at the same Si:P ratios. SiNWs synthesized using Si_3H_8 as the Si precursor [29] can also be P doped using either DPP or $\text{P}(\text{SiMe}_3)_3$ at similar Si:P ratios, as described in the following section.

2.3.1.3 NWs synthesized from trisilane

Silicon nanowires were synthesized from Si_3H_8 precursor using $\text{P}(\text{SiMe}_3)_3$ as the phosphorus precursor at Si:P mole ratios of $5.5 \times 10^5 : 1$, $5.5 \times 10^4 : 1$, and $5.5 \times 10^3 : 1$. The procedures are as follows for a Si:P mole ratio of approximately 10^5 .

A reactant solution was prepared inside the inert atmosphere of a nitrogen- or argon-filled glovebox. The solution contained 27 μL of 0.4 mM $\text{P}(\text{SiMe}_3)_3$, 270 μL of toluene, 550 μL of Au nanocrystals⁹, and 250 μL of Si_3H_8 . The Si:Au mole ratio was 20:1.

The synthesis reaction is a semi-batch process, and the conditions were as follows. A 10-mL tubular titanium reactor was pressurized to 1,000 psi (6.89 MPa)

⁹i.e., equal to 27.5 mg of Au nanocrystals, solution in toluene at a concentration of 50 mg mL^{-1} of Au nanocrystals

by means of an HPLC pump, with the effluent (exit) line closed and pre-heated to a temperature of 450°C. The reactant solution was injected into the reactor by means of an HPLC pump at a volumetric flow rate of 3 mL min⁻¹. The injection time¹⁰ was 1 min. The reactor was allowed to pressurize during injection by maintaining the effluent line closed. After one minute, the injection was terminated, and the final pressure of the reactor was 2,100 psi (14.47 MPa). At the conclusion of the synthesis reaction, the reactor was allowed to cool isochorically in the ambient of the glovebox and, once cool to the touch, was removed from the glovebox and unsealed under a chemical fume hood. The nanowires were extracted manually using a glass pipette and dispersed in toluene or CHCl₃. Then, the collected nanowires were ablated three times via centrifugation at 5,000 rpm in a mixture of toluene, chloroform, and hexane (2:1:1) to remove unreacted precursors.

As with the synthesis of *in-situ* -doped MPS nanowires, the doping level can be adjusted by appropriate dosing of phosphorus precursor to the reaction solution.

2.3.2 Electron Paramagnetic Resonance Spectroscopy (EPR)

EPR was performed using a Bruker EMX Plus X-band spectrometer equipped with a cryostat for studies at 4.2 K. Liquid helium (Industrial Grade, 99.999% purity, 60 L cryogenic liquid shipped in a 304 stainless-steel dewar) was purchased from Praxair (Praxair Distribution, Inc., Austin, TX). The EPR cryostat is equipped with a fitting that allows the delivery of cryogenic liquids from the dewar through a stainless-

¹⁰Because of the higher reactivity and faster decomposition kinetics of Si₃H₈, much shorter reaction times are needed. This short injection/reaction time is in contrast to the 40-min. reaction time for MPS.

steel vacuum-insulated transfer line. Prior to each experiment in which liquid He was used as the cryogen, the vacuum vent of the transfer line was connected to a turbomolecular pump, and the pumping cycle was initiated. The vacuum pressure in the transfer line was allowed to reach at least 5×10^{-6} torr, which required at least 8 hours. Prior to connecting the transfer line to the liquid helium dewar, the transfer line and the cryostat were purged with nitrogen gas from the in-house nitrogen supply in the Welch building of the Department of Chemistry. The transfer line was connected to the dewar by slowly lowering the ventral inlet tube of the transfer line into the primary outlet valve of the dewar. The outlet of the transfer line was then quickly connected to the cryostat, and negative pump pressure was applied to the secondary vent valve of the dewar, such that there would be no back pressure of gases into the liquid He dewar. A temperature control unit was activated, with which the temperature inside the cryostat could be actively monitored throughout the experiment. The system was allowed to cool to 4.2 K, and this temperature was maintained throughout the experiment, provided a steady supply of liquid helium.

Dried samples of undoped and *in-situ*-doped SiNWs were placed in quartz tubes (4-mm, thin-wall, precision quartz EPR tube, Wilmad-LabGlass) for spectral acquisition. When cryogenic cooling was applied, the samples were allowed to cool for several minutes prior to spectral acquisition. Great care was taken to ensure that ice plugs did not form in the portion of the cryostat that holds the sample.

2.3.3 Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES)

Elemental analysis was performed using a Varian ICP-AES to determine the relative amounts of P impurities in *in-situ* doped SiNWs. NWs that had been *in-situ*-doped at Si:P ratios of 10^5 , 10^4 , and 10^3 , as well as undoped NWs (control) were dissolved via wet digestion in 1 M NaOH_(aq) (Fisher Chemical, pellets, Certified ACS, $\geq 97.0\%$) to a stock concentration of approximately 1000 ppm total dissolved solids (TDS), and solutions were obtained at concentrations ranging from 100-1 ppm TDS via serial dilution. Tests were conducted on a range of dilutions in order to optimize signal detection.

2.3.4 Electron Microscopy

Samples of *in-situ*-doped SiNWs dispersed in chloroform were drop cast onto Si wafers for examination via scanning electron microscopy (SEM) using a Zeiss Supra 40 VP microscope operating at an accelerating voltage of 2 kV and a working distance of 2 to 5 mm.

Samples of *in-situ*-doped SiNWs that had been drop cast onto Cu grids coated with lacey carbon (Electron Microscopy Sciences) were examined via transmission electron microscopy (TEM) on a JEOL 2010F microscope¹¹ operating at an accelerating voltage of 200 kV or on an FEI Tecnica Spirit microscope¹² with BioTwin lens

¹¹Located at the Texas Materials Institute (TMI) facility in the Faulkner Nanoscience and Technology building at the University of Texas at Austin

¹²Located at the Electron Microscopy facility of the Institute for Cellular and Molecular Biology (ICMB) at the University of Texas at Austin

configuration, operating at an accelerating voltage of 80 kV.

2.4 Results and discussion

2.4.1 Electron paramagnetic resonance spectroscopy

Figure 2.1 shows the EPR spectrum collected from *in-situ* P-doped SiNWs (Si:P = 10^5) at 4.2 K. Acquisition of an EPR signal using microwave radiation with frequencies in the X band means that the magnetic field strength is in the millitesla range (or units of kilogauss). As a result, when the EPR spectra were acquired, the so-called field center, or the median point in the magnetic field sweep is kept at approximately 3200 Gauss (320 mT).

The clear signal at $g = 1.998$ indicates the presence of paramagnetic P donor states in crystalline Si. Because the EPR spectrum can be considered to be a composite of all the resonant signals within the sample, the presence of paramagnetic donor states from substitutionally incorporated P impurities, results in the appearance of a second peak of smaller magnitude adjacent to the prominent peak from P_B paramagnetic centers. This result is in agreement with that reported by Fukata et al., who studied the effects of *in-situ* doping of silicon nanowires grown by laser ablation or CVD [19, 20, 22].

Figure 2.2 shows the spectrum acquired from undoped (as synthesized) MPS Si nanowires. The only feature of this spectrum is a large symmetrical peak at $g = 2.005$. This peak is attributed to Si dangling bonds, i.e., P_B paramagnetic centers. Given that Si nanowires have a very high surface-to-volume ratio and high aspect ratio, a substantial amount of the material is essentially and Si surface. Surfaces

can, in general, be considered to be large planar defects, in which the coordination around atoms in the crystal structure is much reduced compared to atoms in the bulk. Therefore, silicon atoms at the surface of the nanowire no longer possess a tetrahedral coordination as bulk atoms do, and as a result, many silicon atoms present unpaired electrons at the surface in the form of dangling bonds. These unpaired electrons are responsible for the generation of an EPR signal, such as the one seen in Figure 2.1 [68–70]. .

In the case of TS nanowires, $\text{P}(\text{SiMe}_3)_3$ was used as the P source. The rationale to support this difference in precursor is the following. It was assumed that DPP is an analog to MPS and that thermal decomposition of the two compounds would be similar, *i.e.*, the disproportionation of phenyl groups in the SFLS reaction would lead generation of phosphorus at similar rates as the analogous case of silicon. Because no literature references could be found that dealt with the thermolytic decomposition of DPP at the temperatures and pressures relevant to SFLS synthesis, this conjecture could not be supported by independent results. Nevertheless, the rationale seems justified given the results from EPR showing P incorporation, as seen in Figure 2.1. Furthermore, the assumption was made that in the case of TS, whose decomposition kinetics are quite dissimilar from that of MPS (and also presumably, DPP), a precursor was chosen that could be analogous to TS, namely $\text{P}(\text{SiMe}_3)_3$. The conjecture in this case was that, because the phosphorus atom is already bonded to silicon in the molecule, loss of the three methyl groups (which should occur readily in SFLS synthesis) would be sufficient to allow incorporation of the dopant into silicon nanowires *in-situ* . Again, this rationale seems justified by the fact that P donor states are

indeed detected in EPR spectra from TS nanowires doped *in-situ* with $\text{P}(\text{SiMe}_3)_3$, as can be seen in Figure 2.3.

As yet another route toward incorporation of P dopant, MPS nanowires were doped *in-situ* using $\text{P}(\text{SiMe}_3)_3$. One can observe from the spectrum in Figure 2.4, that a signal from P donor states is detected. However, in contrast to *in-situ* DPP-doped MPS nanowires, there appears to be a difference in the relative intensities of the peak from Si dangling bonds and P donor states, and this difference is perhaps indicative of the different rates of P incorporation using $\text{P}(\text{SiMe}_3)_3$ as the P source compared to DPP.

As a corroboration of the results of SFLS *in-situ* doping, a collaboration was initiated between the Korgel group and Naoki Fukata of Tsukuba University in Tsukuba, Japan. Figure on page 138 in Appendix B shows the EPR spectra at two different microwave power levels. By acquiring a spectrum at different microwave power levels, saturation behavior of the resonance signal is observed. This saturation also occurs in NMR systems, in which the signal amplitude is observed to decrease as the power of the excitation frequency is increased. This saturation behavior results from the phenomena described in §2.2. Furthermore, a side-by-side comparison of *in-situ* DPP-doped MPS silicon nanowires and those grown by the CVD method and *in-situ* doped, which were provided by Fukata, also shows a great degree of correspondence between the observed signals — that is, a large signal attributed to Si dangling bonds adjacent to a smaller peak attributed to P donor states.

In addition, the saturation behavior at various levels of microwave power can also be observed in Figure B.3 located in Appendix B on page 137.

2.4.2 Electron Microscopy

Figure 2.5 shows SEM micrographs of SiNWs *in-situ* P-doped at varying concentrations. One observes that as the Si:P ratio increases, via addition of greater amounts of DPP to the reactant solution, the NW quality decreases (i.e., the number of undesirable products, in the form of amorphous particles and tortuous NWs, increases). The increased presence of dissociated phenyl groups from decomposed DPP might disrupt the formation of silane from MPS disproportionation, and so the degradation in the nanowire quality is likely a result of this disruption of the chemistry of MPS to silane, which one of the main pillars of the SFLS NW growth mechanism [26–29].

SEM micrographs of TS $\text{P}(\text{SiMe}_3)_3$ -doped nanowires are shown in Appendix A on page 122.

Figure 2.6 shows a TEM micrograph MPS nanowires doped at the lowest concentration of phosphorus, Si:P mole ratio of 10^5 , are similar to undoped MPS nanowires.

Figure 2.7 shows a high-resolution TEM micrograph of a MPS nanowire doped at the lowest concentration of phosphorus, Si:P mole ratio of 10^5 . The features observed are similar to undoped MPS nanowires.

Figure 2.9 shows a high-resolution TEM micrograph of a TS nanowire doped at the lowest concentration of phosphorus, Si:P mole ratio of 10^5 . The features observed are similar to undoped TS nanowires.

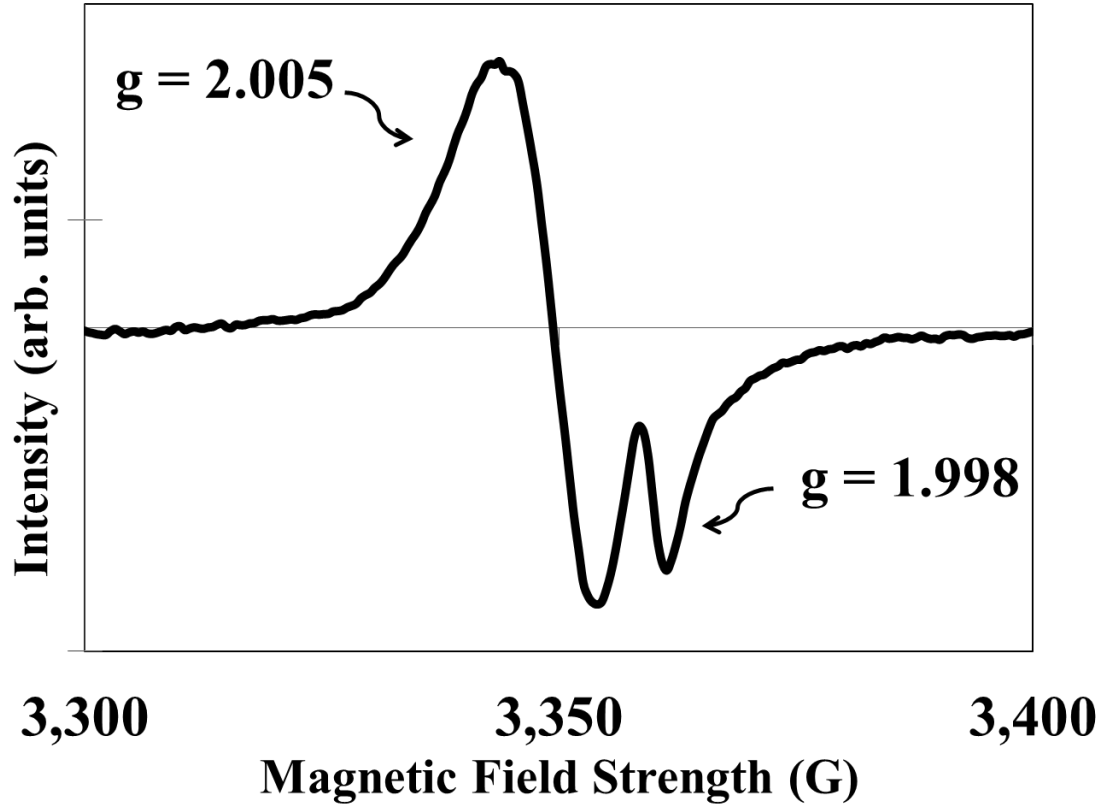


Figure 2.1: EPR spectrum of *in-situ* DPP-doped MPS Si nanowires ($\text{Si:P} = 10^5$) acquired at 4.2 K. The peak centered at 336 mT corresponds to $g = 1.998$ and indicates the presence of P donor states in Si. The inset shows the spectrum gathered from undoped Si nanowires acquired at 4.2 K. The peak at $g = 2.005$ (which is also present in the doped spectrum) is attributed to P_B centers.

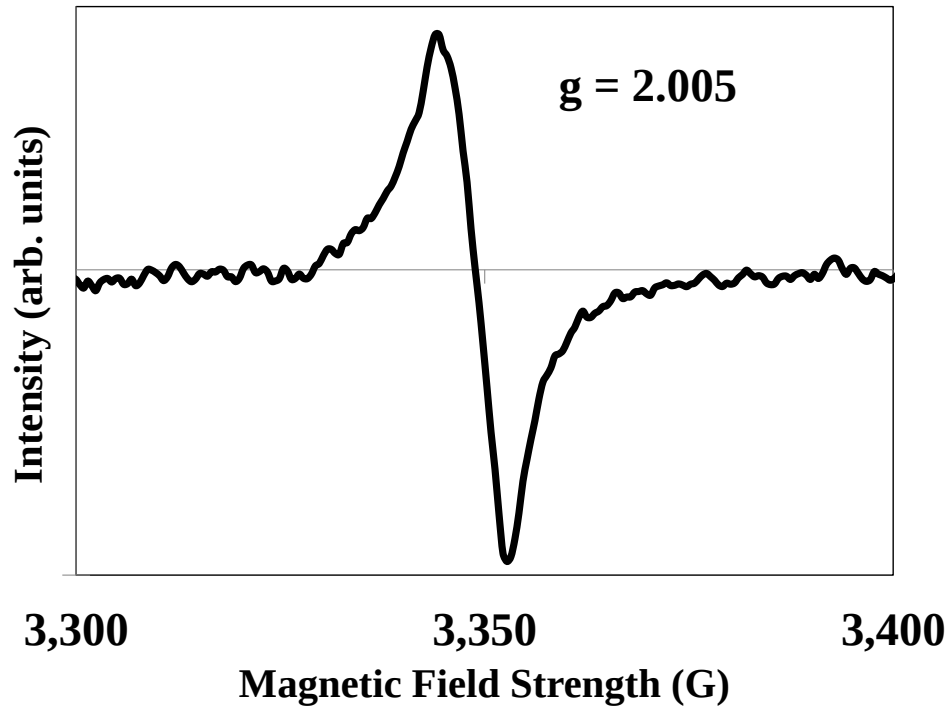


Figure 2.2: EPR spectrum of undoped MPS Si nanowires acquired at 4.2 K. The peak corresponds to $g = 2.005$ and is attributed to Si dangling bonds, *i.e.*, P_B centers.

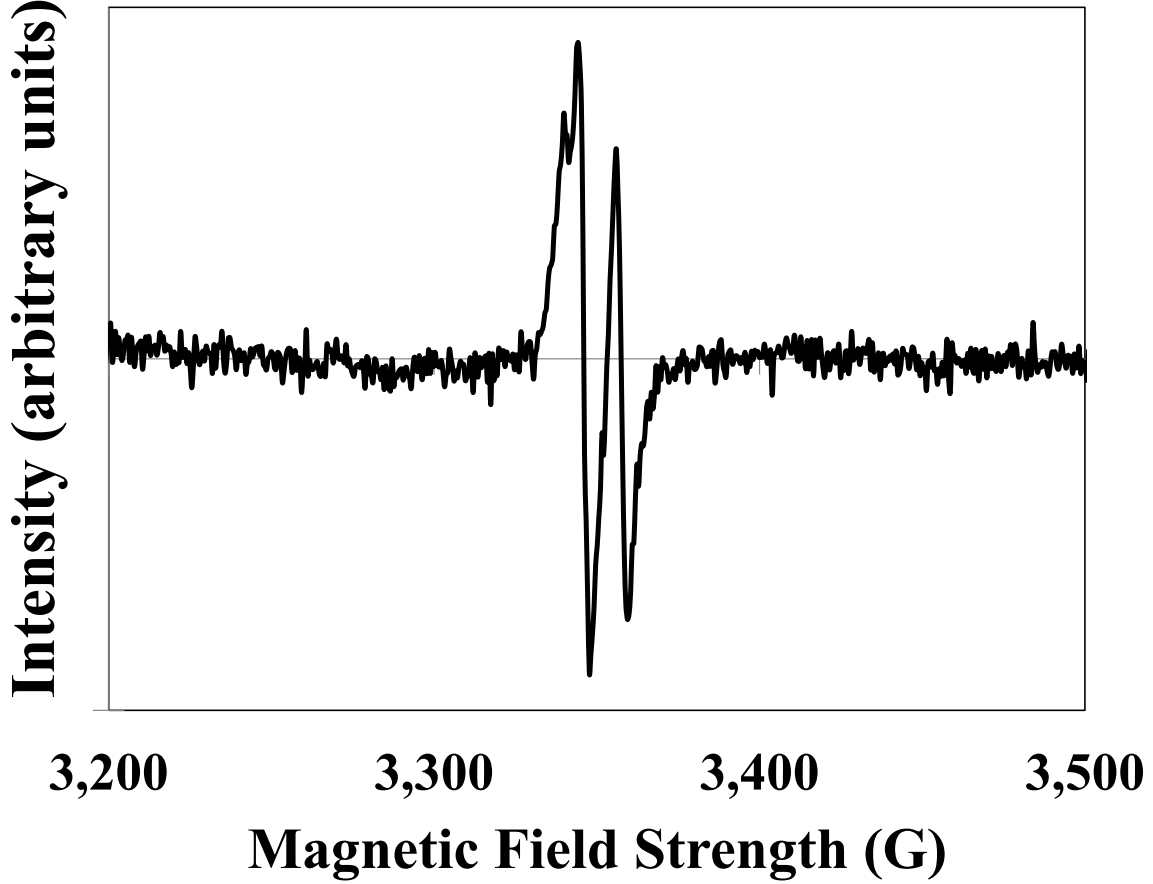


Figure 2.3: EPR spectrum of TS Si nanowires *in-situ* -doped with $\text{P}(\text{SiMe}_3)_3$ at a Si:P mole ratio of 10^5 . The nanowire quality is unaffected by the addition of P dopant. Furthermore, the detection of Si surface states and P donor states indicates that *in-situ* -doping is successful in TS nanowire synthesis using $\text{P}(\text{SiMe}_3)_3$ as the P source. In addition, the relative intensities of the peak resulting from Si dangling bonds and P donor states indicates that the relative number of spins is quite comparable. This result is likely due to the self-passivation of TS nanowires, in contrast to MPS nanowires. TS nanowires readily oxidize in the ambient, and thus the number of Si dangling bonds would be reduced, compared to the case of MPS nanowires at the same P doping level. However, this conjecture assumes that incorporation of phosphorus is comparable in both cases.

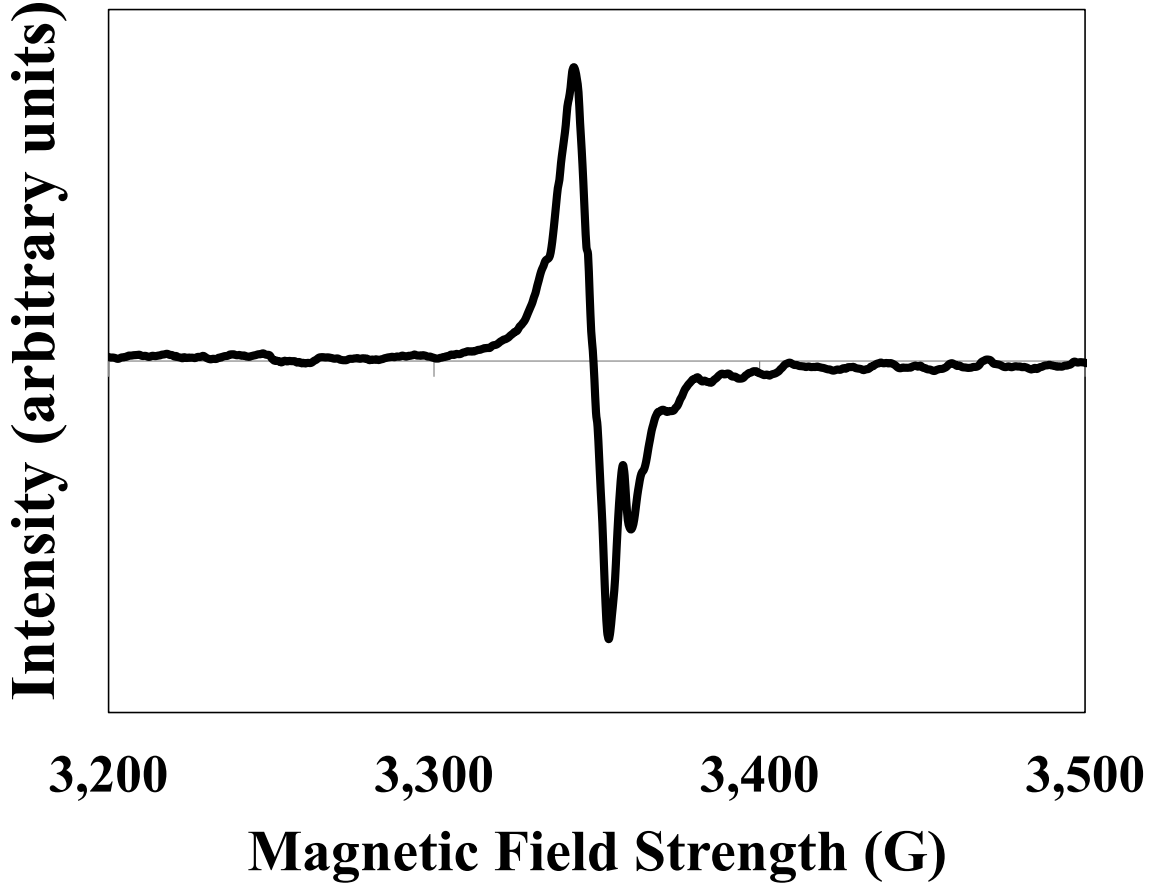


Figure 2.4: EPR spectrum of MPS Si nanowires *in-situ* -doped with $\text{P}(\text{SiMe}_3)_3$ at a Si:P mole ratio of 10^5 . The nanowire quality at this doping level is unaffected by the addition of P dopant. Furthermore, the detection of Si dangling bonds and P donor states indicates that *in-situ* doping is successful using $\text{P}(\text{SiMe}_3)_3$ as the P source. While direct comparison of EPR spectra in terms of signal intensities is not possible in this case, given differences in signal acquisition parameters, it can be said that the relative intensities of the peak from Si dangling bonds and that of the P donor state stands in contrast to the case of DPP-doped nanowires. This results might indicate that P incorporation is reduced in the case of $\text{P}(\text{SiMe}_3)_3$, possibly as a result of a difference in decomposition kinetics compared to DPP.

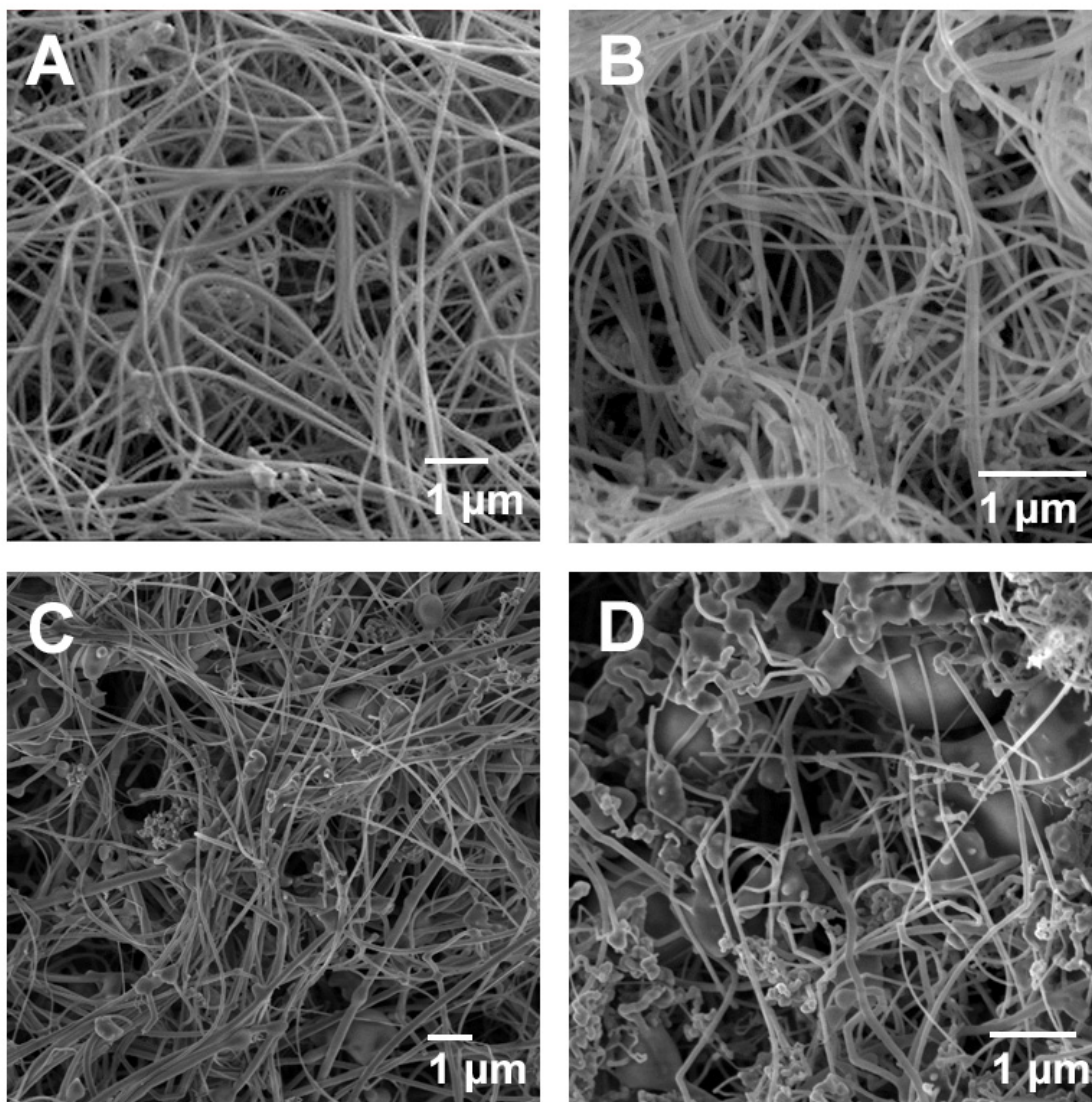


Figure 2.5: SEM micrographs of undoped and *in-situ* DPP-doped MPS SiNWs: (A) undoped MPS SiNWs, and MPS SiNWs doped at Si:P moles ratios of (B) 10^5 , (C) 10^4 , (D) 10^3 . At low dopant concentrations the nanowire quality is not greatly affected, but at a Si:P mole ratio of 10^3 , the nanowire quality is greatly degraded, likely a result of interference with silane formation due to the increased presence of phenyl groups from DPP.

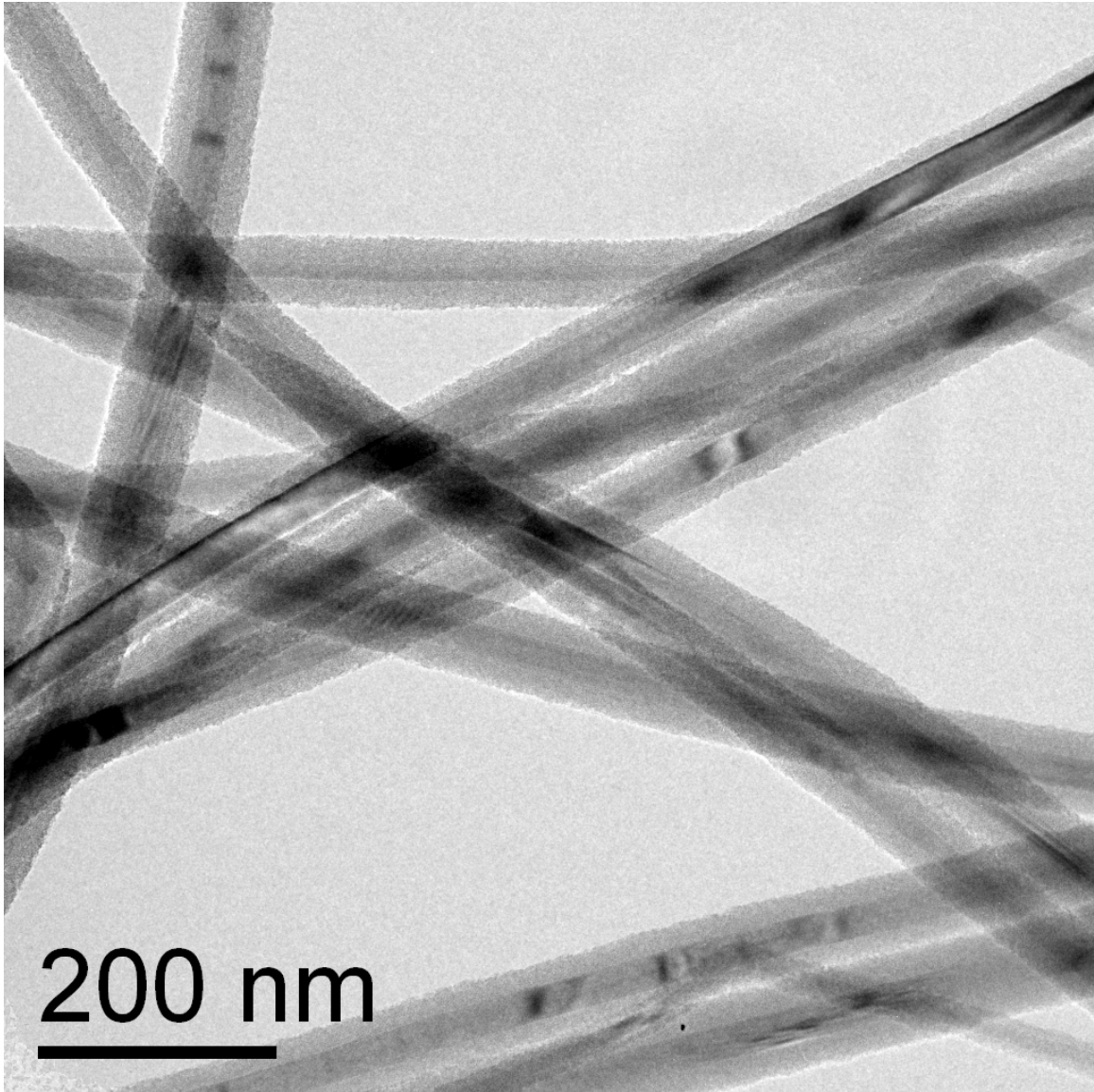


Figure 2.6: Bright-field TEM micrograph of a DPP doped SiNW synthesized from MPS, Si:P mole ratio of 10^5 . A thin shell is observed around each nanowire, which is composed of polyphenylsilane arising from the precursor. Bending fringes are observed as dark spots on the nanowires and are a result of diffraction contrast. The nanowire quality is good and identical to that of undoped MPS nanowires

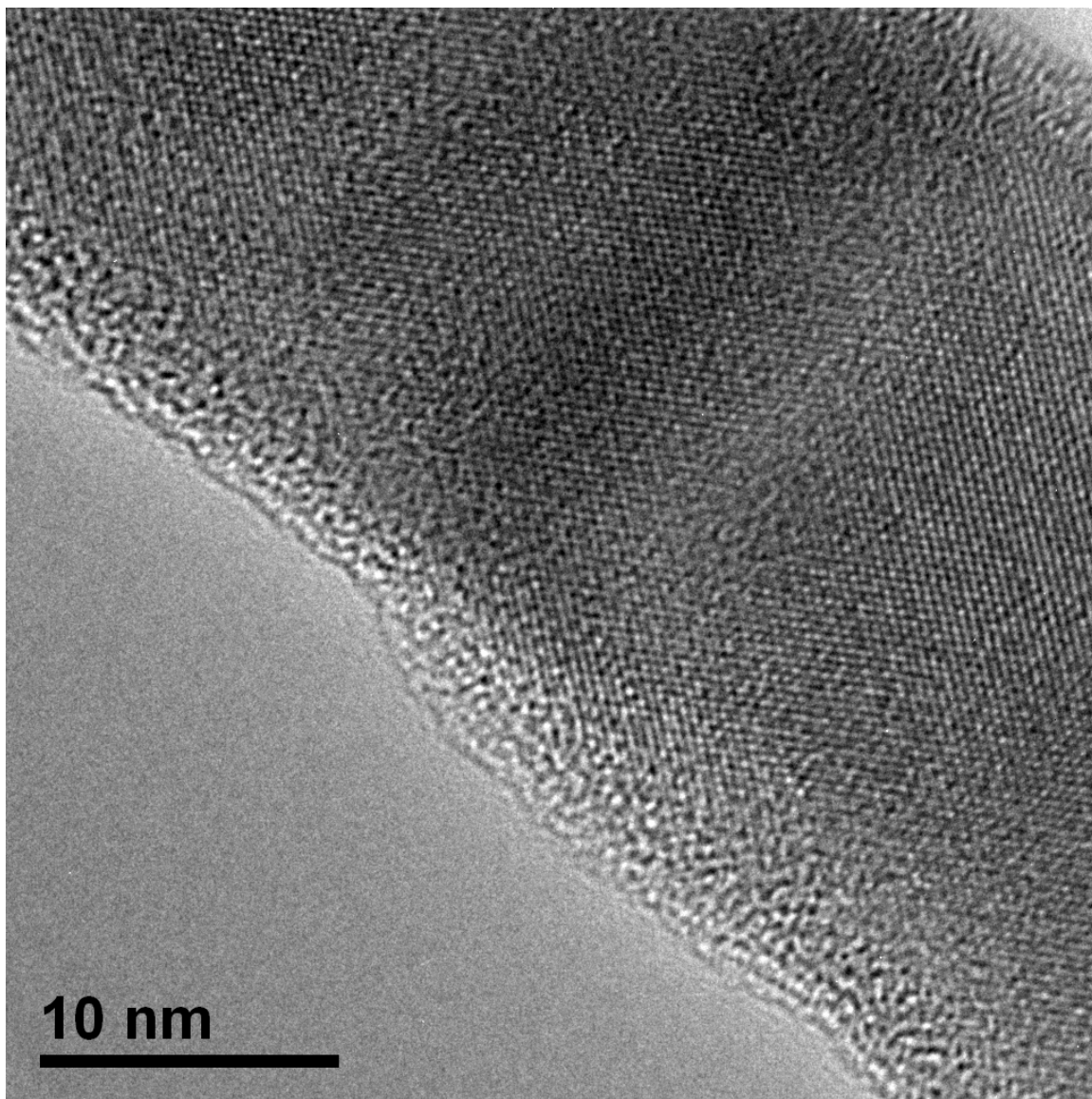


Figure 2.7: High-resolution, bright-field TEM micrograph of a DPP doped SiNW synthesized from MPS, Si:P mole ratio of 10^5 . The crystalline core of the nanowire is observable, as is the amorphous shell. The FFT of this image is shown in Appendix A in Figure A.1 on page A.1.

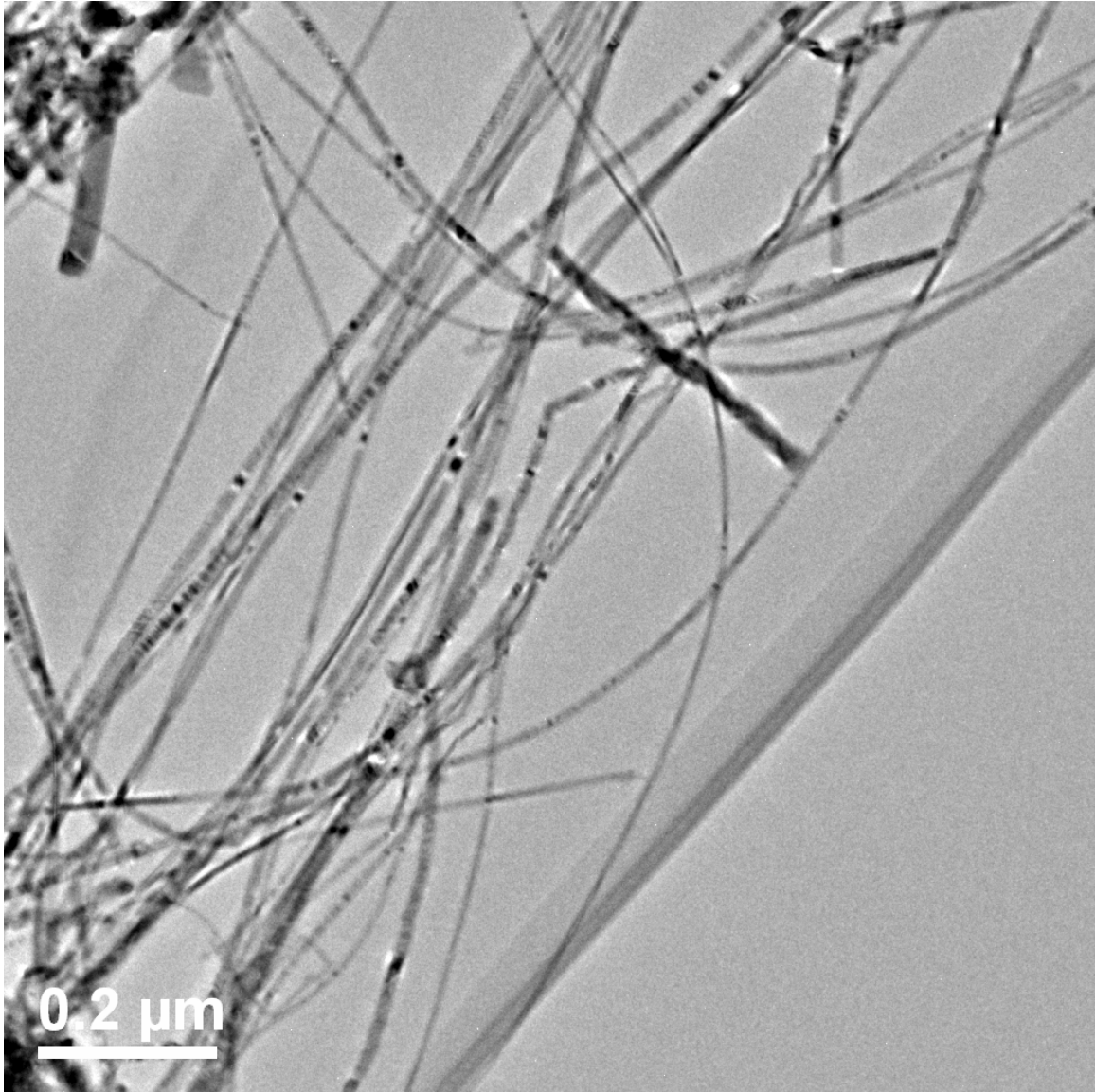


Figure 2.8: Bright-field TEM micrograph of a $\text{P}(\text{SiMe}_3)_3$ -doped SiNW synthesized from TS, Si:P mole ratio of 10^5 . Bending fringes are observed as dark spots on the nanowires and are a result of diffraction contrast. The nanowire quality is good and identical to that of undoped TS nanowires

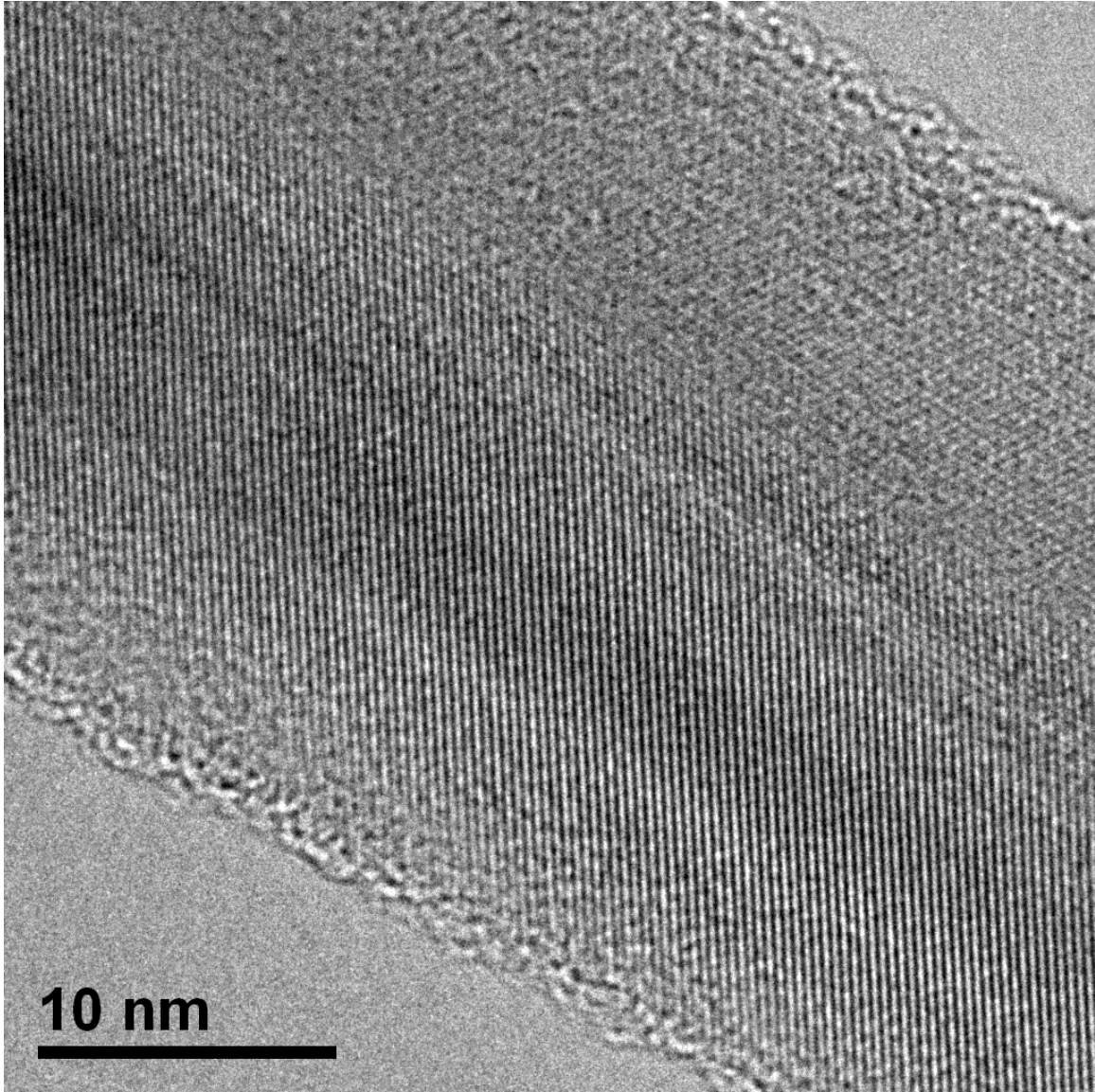


Figure 2.9: High-resolution, bright-field TEM micrograph of a $\text{P}(\text{SiMe}_3)_3$ -doped SiNW synthesized from TS, Si:P mole ratio of 10^5 . The crystalline core of the nanowire is observable, as a thin oxide. The FFT of this image is shown in Appendix A in Figure A.2 on page A.2.

Table 2.1: ICP-AES Results for *in-situ*-doped SiNWs

P dose in SFLS reactor (Si:P ratio)	P concentration detected via ICP-AES (mg/L)
10^3	1.31
10^4	0.18
10^5	0.05*
Undoped SiNWs	0.00
5 ppm P Standard	5.20

* Value below detection threshold

2.4.3 ICP-AES

Table 2.1 shows the results of ICP-AES chemical analysis. The optimum sample concentrations for signal detection had a concentration of Si of 1000 mg L^{-1} (i.e., 1000 ppm). The concentrations of P detected from the *in-situ*-doped NWs track with dose of P added to the SFLS reactant mixture. For example, for the NWs dosed at a Si:P of 10^3 the detected concentration of P is 1.31 mg L^{-1} (Table 2.1); when compared with the concentration of Si for that sample, the resulting Si:P ratio is 1000:1 or 10^3 . This result indicates that the concentration of P dopants in *in-situ*-doped SiNWs can be controlled deterministically and in a linear fashion by addition of the appropriate amount of P precursor to the SFLS reactant mixture.

2.5 Conclusions

It has been clearly demonstrated that the SFLS growth method can be utilized for the *in-situ* doping of silicon nanowires.

SEM characterization has shown that the nanowire quality can be maintained over a doping range of 10^5 to 10^4 Si:P mole ratio. At higher concentrations though,

the disproportionation reaction that is the backbone of the SFLS growth method, is disrupted to such a great degree that nanowire quality as observed in SEM is appreciably reduced — tortuous wires and amorphous particles are predominant at the highest doping concentration of 10^3 Si:P mole ratio.

EPR characterization has proven quite convincingly that P can be incorporated in SFLS grown silicon nanowires *in-situ*. The observation of an electron spin resonance peak at $g = 1.998$ is positive evidence of P donor states in Si. This result is broadly reproducible and can be obtained from MPS nanowires using DPP and $\text{P}(\text{SiMe}_3)_3$ as the P sources as well as in TS nanowires using $\text{P}(\text{SiMe}_3)_3$ as the P source. Differences emerge in the EPR spectrum that are related to the intensities of the two resonance peaks, and these differences may be attributed by conjecture to differences in precursor decomposition rates and thus rates of incorporation, as well as different effects on Si surfaces as a result of the different chemistries of the silicon precursors used.

Lastly, ICP-AES chemical analysis has shown that P is present at level commensurate with the *in-situ* doping levels.

2.6 Acknowledgements

The contribution to this work from Dr. Naoki Fukata is greatly appreciated and acknowledged. His collaboration was essential in developing a deeper understanding and appreciation for the study of paramagnetic defects in silicon nanowires via EPR. His expert attention and willingness to share his knowledge are a testament to his strength as a scientist. The provision of CVD grown nanowires was also greatly

appreciated, as a means to corroborate the results of *in-situ* doping.

In addition, much insight into SFLS growth was obtained through thoughtful discussions with Drs. Vince Holmberg, Aaron Chockla, Timothy Bogart, and Xiaotang Lu. In particular, Dr. Chockla was instrumental in applying the technique of *in-situ* doping to the TS nanowire system, and his efforts are greatly appreciated. Fruitful discussions with Dr. Colin Hessel are also acknowledged.

Dr. Chia-chen Chen is acknowledged for performing ICP-AES and for his insights into sample preparation and dilution techniques.

Lastly, the assistance of Dr. Minh Nguyen of the Holliday group in the Department of Chemistry, is greatly acknowledged and appreciated. His aid was instrumental in configuring the EPR spectrometer for use with liquid helium. He was steadfast in his dedication to learn alongside the author and gain experience in operating cryo-EPR, which had not been done in recent memory at the UT EPR facility.

Chapter 3

Nanowire Field-effect Transistors

“Ci sono soltanto due possibili conclusioni: se il risultato conferma le ipotesi, allora hai appena fatto una misura; se il risultato è contrario alle ipotesi, allora hai fatto una scoperta.”

— Enrico Fermi

3.1 Introduction

Of all the technologies to have emerged from the 20th century, the transistor, and in particular, the metal-oxide semiconductor field-effect transistor (MOSFET) is perhaps the most revolutionary. The ability to be miniaturized at an ever-increasing device densities in an integrated circuit has lead to the ubiquity and penetration of this technology on a vast scale into nearly every facet of modern life¹. This development has been so intense that handheld devices now exceed the specifications, in terms of processor speed, graphics, and memory, that desktop computers boasted a mere 5 or 10 years ago.

¹The transistor was first conceived in a U.S. patent filed in 1925 by Canadian physicist J.E. Lilienfeld. The first demonstration of current amplification was a device built by John Bardeen, Walter Brittain, and William Shockley at Bell Labs in Murray Hill, New Jersey in 1947, for which the three received the 1956 Nobel Prize in Physics. This first device was made of germanium. Later in 1958, Jack Kilby and Robert Noyce working independently would invent the integrated circuit. Several authors have chronicled this fascinating history, and the reader is directed to the references listed in the bibliography [71–76].

The industrial scale manufacturing of semiconductor devices, however, has relied on top-down processes that are beginning to approach fundamental physical limits. Semiconductor nanowires, therefore, have been seen as a potential alternative to, monolithic crystalline silicon, polysilicon, or even thin-film amorphous silicon, as the primary semiconductor base material for fabrication of devices for a number of applications, not least of which is the field-effect transistor. With the development of nanowire growth methods that control the nanowire diameter, surface properties, and even axial distribution of dopant impurities, it is ever-more likely that nanowire-based transistors will become the basis for novel bottom-up semiconductor devices.[1–7, 77–103].

Solution-grown silicon nanowires are also ideal for device fabrication and processing that is itself solution based, such as printable displays and sensors or even devices embedded fabrics and textiles. The scalability of SFLS-grown nanowires may one day couple well with solution-processable techniques with an eye toward industrial manufacture of solution-processed devices [104–107].

3.1.1 Field-effect transistors

Briefly, the functioning of the field-effect transistor hinges on the concept of gate modulation. Because the conductivity of the channel is operationally dependent on an applied gate voltage (among other factors), by varying the gate-to-source voltage the channel can be made highly conductive and allow the passage of a large current from the source to the drain — or become highly resistive and impede the passage of any current. In this way, voltage applied to the gate causes the transistor

to switch between ON (high current) and OFF (low current) states. This behavior is termed the field effect. In addition, within a certain range, a small change in gate voltage results in a large change in the current from source to drain, and the transistor can function as a current amplifier. For this reason, the transistor is such a versatile device in that it can function as a switch or diode in order to perform logic operations or as an amplifier of signals. The curious reader is directed to the text by Streetman and Banerjee for further information of the properties and operation of a wide range of solid-state electronics [108].

In the case of nanowire FETs, the use of Au contacts should result in a Schottky barrier at the interface between the silicon nanowires and the Au contacts. This feature would disfavor n-type characteristics in general, though as will be shown, the device behaviors are rather complex and are likely a result of surface effects in many cases.

3.2 Experimental Details

Silicon nanowires that were doped *in-situ* using MPS and TS as the silicon precursors were incorporated into thin-film devices in order to determine their ability to achieve gate modulation, i.e., to function as rudimentary field-effect transistors².

²The procedures described below are also found in Ch. 2, §2.3 beginning on page 18 and are reproduced here *in nuce* for the convenience of the reader.

3.2.1 Materials

All reagents used in the procedures described here were utilized as received without further purification. Anhydrous toluene (99.8%), chloroform (99.8%), diphenyl phosphine (98%), ethanol (99.9%), dodecanethiol ($\geq 98\%$), tetrachloroaurate trihydrate ($\geq 99\%$), sodium borohydride ($\geq 98\%$), and tetraoctylammonium bromide (98%) were purchased from Sigma-Aldrich. Monophenylsilane ($> 95\%$) was purchased from Gelest (Morrisville, PA). Trisilane (99.99%) was purchased from Voltaix (Branchburg, NJ). Hydrochloric acid (25% v/v) and nitric acid (70%, 15.8 N, Certified ACS Plus) were purchased from Fisher Chemical, and hydrofluoric acid (48 - 51% v/v) was purchased from EMD Chemical.

3.2.1.1 NWs synthesized from MPS

In a typical synthesis reaction, a 28-mL reactant solution was prepared containing anhydrous toluene (ACS grade, Sigma-Aldrich, 99.8%), 40 mg L⁻¹ of dodecanethiol-capped Au nanocrystals (averaging 2 nm in diameter, prepared according to the method enunciated by Brust et al. [67]), and 135 mM MPS (Gelest, $> 95\%$), inside a nitrogen- or argon-filled glovebox. This solution was placed into a stainless steel injection cylinder that was sealed inside the glovebox before being brought into the ambient.

For *in-situ* P doping, DPP (Aldrich, 98%) was added as a P precursor at Si:P mole ratios ranging from 10^5 to 10^3 , which would correspond to doping concentrations of $n = 10^{17}$ to 10^{19} . For example, to obtain a Si:P mole ratio of 10^5 , 1.35 μ M DPP was added to the reactant solution. To obtain a highly dilute solution of DPP, a

one-step serial dilution was performed by using a micropipetter to add approximately 7 μL of DPP to a glass vial containing 5 mL of anhydrous toluene (inside a nitrogen-filled glovebox). This solution was mixed by manual agitation, and a 5- μL aliquot was added to the reactant solution using a micropipetter.

A 10-mL tubular titanium reactor was heated to 490°C in a heating block. The injection cylinder containing the reactant solution was then connected to the reactor system. The headspace of the injection cylinder was eliminated first by flowing a small amount of the reactant solution thru the secondary outlet of a six-way valve. Once a good seal between all connections was established and each line was cleared of potential air bubbles, the reactor was filled with anhydrous toluene at a volumetric flow rate of approximately 1 mL min⁻¹ to a pressure of 1,100 psi (8.27 MPa). Then, the reactor inlet line was closed. The six-way valve was switched to feed the injection cylinder, which was pressurized 1,200 psi (7.58 MPa), and the outlet valve of the injection cylinder was opened. Then, the six-way valve was then switched to connect the injection cylinder outlet line to the reactor inlet line. The toluene feed from the HPLC pump was momentarily paused with all valves open except for the reactor inlet, to ensure proper seals throughout the system. Then, the toluene feed was restarted. At this point, the volumetric flow rate of the HPLC pump was reduced to 0.5 mL min⁻¹, the reactor inlet valve was opened, and the pressure was allowed to increase to 1,400 psi (9.65 MPa) with the reactor outlet closed. Once a pressure of 1,450 psi (10 MPa) was reached, the reactor outlet valve was opened. A chronometer was set for a reaction time of 40 minutes, and the pressure throughout the system was maintained at 1,500 $\pm$ 50 psi (10.34 $\pm$ 0.34 MPa) by means of a manual millimeter valve. A

glass vial was connected to the exit line by means of a septum stopper in order to collect the effluent from the reactor. At the conclusion of 40 minutes, the synthesis reaction was terminated, the reactor was sealed, the HPLC pump was shut off, the variac power was also terminated, and the upper portion of the heating block was removed to expose the reactor, and the reactor was allowed to cool isochorically in the ambient of the fume hood. Once cool to the touch, the reactor was unsealed under a chemical fume hood. The nanowires were extracted manually using a glass pipette and dispersed in toluene. Then, the collected nanowires were ablated three times via centrifugation (Eppendorf, model 5804R) at 5,000 rpm in a mixture of toluene, chloroform, and hexane (2:1:1) to remove unreacted precursors. A similar procedure was carried out using tris(trimethylsilyl)phosphine ($\text{P}(\text{SiMe}_3)_3$, Sigma-Aldrich, 95%) instead of DPP as the P dopant for *in-situ* doping at the same Si:P ratios. SiNWs synthesized using Si_3H_8 as the Si precursor [29] can also be P doped using either DPP or $\text{P}(\text{SiMe}_3)_3$ at similar Si:P ratios, as described in the following section.

3.2.1.2 NWs synthesized from trisilane

Silicon nanowires were synthesized from Si_3H_8 precursor using $\text{P}(\text{SiMe}_3)_3$ as the phosphorus precursor. The procedures are as follows for a Si:P mole ratio of 10^5 .

A reactant solution was prepared inside the inert atmosphere of a nitrogen- or argon-filled a glovebox. The solution contained 27 μL of 0.4 mM $\text{P}(\text{SiMe}_3)_3$, 270 μL of toluene, 550 μL of Au nanocrystals³, and 250 μL of Si_3H_8 . The Si:Au mole ratio

³i.e., equal to 27.5 mg of Au nanocrystals, solution in toluene at a concentration of 50 mg mL^{-1} of Au nanocrystals

was 20:1.

The synthesis reaction is a semi-batch process, and the conditions were as follows. A 10-mL tubular titanium reactor was pressurized to 1,000 psi (6.89 MPa) by means of an HPLC pump, with the effluent (exit) line closed and pre-heated to a temperature of 450°C. The reactant solution was injected into the reactor by means of an HPLC pump at a volumetric flow rate of 3 mL min⁻¹. The injection time⁴ was 1 min. The reactor was allowed to pressurize during injection by maintaining the effluent line closed. After one minute, the injection was terminated, and the final pressure of the reactor was 2,100 psi (14.47 MPa). At the conclusion of the synthesis reaction, the reactor was allowed to cool isochorically in the ambient of the glovebox and, once cool to the touch, was removed from the glovebox and unsealed under a chemical fume hood. The nanowires were extracted manually using a glass pipette and dispersed in toluene. Then, the collected nanowires were ablated three times via centrifugation (Eppendorf, model 5804R) at 5,000 rpm in a mixture of toluene, chloroform, and hexane (2:1:1) to remove unreacted precursors.

The above procedure produces nanowires with a desired Si:P mole ratio of 10⁵. As in the case of MPS silicon nanowires doped *in-situ* with DPP, the doping level can be adjusted simply by varying the quantity of phosphorus precursor that is added to the reaction mixture in order to reach the desired mole ratio of silicon to phosphorus.

⁴Because of the higher reactivity and faster decomposition kinetics of Si₃H₈, much shorter reaction times are needed. This short injection/reaction time is in contrast to the 40-min. reaction time for MPS.

3.2.2 Nanowire Field-Effect Transistors

Back-gated NWFETs were fabricated using Si wafers, with approximately 200 nm of thermally grown SiO_2 dielectric, printed with interdigitated arrays (IDAs) of Au contacts, with spacings of 2.5, 5, 10, and 20 μm between the digits. Undoped and *in-situ*-doped SiNWs were dispersed at a concentration of 1 mg of nanowires per 1 mL of solvent in either anisole or chloroform via sonication at room temperature for periods of up to 3 hours or until a homogeneous dispersion was obtained (typically an hour). Then, a clean, printed wafer was affixed to the motorized arm of an automated dipping apparatus. This apparatus was built in house and was used to dip the wafer in the NW solution 10 times along the vertical axis at a speed of 10 mm/min, via computer control in an automated fashion, in order to deposit the NWs onto the wafer via capillary action. Dipping in this way aligns the NWs parallel to the dipping direction. Devices whose digits were oriented perpendicular to the NW alignment direction (*vide infra* Fig. 3.2) were then tested in a Karl Süss probe station using a Keithley Instruments Semiconductor Characterization System, model 4200⁵. A three-probe arrangement was used with one probe connected to the gate and the other two probes to the contact pads of the interdigitated array. For determination of the transfer characteristics, the gate voltage (V_{gate}) was swept at a constant rate of 10 V s⁻¹ between 20 V and -30 V at source-drain bias voltages (V_{sd}) of 1 V and 2 V. Three scans per measurement were performed.

⁵Measurements were carried out in an isolation chamber equipped with a stage to prevent vibration. The measurement chamber was located in the clean room in of the Faulkner Nanoscience and Technology building of the University of Texas.

3.2.3 Chemical Etching of Si Nanowires for FETs

In some cases, as an attempt to improve device performance, a chemical etch was performed on Si nanowires prior to FET confection. The etching procedure is carried out in two steps. First, an etch with hydrofluoric acid ($\text{HF}_{(\text{aq})}$) was performed to remove a thin shell of Si that is present around the Au seed in trisilane nanowires. For MPS nanowires, this HF etch has been shown to partially remove the polyphenylsilane shell that coats nanowires synthesized with this precursor. Then, an etch is carried out using *aquaregia* to remove the Au seed from the nanowire tips. Initially, a second HF etch was performed, identical to the one described below, in order to remove a substoichiometric SiO_x oxide that may form as a result of the strong oxidizing conditions of the *aqua regia* etch, but this second HF etch was not shown to substantially improve the device performance and was deemed unnecessary and time-consuming, such that in most cases, it was not warranted. The procedure described below is the two-step etch that was performed in all cases, save those cases in which another etching procedure was explicitly carried out.

Hydrofluoric acid etch The HF etching procedure is as follows. Working in a chemical fume hood designed for the use of HF ⁶, 20 mg of Si nanowires are dissolved in a sufficient amount of chloroform (CHCl_3) to adequately wet the nanowires. Next, this mixture is placed into a plastic beaker containing 10 mL of an HF etching solution

⁶Personnel must be equipped with full personal protective equipment as HF is an extremely corrosive liquid, is known to have extremely adverse health effects upon contact with the skin, is slow acting, and can disrupt nerve function, leaving exposed individuals unaware of their contact up to 24 hours after exposure when burns symptoms begin to present.

composed of HF (48%, EMD Chemicals), deionized water (DI H₂O) and ethanol (EtOH, 99.9%) in a volume/volume (v/v) ratio of 1:1:1. An additional 10 mL of CHCl₃ was added, and the mixture was stirred vigorously to form an emulsion, with the aid of a magnetic stirring on a hotplate at room temperature. The emulsion was allowed to stir vigorously for 20 minutes.

After this time had elapsed, the stirring was ceased, and the mixture was allowed to rest until the emulsion had phase-separated. The upper phase is the aqueous phase, and the nanowires have the tendency to at the liquid-liquid interface of the aqueous and organic phases. Thus, a plastic pipette was used to carefully remove the aqueous phase, leaving the nanowires dispersed in the organic phase.

This dispersion was then placed into a plastic centrifuge tube with 10 mL of DI H₂O in order to remove any remaining aqueous etching solution. The centrifuge tube was then tightly sealed, and the mixture was agitated manually with great vigor. Then, the mixture was then allowed to phase separate, the aqueous portion was carefully extracted with the use of a plastic pipette, an additional 10 mL of DI H₂O was added, the centrifuge tube was sealed, and the mixture was vigorously agitated. The mixture was then allowed to phase separate, the aqueous portion was extracted, and approximately 10 mL of EtOH was added to the solution. This solution was then subjected to centrifugation at 5,600 rpm for 5 minutes. The solution was ablated two more times by centrifugation under the same conditions. The supernatant was then decanted off the nanowires and discarded, with great care taken to remove as much liquid without extracting any nanowires. Finally, the nanowires were dispersed once again in approximately 20 mL of CHCl₃.

***Aqua regia* etch** To carry out the *aqua regia* etch, 12 to 13 mL of *aqua regia* was prepared containing hydrochloric acid (HCl, 12.1 N, Fisher) and nitric acid (HNO₃, 15.8 N, Fisher) in a ratio of 1:3 HNO₃:HCl v/v. This solution was added to the nanowires dispersed in 20 mL of CHCl₃ in a glass beaker. An emulsion was achieved by vigorous magnetic stirring on a hotplate at room temperature. The emulsion was allowed to stir vigorously for two hours. After this time has elapsed, the nanowires were extracted using the same procedure of phase separation described above. The nanowires were ablute twice in DI H₂O and twice in EtOH via centrifugation, as described above. Lastly, the nanowires were collected and dispersed in EtOH.

Finally, the nanowires were dried in a rotary evaporator and weighed in order to determine their mass accurately for the purposes of FET confection.

3.3 Results and Discussion

3.3.1 Undoped nanowires

Figure 3.1 shows the control sample of undoped MPS nanowires. These devices are typical of undoped MPS nanowires. They display appreciably large ON/OFF ratios and a large degree of hysteresis. Relevant values related to the device performance can be found in Table C.1 in Appendix A on page 147.

The large hysteresis exhibited by these devices is factor that can affect the device performance and in particular the mobility. It has been shown [101, 104] that the presence of hydroxyl groups (OH•) on the surface of a SiO₂ gate dielectric can interact with the surfaces of the Si nanowires to generate trap states that can scatter

charge carriers and impede their conduction. This phenomenon of surface trap states is observed as hysteresis during the sweep of the gate voltage. Hysteresis refers to a shift in the threshold voltage when the gate voltage is swept from a positive gate-to-source voltage to a negative gate-to-source voltage, compared to the value of the threshold voltage when sweeping the gate voltage from a negative gate-to-source voltage to a positive gate-to-source voltage. This behavior is considered undesirable in real-world conditions of device operation, although hysteresis can be controlled to some extent by minimizing the magnitude of the gate voltage sweep and by other means that are beyond the scope of this discourse. in addition,

Nevertheless, the hysteretic character of the FET devices reported here should be considered a basis of comparison for the purposes of this study.

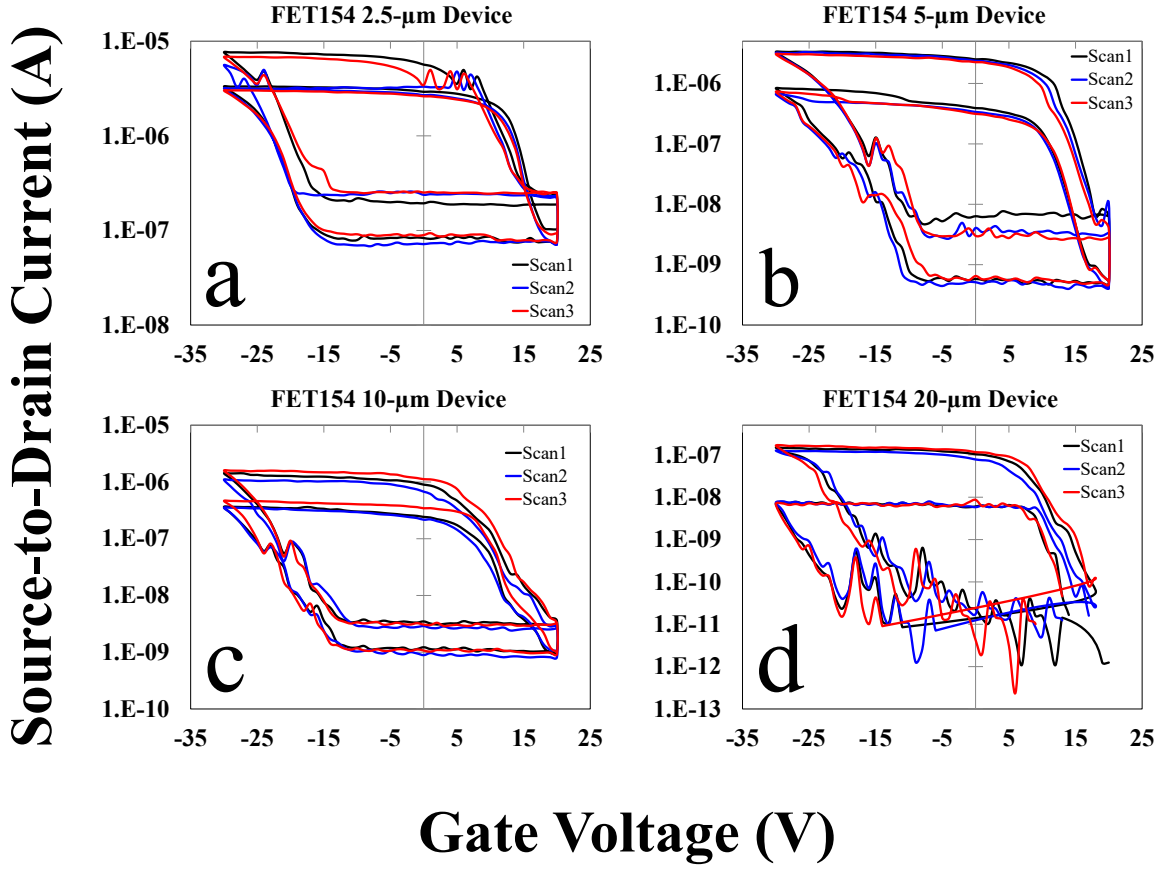


Figure 3.1: **FET 154** – Transfer Characteristics of **undoped Si nanowires** synthesized from MPS precursor – Each of the four devices tested consists of an interdigitated array of gold contacts with spacing between the digits of (a) $2.5\ \mu\text{m}$, (b) $5\ \mu\text{m}$, (c) $10\ \mu\text{m}$, and (d) $20\ \mu\text{m}$. Each plot is a composite of 3 scans of the gate voltage (V_{gate}) from 20 V to -30 V at two values of applied source-to-drain bias voltage (V_{sd}), i.e., 1 V and 2 V. In general, at $V_{sd} = 2\ \text{V}$, the source-to-drain ON current I_{ON} is higher than that of the curve at $V_{sd} = 1\ \text{V}$. The transfer curves are typical of undoped as-synthesized MPS Si nanowires. The curves display highly variable ON/OFF ratios that range from approximately 400 to approximately 1×10^5 , with typical values of c. 500. In addition, the devices are characterized by large hysteresis of typically 30 to 40 V. Values of the standard parameters measured for each of the devices are tabulated in Table C.1 found in Appendix A on page 147. Optical micrographs corresponding to these devices are found in Fig. 3.2 on page 54

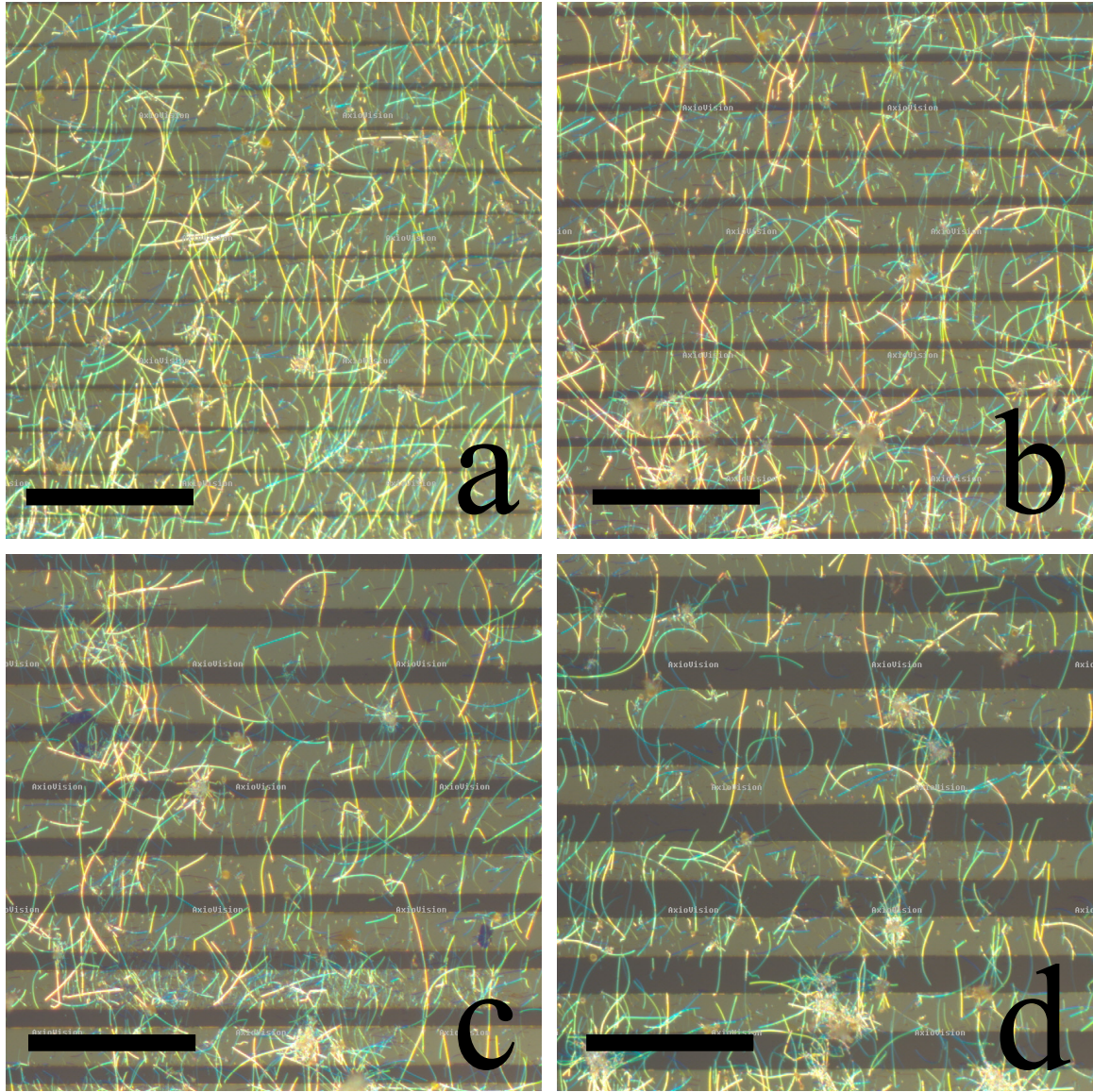


Figure 3.2: **FET 154** –Optical micrographs of **undoped Si nanowires** synthesized from MPS precursor – The images show the interdigitated arrays of gold contacts that comprise the FET devices. The light-colored filamentous objects seen in the micrographs are undoped SiNWs synthesized from MPS – (a) 2.5- μm device; (b) 5- μm device; (c) 10- μm device; (d) 20- μm device. The scale bars are equal to 100 μm . The nanowire coverage of this FET is quite dense. The FET was dipped ten times in chloroform in a solution of SiNWs at a nanowire concentration of 1 mg/mL. The corresponding transfer curves are found in Fig. 3.1 on page 53.

3.3.2 DPP-doped MPS Nanowires

3.3.2.1 Lightly-doped MPS Nanowires - $\text{Si:P} = 10^5$

The FET transfer curves shown in Figure 3.3 exhibit a high degree of signal noise and in general little can be gleaned from these data. Although relatively large currents, in some cases in the microamp range, are observed, there is a high degree of inhomogeneity in the signal. Gate modulation is observed despite the noise.

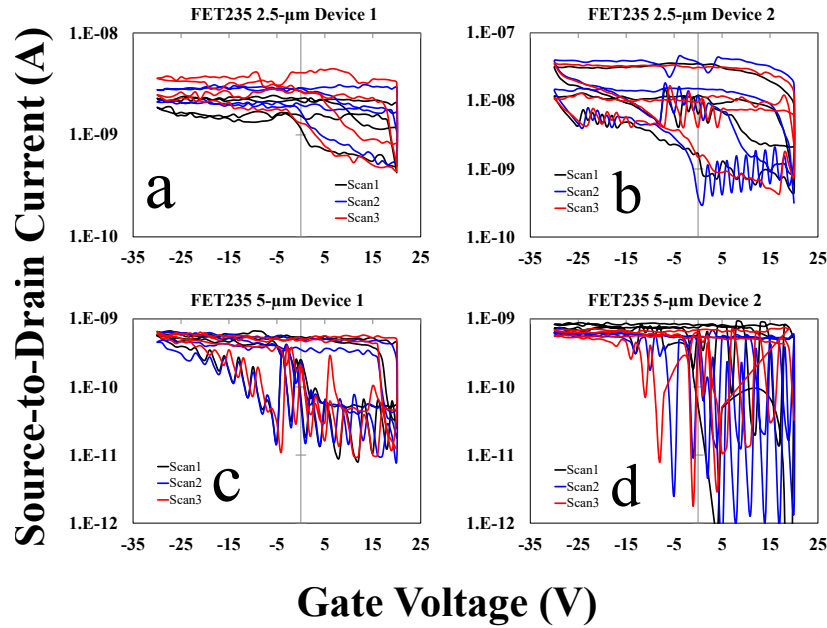


Figure 3.3: **FET 235** – Transfer Characteristics of *in-situ* DPP-doped SiNWs synthesized from MPS precursor at a Si:P ratio of 10^5 – 2.5-μm (a) device 1 and (b) device 2; 5-μm (c) device 1 and (d) device 2. — These devices exhibit a great degree of noise and signal inhomogeneities. The device in (a) appears to show a small degree of hysteresis and reasonably high current, but curve exhibits great variance, perhaps due to the poor quality of the nanowire batch. Optical micrographs for these devices were not available.

3.3.2.2 Moderately-doped MPS Nanowires - Si:P = 10^4

In contrast to the behavior observed in the previous devices, there is no gate modulation observed for these FETs, made from silicon nanowires that were doped at a Si:P mole ratio of 10^4 .

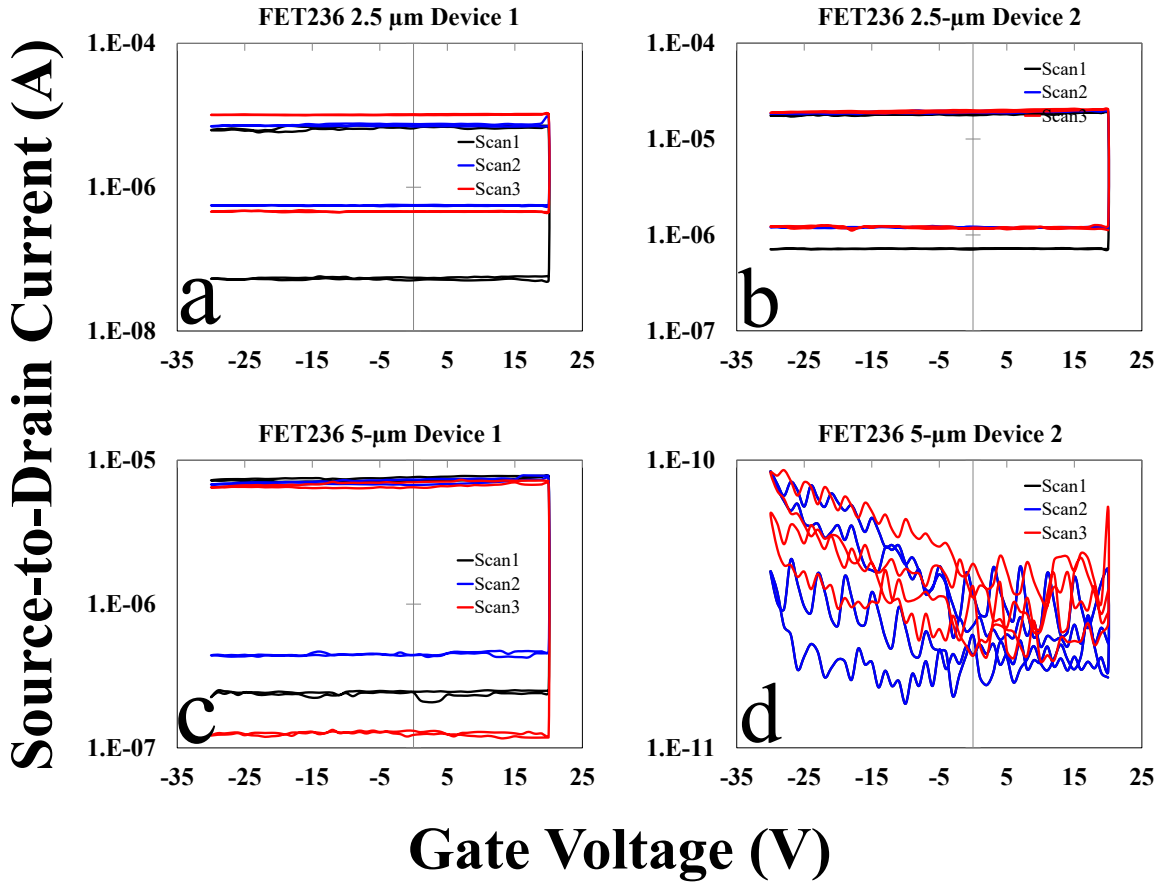


Figure 3.4: **FET 236** – Transfer Characteristics of *in-situ* DPP-doped SiNWs synthesized from MPS precursor at a Si:P ratio of 10^4 – 2.5- μm (a) device 1 and (b) device 2; 5- μm (c) device 1 and (d) device 2. — No gate modulation is observed for these devices, and the device in (d) presents too much noise to distinguish any features worthy of mention.

3.3.2.3 Heavily-doped MPS Nanowires - Si:P = 10^3

Lastly, devices made with the most heavily doped nanowires show similar behavior to those in the previous dataset, with no observable gate modulation and a great degree of noise in some cases.

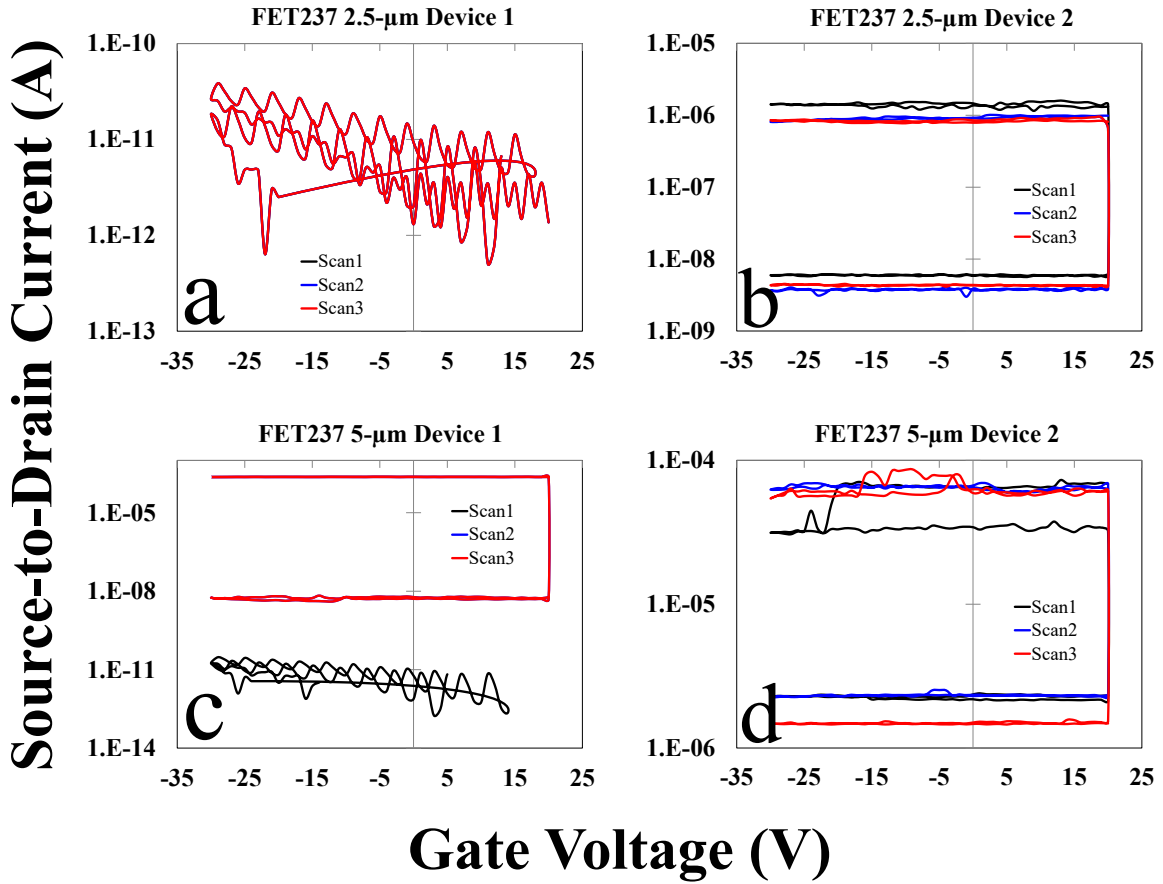


Figure 3.5: **FET 237** – Transfer Characteristics of *in-situ* DPP-doped SiNWs synthesized from MPS precursor at a Si:P ratio of 10^3 – 2.5-μm (a) device 1 and (b) device 2; 5-μm (c) device 1 and (d) device 2. – No gate modulation is observed.

3.3.3 The effect of chemical etching on FET characteristics of DPP-doped MPS nanowires

3.3.3.1 Lightly-doped, unetched, MPS Nanowires - Si:P = 10^5

The figure below shows the transfer curves for FETs made from lightly-doped MPS nanowires. Compared to the devices in Figure 3.3, these devices still exhibit a very poor performance, but in this case, hysteresis appears to be greater for one of the 2.5- μm devices, subfigure (a), while for the other device there is no modulation and no hysteresis. These results are an indication that device performances are highly variable, even when nanowires of comparable quality and composition are used. Factors such as nanowire coverage are difficult to control, and environmental factors might also play a role, given that the presence of water molecules adsorbed to the surface of the device wafer could play a role in charge carrier trapping at the interface between the silicon nanowire surfaces and the gate dielectric surface [101, 104].

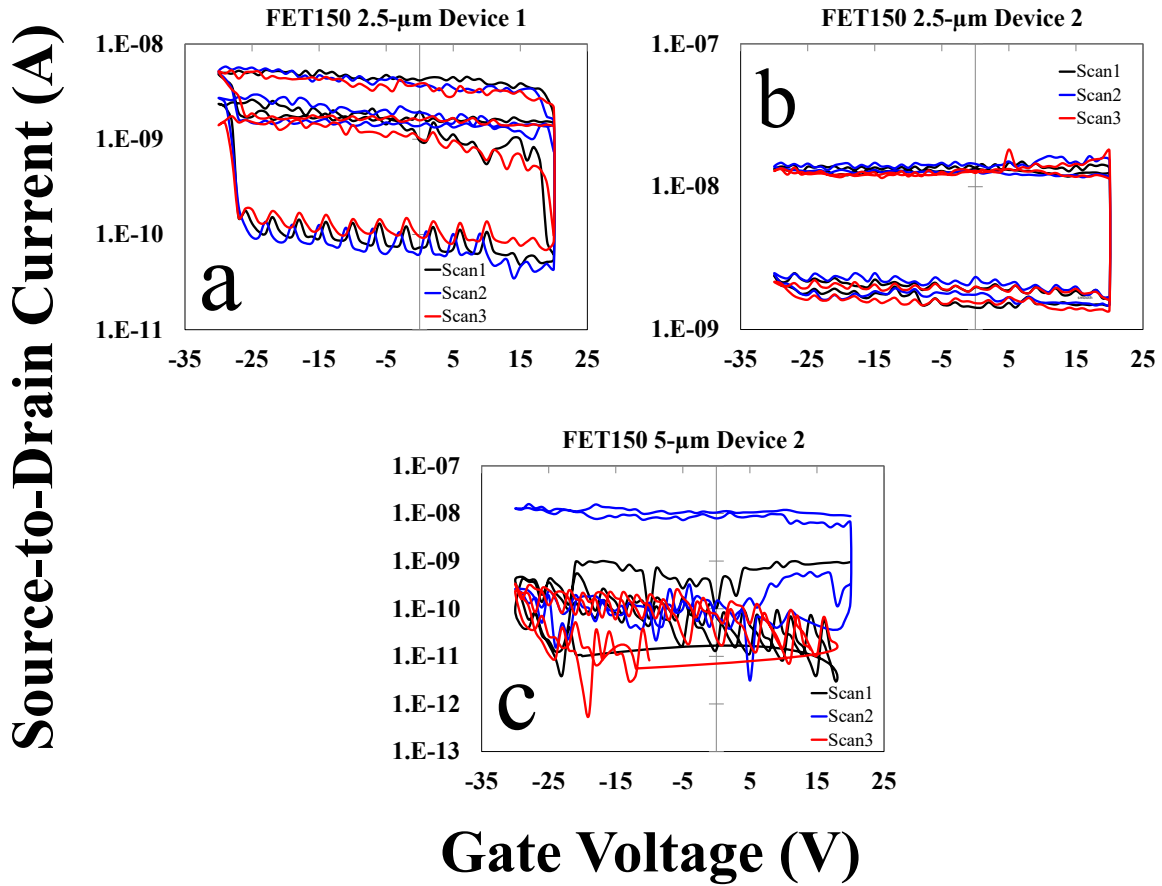


Figure 3.6: **FET 150** – Transfer Characteristics of *in-situ* DPP-doped SiNWs synthesized from MPS precursor at a Si:P ratio of 10^5 . The nanowires were not etched after synthesis. – 2.5- μm (a) device 1 and (b) device 2; (c) 5- μm device. These devices exhibit much different behavior from those in Figure ?? . Optical micrographs corresponding to these devices are found in Fig. 3.7 on page 60.

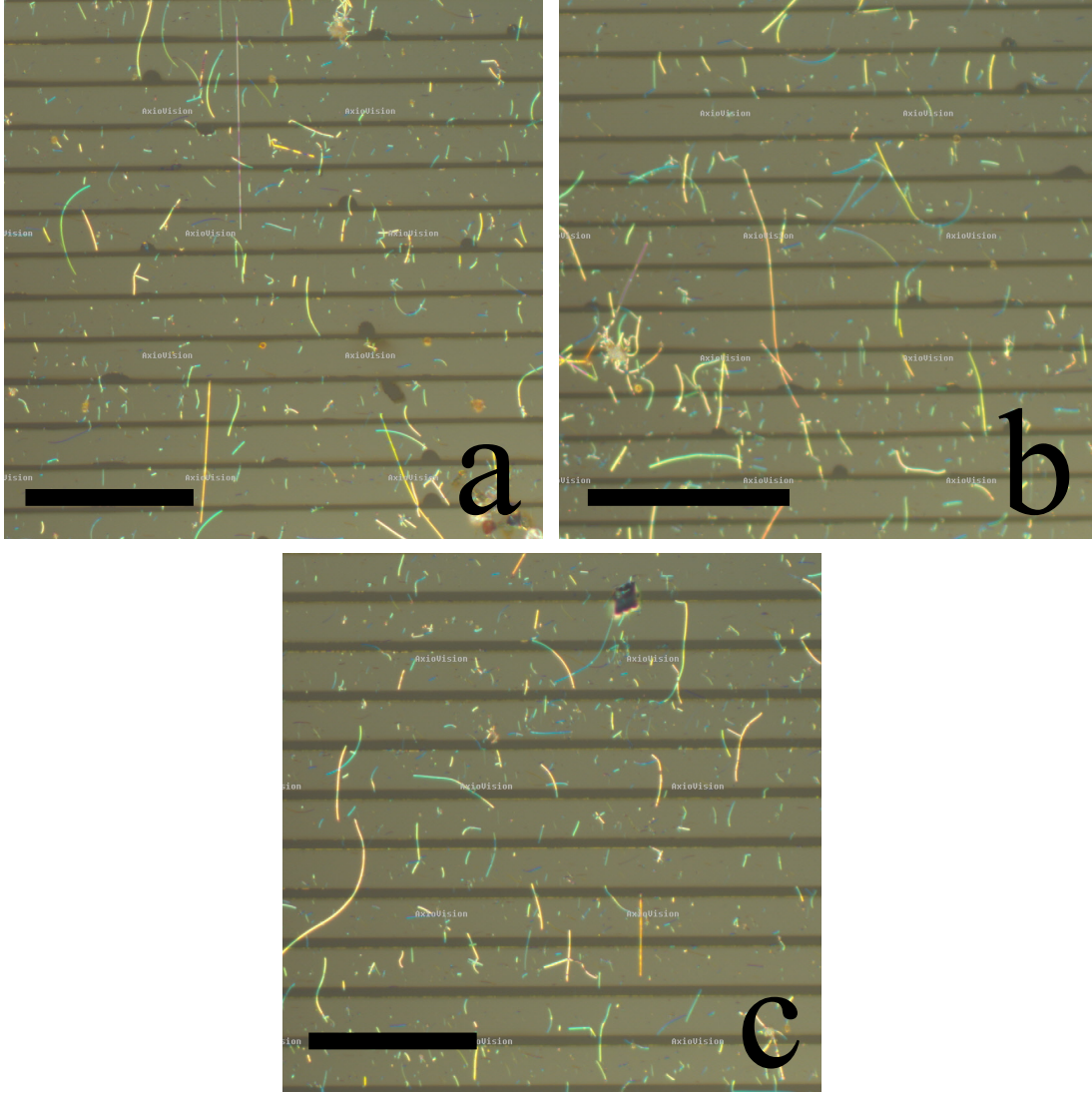


Figure 3.7: **FET 150** – Optical micrographs of *in-situ* DPP-doped SiNWs synthesized from MPS precursor at a Si:P ratio of 10^5 – The images show the interdigitated arrays of gold contacts that comprise the FET devices. The light-colored filamentous objects seen in the micrographs are doped SiNWs (Si:P = 10^5) – $2.5\text{-}\mu\text{m}$ (a) device 1 and (b) device 2; (c) $5\text{-}\mu\text{m}$ device. The scale bars are equal to $100\text{ }\mu\text{m}$. The nanowire coverage of this FET is somewhat sparse. For these devices, there are still a number of nanowires that bridge the gaps between the digits, but in general the device performance is poor with rather low values of I_{sd} . The corresponding transfer curves are found in Fig. 3.6 on page 59.

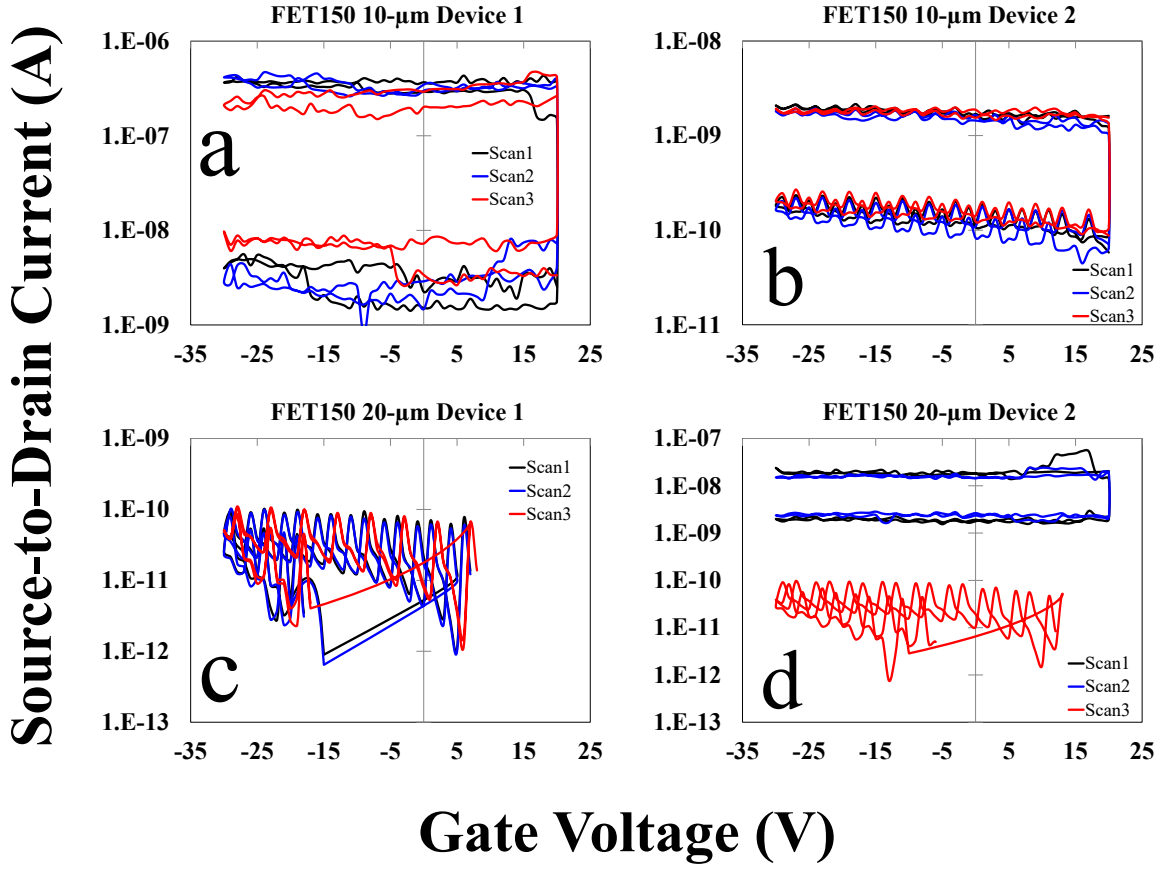


Figure 3.8: **FET 150** – Transfer Characteristics of *in-situ* DPP-doped SiNWs synthesized from MPS precursor at a Si:P ratio of 10^5 . The nanowires were not etched after synthesis. – 10- μm (a) device 1 and (b) device 2; 20- μm (c) device 1 and (d) device 2. Optical micrographs corresponding to these devices are found in Fig. 3.9 on page 62.

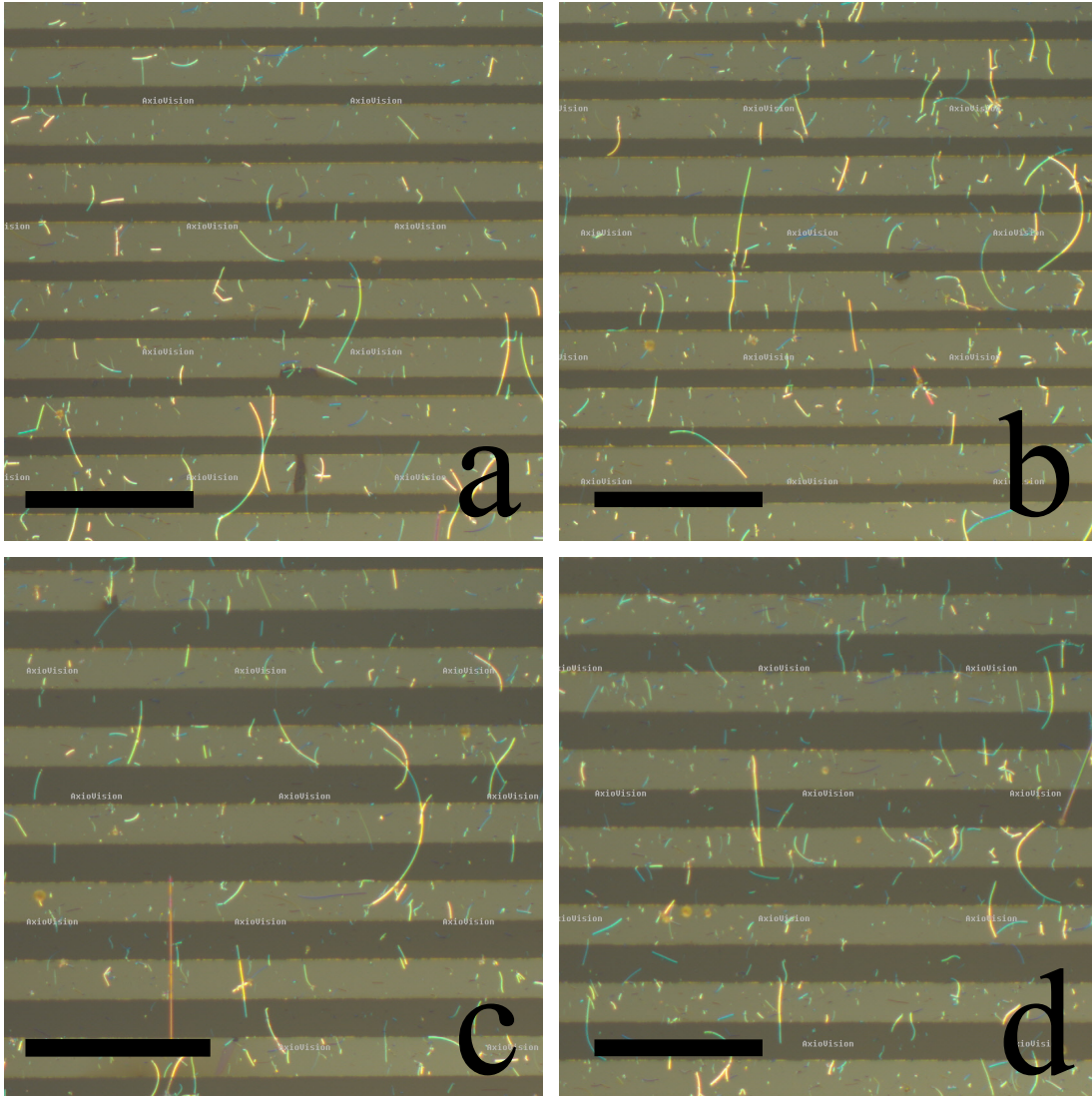


Figure 3.9: **FET 150** – Optical micrographs of *in-situ* DPP-doped SiNWs synthesized from MPS precursor at a Si:P ratio of 10^5 – The images show the interdigitated arrays of gold contacts that comprise the FET devices. The light-colored filamentous objects seen in the micrographs are doped SiNWs ($\text{Si:P} = 10^5$) – 10- μm (a) device 1 and (b) device 2; 20- μm (c) device 1 and (d) device 2. The scale bars are equal to 100 μm . The nanowire coverage of this FET is somewhat sparse. For these devices, few nanowires that bridge the gaps between the digits, and the device performance is poor as a result. The corresponding transfer curves are found in Fig. 3.8 on page 61.

3.3.3.2 Lightly-doped and etched MPS Nanowires - Si:P = 10^5

The devices in Figure 3.10 present interesting behavior, especially in the case of the 2.5- μm device. The transfer curves for this device are plotted separately in Figure 3.3.3.2 on page 68.

The Si nanowires used for this device were taken from the same batch as those used for FET 150 (Fig. 3.6, page 59). However, prior to confecting the FET device, the Si nanowires were subjected to treatment in aqua regia for a period of 3 minutes and were subsequently ablated in deionized water, desiccated using a rotary evaporator, and dispersed in chloroform at a concentration of 1 mg of Si nanowires to 1 mL of chloroform. When compared to FET 150, the behavior of the 2.5- μm device 1 appears to show a small degree of n-type gate modulation, especially at a bias of $V_{sd} = 2$ V. However, the 2.5- μm device 1 does not show this behavior, and in general the curves exhibit a large degree of hysteresis. The scans for this 2.5- μm device 1 are plotted separately in Fig. 3.3.3.2. Values of the standard parameters measured for each of the devices are tabulated in Table C.2 found in Appendix A on p. 148.

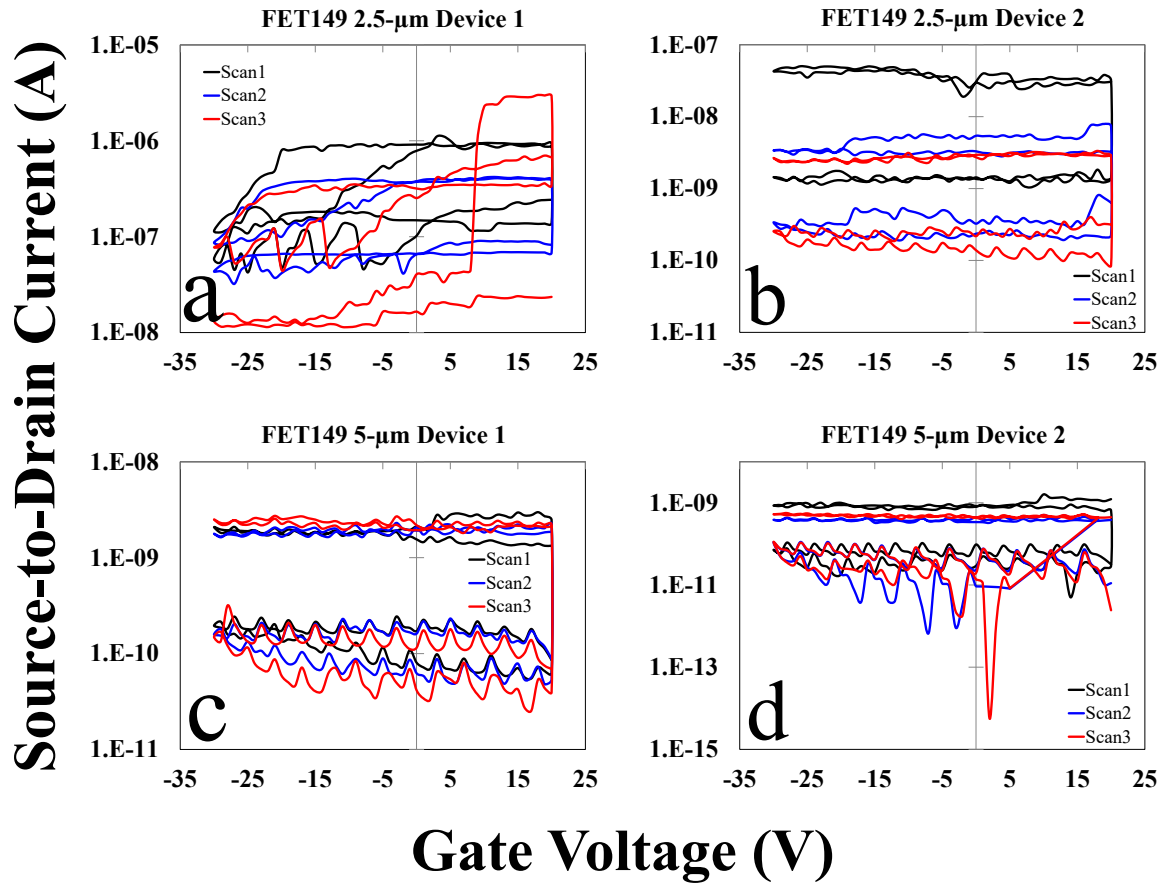


Figure 3.10: **FET 149** – Transfer Characteristics of *in-situ* DPP-doped SiNWs synthesized from MPS precursor at a Si:P ratio of 10^5 – 2.5-μm (a) device 1 and (b) device 2; 5-μm (c) device 1 and (d) device 2.

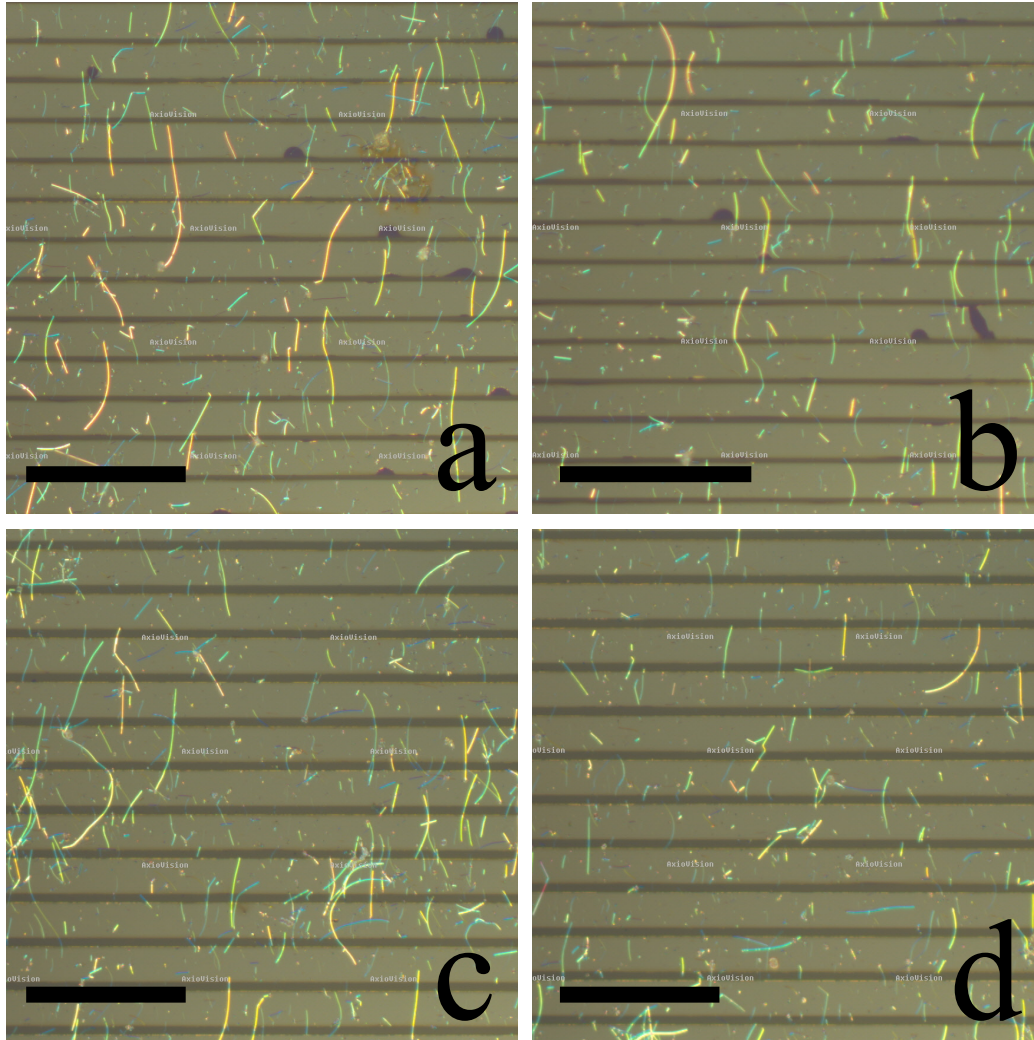


Figure 3.11: **FET 149** – Optical micrographs of *in-situ* DPP-doped SiNWs synthesized from MPS precursor at a Si:P ratio of 10^5 – The images show the interdigitated arrays of gold contacts that comprise the FET devices. The light-colored filamentous objects seen in the micrographs are doped SiNWs (Si:P = 10^5) that were subsequently etched in aqua regia prior to FET confection, according to the procedure described above. – 2.5- μm (a) device 1 and (b) device 2; 5- μm (c) device 1 and (d) device 2. The scale bars are equal to 100 μm . The nanowire coverage of this FET is somewhat sparse. For these devices, there are still a number of nanowires that bridge the gaps between the digits, but in general the device performance is poor with rather low values of I_{sd} . The corresponding transfer curves are found in Fig. 3.10 on p. 64

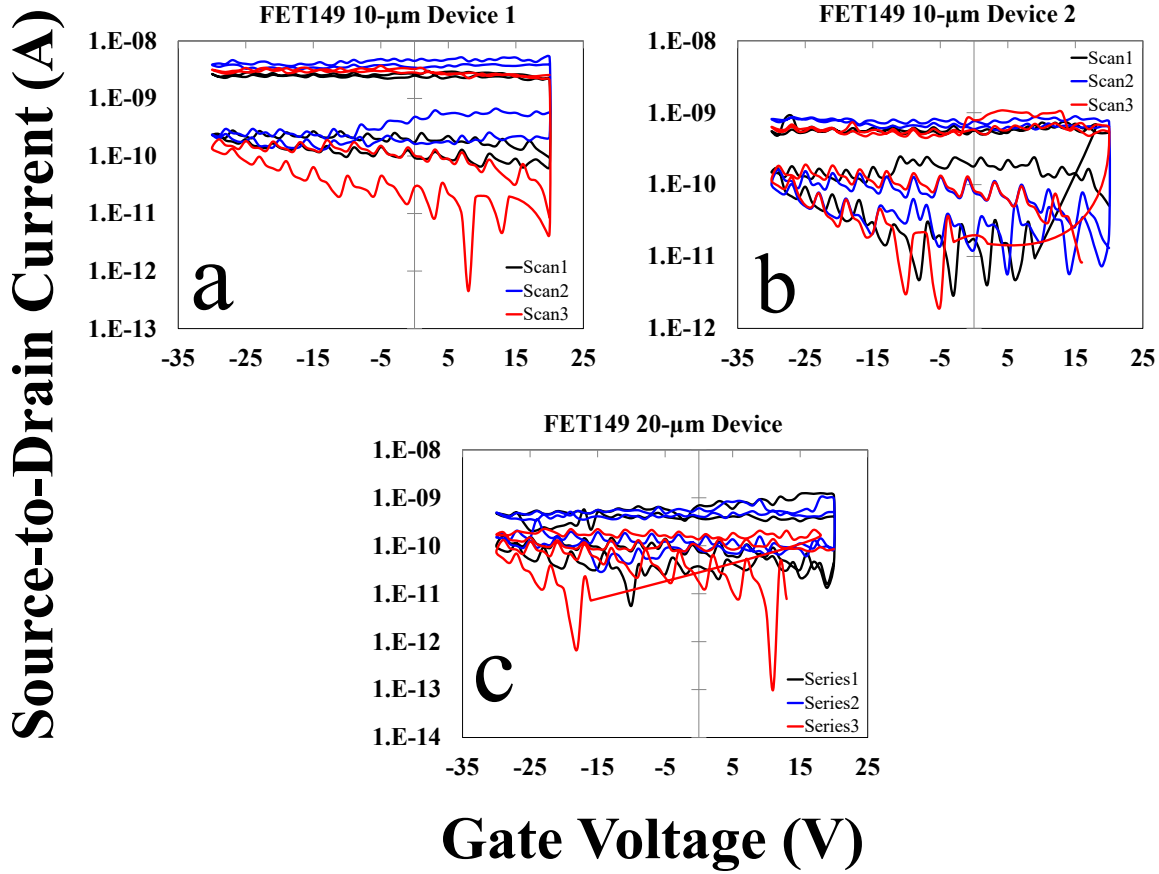


Figure 3.12: **FET 149** – Transfer Characteristics of *in-situ* DPP-doped SiNWs synthesized from MPS precursor at a Si:P ratio of 10^5 – 10- μm (a) device 1 and (b) device 2; (c) 20- μm . – The Si nanowires used for this device were taken from the same batch as those used for FET 150 (Fig. 3.6, page 59). However, prior to confecting the FET device, the Si nanowires were subjected to treatment in aqua regia for a period of 3 minutes and were subsequently ablated in deionized water, desiccated using a rotary evaporator, and dispersed in chloroform at a concentration of 1 mg of Si nanowires to 1 mL of chloroform. Values of the standard parameters measured for each of the devices are tabulated in Table C.2 found in Appendix A on page 148. Optical micrographs corresponding to this device are found in Fig. 3.13 on p. 67.

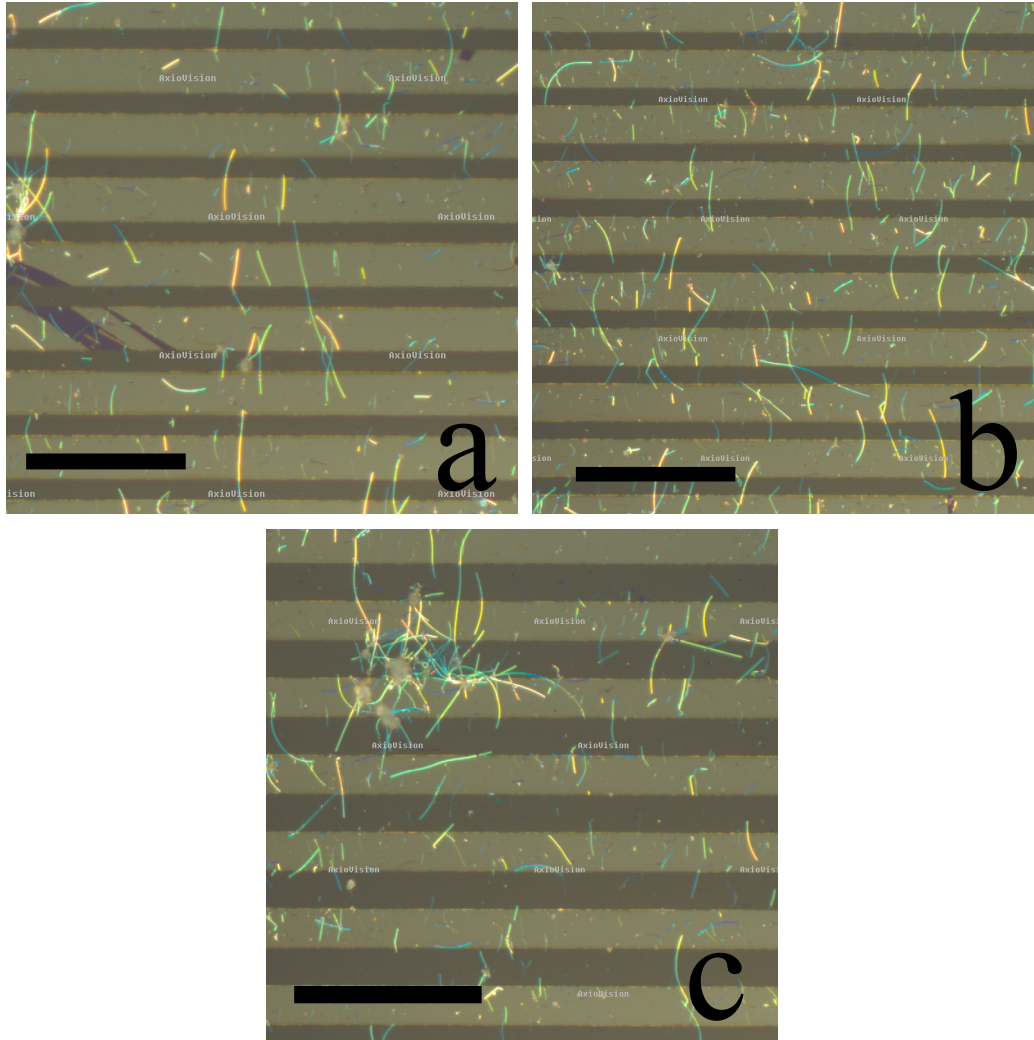


Figure 3.13: **FET 149** – Optical micrographs of *in-situ* DPP-doped SiNWs synthesized from MPS precursor at a Si:P ratio of 10^5 – The images show the interdigitated arrays of gold contacts that comprise the FET devices. The light-colored filamentous objects seen in the micrographs are doped SiNWs (Si:P = 10^5) that were subsequently etched in aqua regia according to the procedure described above – 10- μ m (a) device 1 and (b) device 2; (c) 20- μ m device. The scale bars are equal to 100 μ m. The nanowire coverage for this FET is rather sparse, and at these large device spacings there are few nanowires that bridge the gaps between the digits, which results in poor device performance and very low values of I_{sd} . The corresponding transfer curves are found in Fig. 3.12 on p. 66.

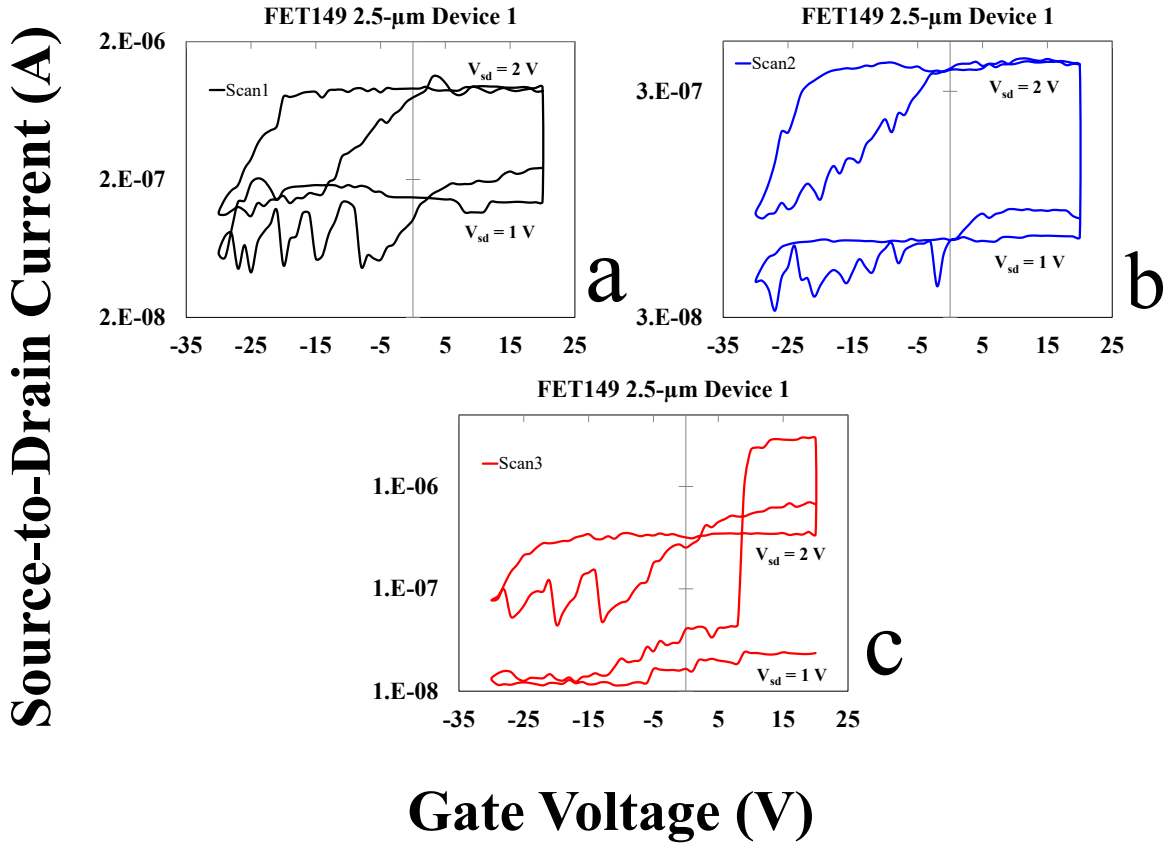


Figure 3.14: **FET 149 – 2.5- μm device 1** – Transfer Characteristics of *in-situ* **DPP-doped SiNWs** synthesized from MPS precursor at a Si:P ratio of 10^3 – the three individual scans for the 2.5- μm device 1 (shown as a composite in Fig. 3.10) are here plotted separately in order to better elucidate what appears to be n-type gate modulation, Values of the standard parameters measured for each of the devices are tabulated in Table C.2 found in Appendix A on page 148. Optical micrographs corresponding to this device are found in Fig. 3.11(a) on page 65.

3.3.4 TMSP-doped TS nanowires

3.3.4.1 Moderately-doped TS Nanowires - Si:P = 10^4

Figures 3.15 and 3.17 show the device performances for FETs made with TS SiNWs doped *in-situ* with $\text{P}(\text{SiMe}_3)_3$ at a Si:P ratio of 5×10^4 . These devices again exhibit ambipolar-type behavior. This could be indicative of the effects of *in-situ* doping. As has been seen in other devices, the p-type behavior is likely due to the presence of surface charges. However, if a sufficiently high concentration of charge carriers from donor states are present to match the p-type effects of the surface charges, ambipolar behavior would be observed. In particular, the $10\text{-}\mu\text{m}$ device shown in Figure 3.17(c), shows strong ambipolarity, that at positive gate voltages tends towards quasi-n-type behavior. Again, this is a conjecture based upon inferences from the data at hand, but the conjecture may be justified in the context of the data presented here and rationales based in the literature.

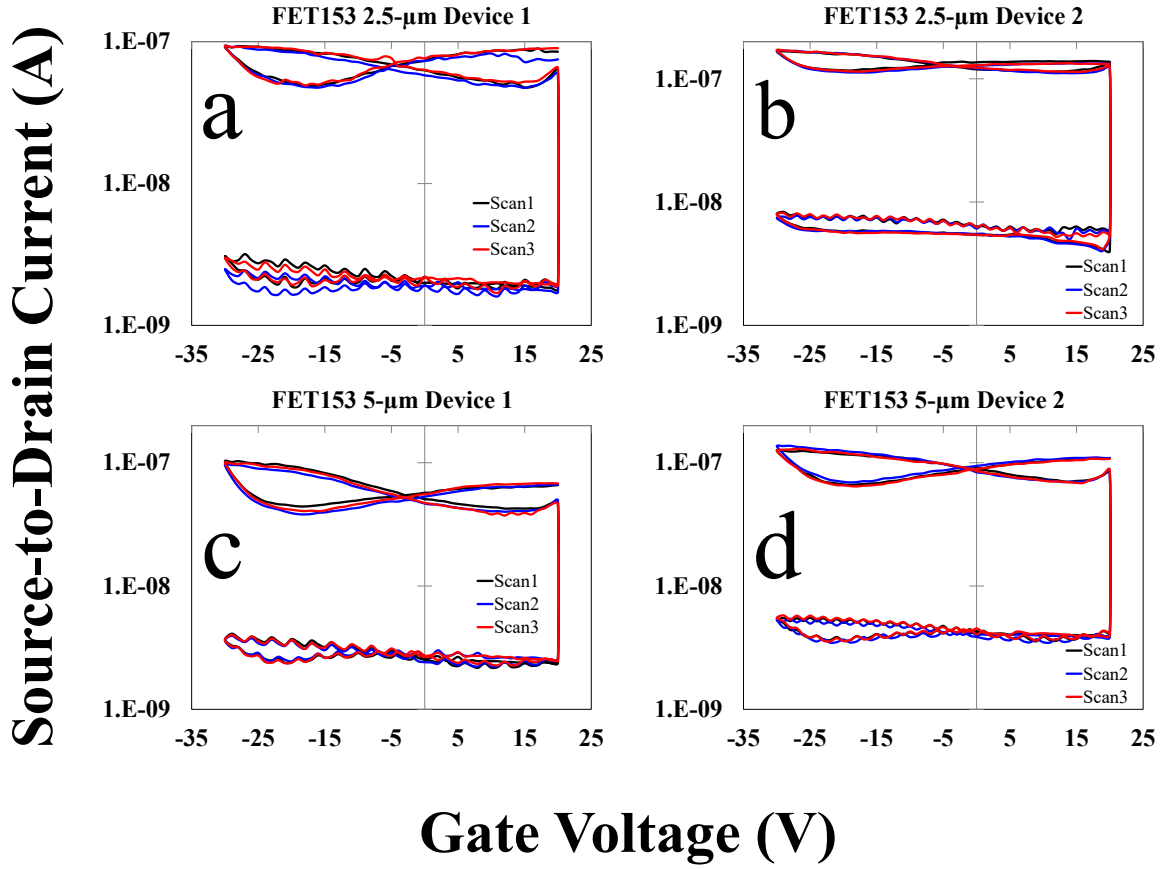


Figure 3.15: **FET 153** – Transfer Characteristics of SiNWs doped *in-situ* with **tris(trimethylsilyl)phosphine** synthesized from Si_3H_8 precursor at a Si:P ratio of 5×10^4 – 2.5- μ m (a) device 1 and (b) device 2; 5- μ m (c) device 1 and (d) device 2. Optical micrographs corresponding to these devices are found in Fig. 3.16 on page 71

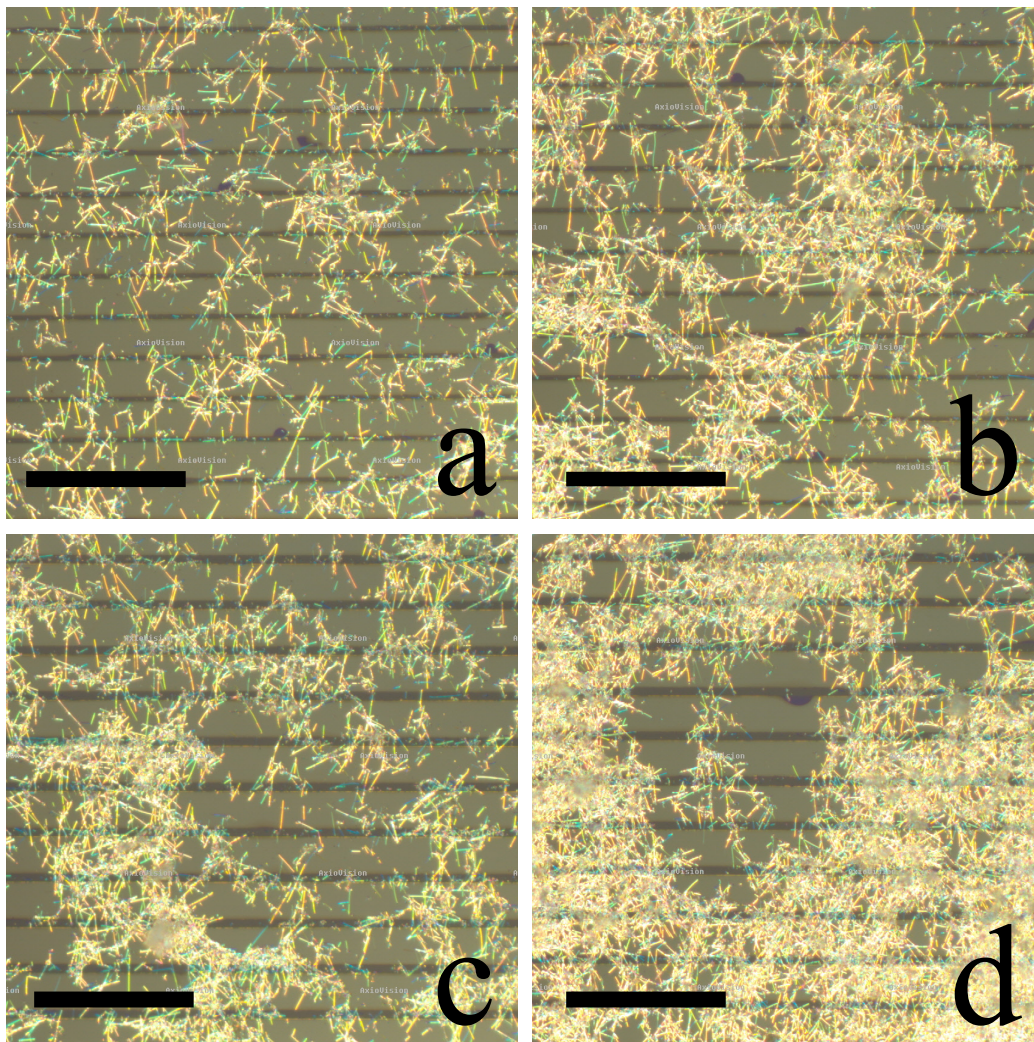


Figure 3.16: **FET 153** – Optical micrographs of SiNWs doped *in-situ* with **tris(trimethylsilyl)phosphine** synthesized from Si_3H_8 precursor at a Si:P ratio of 5×10^4 – The images show the interdigitated arrays of gold contacts that comprise the FET devices. The light-colored filamentous objects seen in the micrographs are *in-situ* -doped Si_3H_8 SiNWs (Si:P = 5×10^4) – 2.5- μm (a) device 1 and (b) device 2; 5- μm (c) device 1 and (d) device 2.. The scale bars are equal to 100 μm . The nanowire coverage of this FET is quite dense. The FET was dipped three times in chloroform in a solution of SiNWs at an increased concentration of 10 mg/mL. The corresponding transfer curves are found in Fig. 3.15 on page 70.

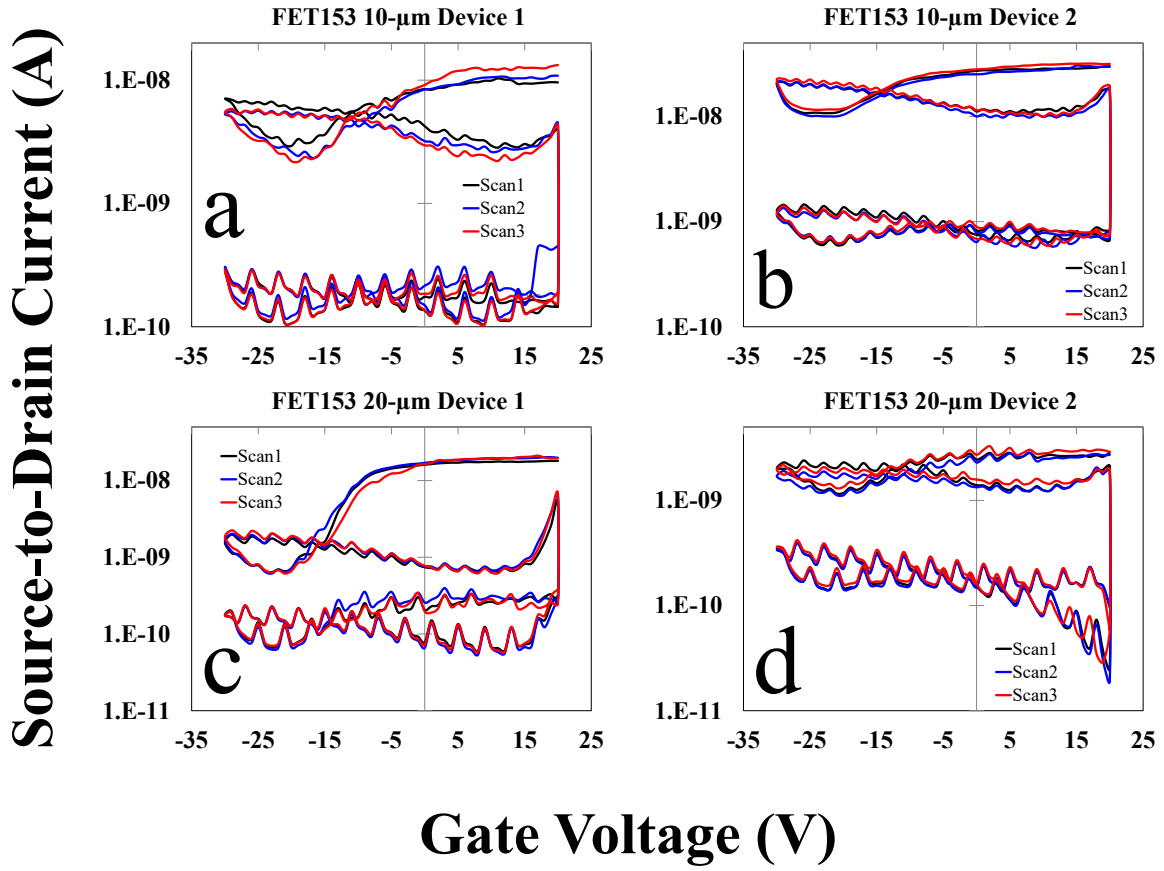


Figure 3.17: **FET 153** – Transfer Characteristics of SiNWs doped *in-situ* with tris(trimethylsilyl)phosphine synthesized from Si_3H_8 precursor at a Si:P ratio of 5×10^4 – 10- μm (a) device 1 and (b) device 2; 20- μm (c) device 1 and (d) device 2. Optical micrographs corresponding to these devices are found in Fig. 3.18 on page 73

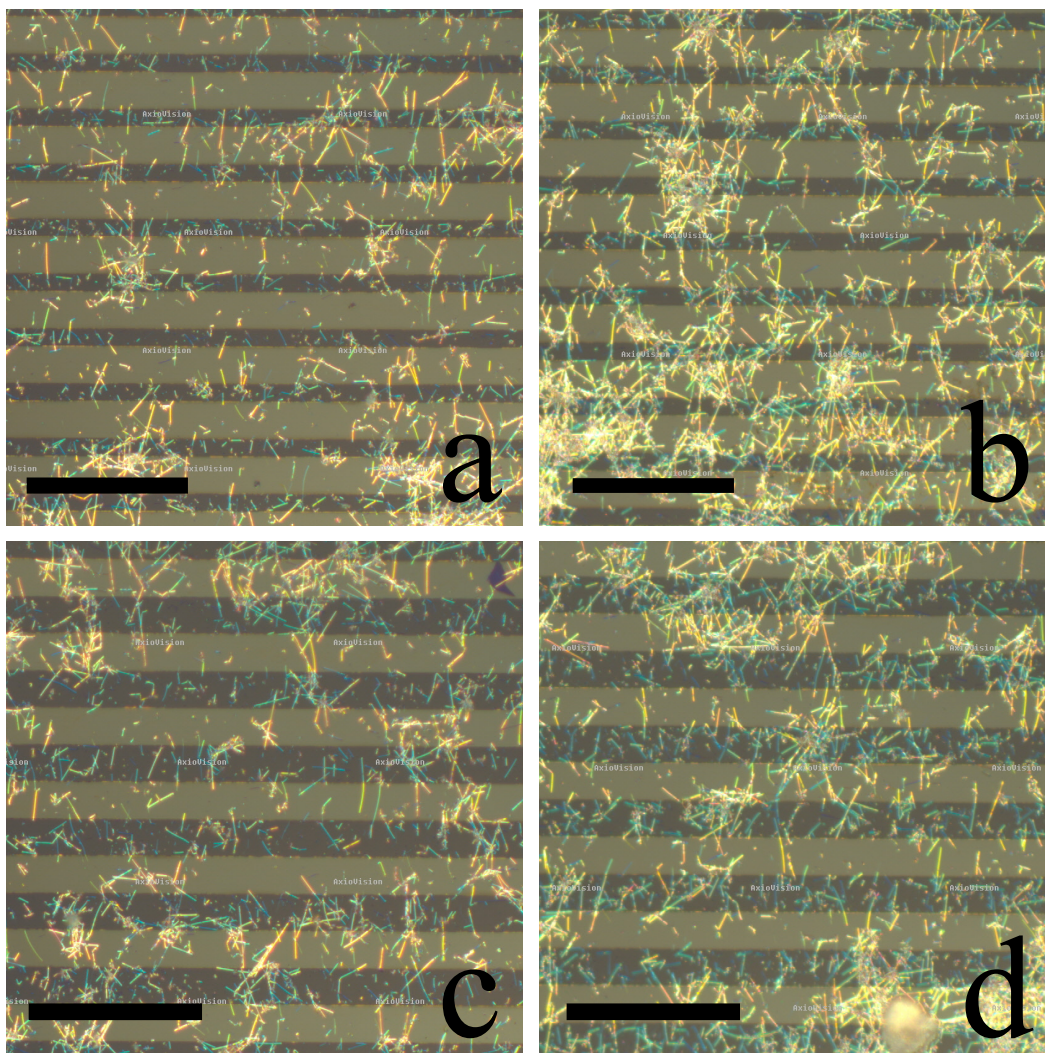


Figure 3.18: **FET 153** – Optical micrographs of SiNWs doped *in-situ* with **tris(trimethylsilyl)phosphine** synthesized from Si_3H_8 precursor at a Si:P ratio of 5×10^4 – The images show the interdigitated arrays of gold contacts that comprise the FET devices. The light-colored filamentous objects seen in the micrographs are *in-situ* -doped Si_3H_8 SiNWs (Si:P = 5×10^4) – 10- μm (a) device 1 and (b) device 2; 20- μm (c) device 1 and (d) device 2.. The scale bars are equal to 100 μm . The nanowire coverage of this FET is good. The FET was dipped three times in chloroform in a solution of SiNWs at an increased concentration of 10 mg/mL. The corresponding transfer curves are found in Fig. 3.17 on page 72.

3.3.4.2 Heavily-doped MPS Nanowires - Si:P = 10^3

Lastly, Figures 3.19 and 3.21 show the FET performance for highly-doped TS nanowires synthesized with Si_3H_8 as the P source. As in the case of Figures reffig:FET153 and 3.17, these devices show ambipolar characteristics that tend toward n-type, particular in the 10- μm devices in Figure 3.21(a) and 3.21(b).

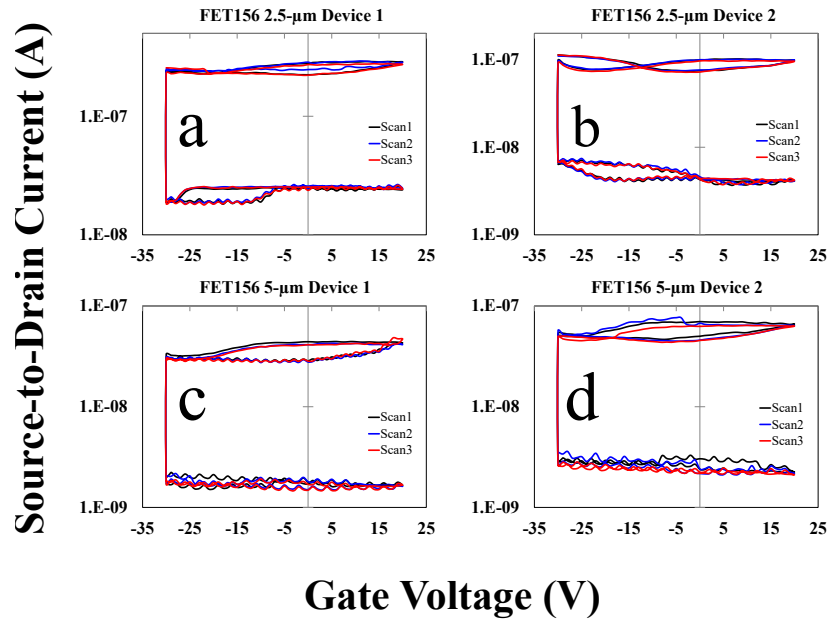


Figure 3.19: **FET 156** – Transfer Characteristics of SiNWs doped *in-situ* with tris(trimethylsilyl)phosphine synthesized from Si_3H_8 precursor at a Si:P ratio of 5×10^3 – 2.5- μm (a) device 1 and (b) device 2; 5- μm (c) device 1 and (d) device 2. These devices present an behavior that appears to be n-type and exhibits hysteresis but with ON/OFF ratios that are quite small (~ 10). The gate modulation in the second 2.5- μm device (b) produces a double eyelet or figure-8 morphology in the curves because at positive V_{gate} , I_{sd} is dominated by electrons in the channel, presumably as a result of doping, yet, at negative V_{gate} , the presence of positive charge carriers (present on NW surfaces) are predominant. However, the other three devices show predominantly weak n-type behavior with hysteresis. the Optical micrographs corresponding to these devices are found in Fig. 3.20 on page 75

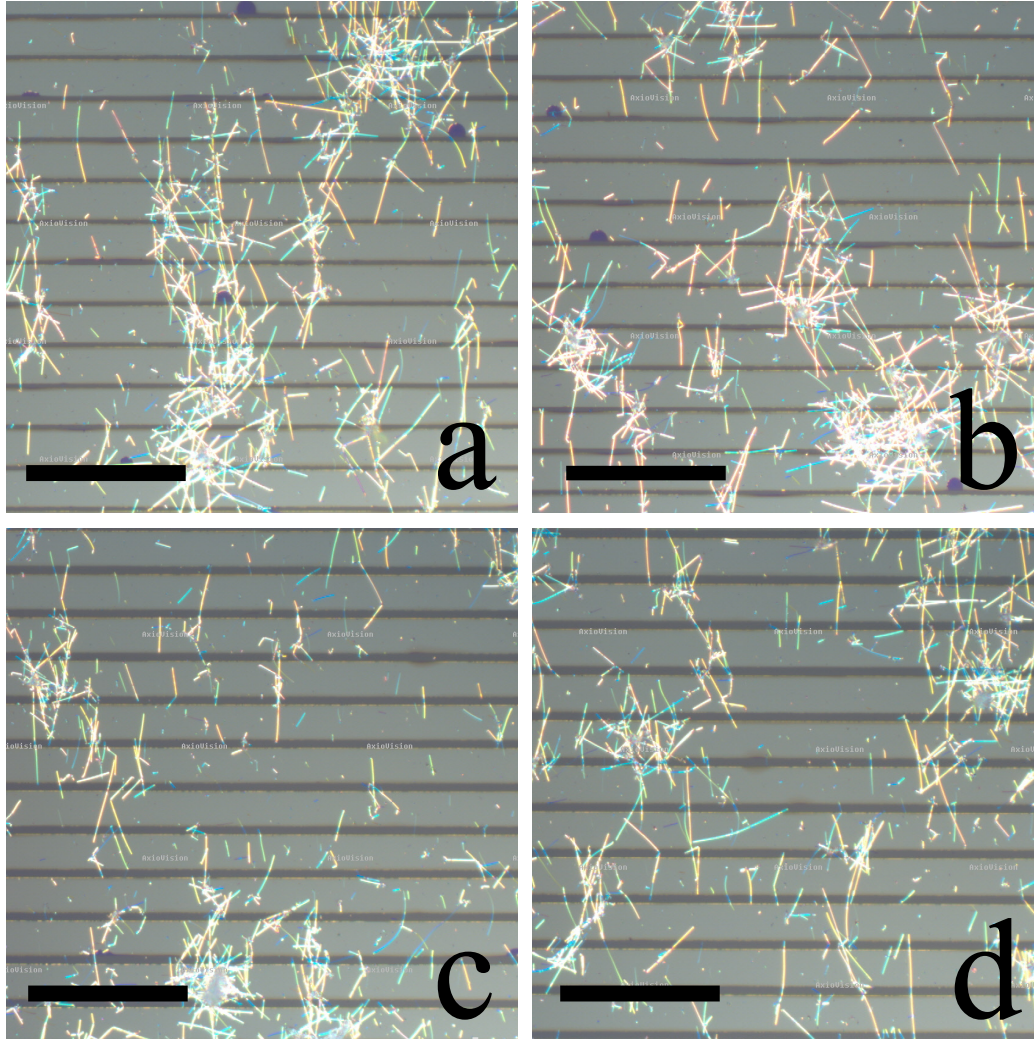


Figure 3.20: **FET 156** – Optical micrographs of SiNWs doped *in-situ* with **tris(trimethylsilyl)phosphine** synthesized from Si_3H_8 precursor at a Si:P ratio of 5×10^3 – The images show the interdigitated arrays of gold contacts that comprise the FET devices. The light-colored filamentous objects seen in the micrographs are *in-situ* -doped Si_3H_8 SiNWs (Si:P = 5×10^3) – (a) 2.5- μm device; (b) 5- μm device; (c) 10- μm device; (d) 20- μm device. The scale bars are equal to 100 μm . The nanowire coverage of this FET is less dense but still adequate. The FET was dipped 10 times in chloroform in a solution of SiNWs at a nanowire concentration of 1 mg/mL. The corresponding transfer curves are found in Fig. 3.19 on page 74.

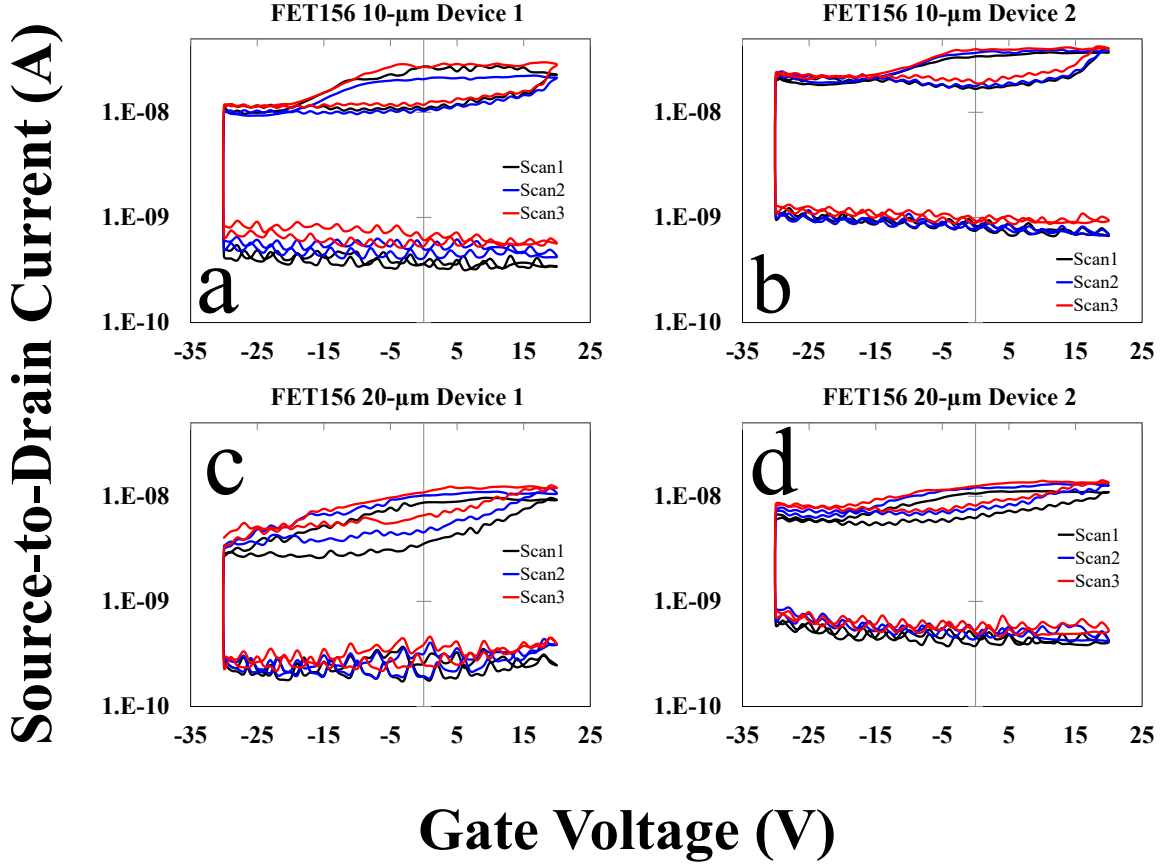


Figure 3.21: **FET 156** – Transfer Characteristics of SiNWs doped *in-situ* with tris(trimethylsilyl)phosphine synthesized from Si_3H_8 precursor at a Si:P ratio of 5×10^3 – 10- μ m (a) device 1 and (b) device 2; 20- μ m (c) device 1 and (d) device 2. As in Figure ??, the gate modulation produces weak n-type with low ON/OFF ratio and hysteresis because at positive V_{gate} , I_{sd} is dominated by electrons in the channel, presumably as a result of doping, yet, at negative V_{gate} , the presence of positive charge carriers (present on NW surfaces) are predominant. In general, an increase in the channel length leads to an increase in the transresistance, and thus I_{sd} is lower for these devices, compared to the devices in Figure ??, which are on the same FET wafer and contain the nanowires from the same dispersion. Optical micrographs corresponding to these devices are found in Fig. 3.22 on page 77

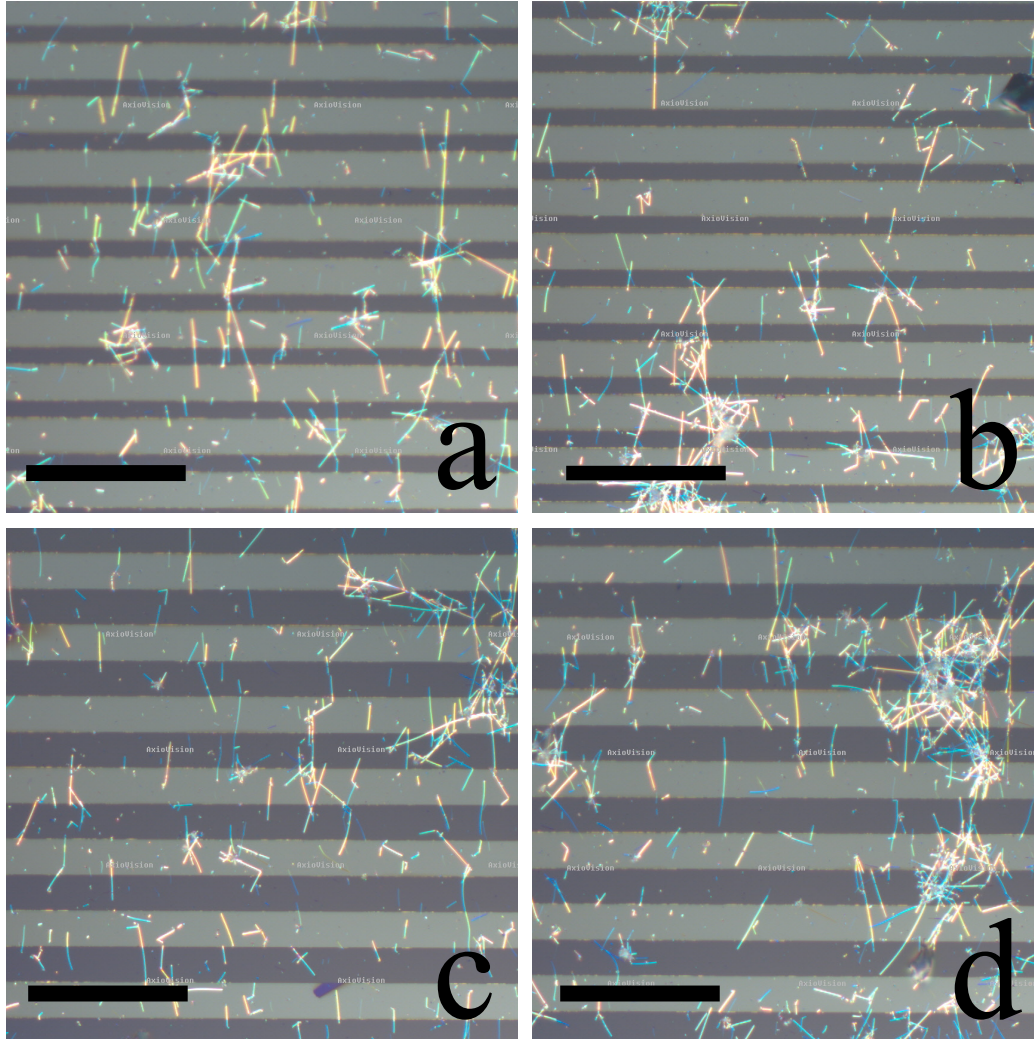


Figure 3.22: **FET 156-2** – Optical micrographs of **SiNWs doped *in-situ* with tris(trimethylsilyl)phosphine** synthesized from Si_3H_8 precursor at a Si:P ratio of 5×10^3 – The images show the interdigitated arrays of gold contacts that comprise the FET devices. The light-colored filamentous objects seen in the micrographs are *in-situ* -doped Si_3H_8 SiNWs (Si:P = 5×10^3) – (a) 2.5- μm device; (b) 5- μm device; (c) 10- μm device; (d) 20- μm device. The scale bars are equal to 100 μm . The nanowire coverage of this FET is less dense but still adequate. The FET was dipped ten times in chloroform in a solution of SiNWs at a nanowire concentration of 1 mg/mL. The corresponding transfer curves are found in Fig. 3.21 on page 76.

3.4 Conclusions

FET studies of *in-situ* doped silicon nanowires reveal a wide array of characteristics, not all of which are attributable to *in-situ* n-type doping with phosphorus. In many cases, it would appear that surface effects related to the presence of trap states and electrostatic charging are the primary causes of the transfer characteristics observed. Some devices show strong ambipolar behavior—tending towards n-type behavior—but more analysis is need to understand the interplay between surface states and high n-type dopant concentrations, especially in TS nanowires doped with $\text{P}(\text{SiMe}_3)_3$.

Further studies should conducted to isolate the origins of these effects through more precise modification of the surface chemistry of the nanowires. In addition, single-nanowire devices can be fabricated via photolithography or electron-beam lithography in a relatively facile and straightforward manner. Such devices should be fabricated with nickel or titanium metal contacts to ensure the formation of contacts that do not result in a barrier to charge injection, as might be the case for the devices presented here that use Au contacts.

3.5 Acknowledgements

The author wishes to thank Dr. Aaron Chockla for the TS nanowire synthesis, as well as Dr. Xiaotang Lu for assistance in corroborating and independently reproducing the *in-situ* doping procedures, and Dr. Timothy Bogart and Rebecca McKeever for help with procedures related to FET confection and testing.

Chapter 4

Ion implantation on silicon nanowires

“We have found it of paramount importance that in order to progress we must recognize our ignorance and leave room for doubt. Scientific knowledge is a body of statements of varying degrees of certainty — some most unsure, some nearly sure, but none absolutely certain.”

— Richard Feynman, in *The Value of Science*,
1955

4.1 Introduction

Ion implantation is an essential processing step in the fabrication of metal–oxide–semiconductor field-effect transistors (MOSFETs) and other semiconductor devices because it allows for the controlled doping of the semiconductor in specific regions of the device and at specific concentrations, by adjustment of ion dose and area of dosage [43, 109–119]. A beam of dopant ions is accelerated toward a target, typically a wafer of a semiconductor material, at a particular voltage and areal density, and these accelerated ions impact the target and are implanted into the crystal structure of that material. Because ion implantation tends to produce structural changes in the crystal structure of the target material that oftentimes results in amorphization, or a loss of long-range crystalline order of atoms in the material, thermal annealing

is applied to regain crystallinity and to incorporate the dopants substitutionally into the atomic sites of the semiconductor crystal structure, which leads to the production of donor and/or acceptor states depending on the valence of the dopant atom relative to the semiconductor atom.

4.1.1 Motivations

For this study, Si nanowires mats were subjected to ion implantation with P and B at targeted dopant concentrations of 10^{17} and 10^{18} atoms cm^{-3} . Because ion implantation is a common processing step for fabrication of semiconductor devices, it was selected as a potential alternative method to achieve controlled doping of Si nanowires, with the ultimate goal of incorporating doped Si nanowires in electronic devices. Although relatively cheap and cost-effective, the choice of ion implantation of nanowire mats might not appear to be entirely prudent or efficient, given that nanowire mats are of extremely low density, typically containing upwards of 90% void space. Thus, ion implantation of a specified dose area that is comprised mainly of void space would seem counter-productive. Nonetheless, because ion implantation is such a well-adapted and facile component of the semiconductor processing pipeline, the decision was made to undergo the study of ion implantation of nanowire mats as a means of *ex-situ* chemical doping, and the results of this study serve as a point of comparison with *in-situ* doping of Si nanowires by means of SFLS synthesis, especially given the fact that at high doping concentrations (*i.e.*, 10^{19}), the *in-situ* method becomes unattractive as a means of a vehicle for delivering dopant impurities because large concentrations of the dopant precursor (*i.e.*, MPS or $\text{P}(\text{SiMe}_3)_3$) interfere with

the synthesis chemistry, thereby resulting on nanowires that are of considerably poor quality in terms of crystallinity, aspect ratio, the presence of undesirable side products such as homogeneously nucleated particles of unreacted or semi-reacted phenylsilanes, the presence of tortuous wires, etc.

Ion implantation could afford an avenue for controlled doping without considerable alteration of the nanowire morphology and without introduction of undesirable materials as a result of chemical synthesis. It will be shown through SEM and TEM that ion implantation does not result in widespread changes to the nanowire morphology. TEM characterization has revealed that widespread amorphization—which is a typical consequence of ion implantation of *bulk* silicon and necessitates post-implantation annealing, which is a thermal process by which silicon which was made amorphous by damage incurred during ion bombardment can regain its crystallinity—*does not* occur after ion implantation of Si nanowires. EPR studies, however, reveal that significant structural modification of the nanowire surfaces does occur upon ion implantation, despite the fact that widespread nanowire amorphization is not observed in TEM studies. The level of structural modification as a result of ion implantation is substantial, and significant differences are observed in the EPR spectra of ion-implanted nanowires compared to as-synthesized nanowires. In particular, as discussed in Chapter 2, the predominant feature in the EPR spectra of as-synthesized and *in-situ* -doped Si nanowires is a large resonance peak located at $g = 2.005$, which is consistent with P_b centers. As will be discussed, the EPR spectra of Si nanowires after ion implantation possess features not seen heretofore—namely, the spectra are highly asymmetric, appearing to contain a substantial contribution from signals cen-

tered at $g = 2.002$, which would be consistent with the presence of SiO_x defects.

4.2 Experimental Details

As a comparison, two batches of Si nanowires, one synthesized from MPS precursor and another synthesized from trisilane precursor, were subjected to ion implantation of phosphorus¹.

4.2.0.1 Materials

All reagents used in the procedures described here were utilized as received without further purification. Anhydrous toluene (99.8%), chloroform (99.8%), diphenyl phosphine (98%), ethanol (99.9%), dodecanethiol ($\geq 98\%$), tetrachloroaurate trihydrate ($\geq 99\%$), sodium borohydride ($\geq 98\%$), and tetraoctylammonium bromide (98%) were purchased from Sigma-Aldrich. Monophenylsilane ($> 95\%$) was purchased from Gelest (Morrisville, PA). Trisilane (99.99%) was purchased from Voltaix (Branchburg, NJ). Hydrochloric acid (25% v/v) and nitric acid (70%, 15.8 N, Certified ACS Plus) were purchased from Fisher Chemical, and hydrofluoric acid (48 - 51% v/v) was purchased from EMD Chemical. Liquid helium (Industrial Grade, 99.999% purity, 60 L cryogenic liquid shipped in a 304 stainless-steel dewar), forming gas (compressed gas mixture of H_2 [5.7%] and N_2 [balance]), and nitrogen gas (compressed gas, 99.999%) were purchased from Praxair (Praxair Distribution, Inc., Austin, TX).

¹The procedures described below are also found in Ch. 2, §2.3 beginning on page 18 and are reproduced here *in nuce* for the convenience of the reader.

4.2.0.2 NWs synthesized from MPS

In a typical synthesis reaction, a 28-mL reactant solution was prepared containing anhydrous toluene (ACS grade, Sigma-Aldrich, 99.8%), 40 mg L⁻¹ of dodecanethiol-capped Au nanocrystals (averaging 2 nm in diameter, prepared according to the method enunciated by Brust et al. [67]), and 135 mM MPS (Gelest, > 95%), inside a nitrogen- or argon-filled glovebox. This solution was placed into a stainless steel injection cylinder that was sealed inside the glovebox before being brought into the ambient.

A 10-mL tubular titanium reactor was heated to 490°C in a heating block². The injection cylinder containing the reactant solution was then connected to the reactor system. The headspace of the injection cylinder was eliminated first by flowing a small amount of the reactant solution thru the secondary outlet of a six-way valve. Once a good seal between all connections was established and each line was cleared of potential air bubbles, the reactor was filled with anhydrous toluene at a volumetric flow rate of approximately 1 mL min⁻¹ to a pressure of 1,100 psi (8.27 MPa). Then, the reactor inlet line was closed. The six-way valve was switched to feed the injection cylinder, which was pressurized 1,200 psi (7.58 MPa), and the outlet valve of the injection cylinder was opened. Then, the six-way valve was then switched to connect the injection cylinder outlet line to the reactor inlet line. The toluene feed from the HPLC pump was momentarily paused with all valves open except for the reactor inlet, to ensure proper seals throughout the system. Then, the toluene feed was restarted.

² *Vide* Chapter 2, §2.3.1

At this point, the volumetric flow rate of the HPLC pump was reduced to 0.5 mL min⁻¹, the reactor inlet valve was opened, and the pressure was allowed to increase to 1,400 psi (9.65 MPa) with the reactor outlet closed. Once a pressure of 1,450 psi (10 MPa) was reached, the reactor outlet valve was opened. A chronometer was set for a reaction time of 40 minutes, and the pressure throughout the system was maintained at 1,500 ± 50 psi (10.34 ± 0.34 MPa) by means of a manual millimeter valve. A glass vial was connected to the exit line by means of a septum stopper in order to collect the effluent from the reactor. At the conclusion of 40 minutes, the synthesis reaction was terminated, the reactor was sealed, the HPLC pump was shut off, the variac power was also terminated, and the upper portion of the heating block was removed to expose the reactor, and the reactor was allowed to cool isochorically in the ambient of the fume hood. Once cool to the touch, the reactor was unsealed under a chemical fume hood. The nanowires were extracted manually using a glass pipette and dispersed in toluene. Then, the collected nanowires were ablated three times via centrifugation (Eppendorf, model 5804R) at 5,000 rpm in a mixture of toluene, chloroform, and hexane (2:1:1) to remove unreacted precursors. SiNWs synthesized using Si₃H₈ as the Si precursor [29, 33], which shall be described below.

4.2.0.3 NWs synthesized from trisilane

Silicon nanowires were synthesized from Si₃H₈ precursor. The procedures are as follows. A reactant solution was prepared inside the inert atmosphere of a nitrogen- or argon-filled a glovebox. The solution contained 270 μL of toluene, 550 μL of Au

nanocrystals³, and 250 μL of Si_3H_8 . The Si:Au mole ratio was 20:1.

The synthesis reaction is a semi-batch process, and the conditions were as follows. A 10-mL tubular titanium reactor was pressurized to 1,000 psi (6.89 MPa) by means of an HPLC pump, with the effluent (exit) line closed and pre-heated to a temperature of 450°C. The reactant solution was injected into the reactor by means of an HPLC pump at a volumetric flow rate of 3 mL min⁻¹. The injection time was 1 min. The reactor was allowed to pressurize during injection by maintaining the effluent line closed. After one minute, the injection was terminated, and the final pressure of the reactor was 2,100 psi (14.47 MPa). At the conclusion of the synthesis reaction, the reactor was allowed to cool isochorically in the ambient of the glovebox and, once cool to the touch, was removed from the glovebox and unsealed under a chemical fume hood. The nanowires were extracted manually using a glass pipette and dispersed in toluene. Then, the collected nanowires were ablated three times via centrifugation (Eppendorf, model 5804R) at 5,000 rpm in a mixture of toluene, chloroform, and hexane (2:1:1) to remove unreacted precursors.

For ion-implantation, as-synthesized nanowire slurries (MPS and TS nanowires dispersed in chloroform at concentrations of c. 10 mg/mL) were nanowire mats were formed by casting nanowire slurries into two large rectangular mold consisting of a teflon trough and an aluminum frame. The solvent was allowed to evaporate in the ambient of a chemical fume hood. To remove the mats, a sharp edge of stainless steel

³i.e., equal to 27.5 mg of Au nanocrystals, solution in toluene at a concentration of 50 mg mL⁻¹ of Au nanocrystals

razor blade was used to cut free the mats from the edge of the aluminum frame⁴. Then, the aluminum frame was released from the edges of the teflon trough with great care. Delamination of the nanowire mats from the teflon trough was aided with the use of the blade.

For boron implantation, two long strips were cut from both the MPS mat and the TS mat and were placed on to an undoped monocrystalline Si wafers (6 in. in diameter whose surfaces exhibited thermally grown oxide) and then two aluminum frame frames were placed on top of the mats, with the mats positioned precisely between the borders of the frames and Si wafer. The frames were affixed to the wafers by copper tape⁵.

For ion-implantation phosphorus, the remainder of the large MPS and TS nanowire mats were sandwiched between aluminum frames and affixed to the wafers with copper tape⁶.

These wafers with the nanowire mats packed securely into polypropylene wafer holders and were sent via the post to Core Systems in Sunnyvale, CA, USA for ion implantation. The implantation was carried out at two targeted concentrations of P: 10^{17} and 10^{19} atoms cm^{-3} .

⁴This procedure was performed with great care because, although nanowire mats are typically free-standing, and self supporting, they have a structural integrity akin to that of thin tissue paper and can also easily shred.

⁵FET device data for these samples are located in Appendix C.

⁶Two small square-shaped pieces were cut from these large mats and affixed to a smaller rectangular aluminum frame that could be positioned into the slots of the other two sets of aluminum frames for the purposes of co-coping, i.e., the wafer labeled (A) in Figure 4.1 on page 90 was implanted with P along with the smaller frame (C), which was then removed from wafer (A) and placed on to wafer (B) for implantation with B. The results of co-doped ion implantation are not presented in this thesis.

The ion doses⁷ during implantation for a targeted dopant concentration of 10^{17} atoms cm^{-3} in silicon, were 3×10^{13} ions cm^{-2} for boron and 1.9×10^{13} ions cm^{-2} for phosphorus. The ion doses during implantation for a targeted dopant concentration of 10^{19} atoms cm^{-3} in silicon, were 3×10^{15} ions cm^{-2} for boron and 1.9×10^{15} ions cm^{-2} for phosphorus.

The accelerating voltage for implantation was 200 keV, and the tilt angle⁸ of the wafers with respect to the axis of ion beam incidence was 7° .

4.2.1 Electron paramagnetic resonance spectroscopy

EPR spectroscopy was performed using a Bruker EMX Plus X-band spectrometer equipped with a cryostat for studies at 4.2 K⁹. Liquid helium (Industrial Grade, 99.999% purity, 60 L cryogenic liquid shipped in a 304 stainless-steel dewar) was purchased from Praxair (Praxair Distribution, Inc., Austin, TX). Dried samples of undoped and ion-implanted Si nanowires were placed in quartz tubes (4-mm outer diameter, thin-walled, precision quartz EPR tube, Wilmad-LabGlass) for spectral acquisition.

⁷which is a term that refers to the areal density of ions on the surface of the target [120]

⁸The target is held at a tilt angle relative to the beam incidence direction in order to avoid “channeling”, in which the path of incident ions through the silicon crystal structure follows relatively open and unimpeded channels, such as along crystallographic directions where the interatomic separation distance is large. This channeling leads to unpredictable ion penetration into the crystal structure and thus indeterminate depths of penetration [120].

⁹In some cases, liquid nitrogen was used when the signal was sufficiently strong at temperatures of approximately 77 K. Liquid nitrogen was supplied from the house supply in the Department of Chemistry. The same cryostat as for liquid helium was used to maintain proper cooling.

4.2.2 Nanowire Field-Effect Transistors

Back-gated NWFETs were fabricated using Si wafers, with approximately 200 nm of thermally grown SiO_2 dielectric, printed with interdigitated arrays (IDAs) of Au contacts, with spacings of 2.5, 5, 10, and 20 μm between the digits. Undoped and ion-implantated SiNWs were dispersed at a concentration of 1 mg of nanowires per 1 mL of solvent in either anisole or chloroform via sonication at room temperature for periods of up to 3 hours or until a homogeneous dispersion was obtained (typically an hour). Then, a clean, printed wafer was affixed to the motorized arm of an automated dipping apparatus. This apparatus was built in house and was used to dip the wafer in the NW solution 10 times along the vertical axis at a speed of 10 mm/min, via computer control in an automated fashion, in order to deposit the NWs onto the wafer via capillary action. Dipping in this way aligns the NWs parallel to the dipping direction. Devices whose digits were oriented perpendicular to the NW alignment direction (*vide supra* Fig. 3.2 on page 54) were then tested in a Karl Süss probe station using a Keithley Instruments Semiconductor Characterization System, model 4200. A three-probe arrangement was used with one probe connected to the gate and the other two to the contact pads of the interdigitated array. For determination of the transfer characteristics, the gate voltage (V_{gate}) was swept at a constant rate of 10 V s⁻¹ between 20 V and -30 V at source-drain bias voltages (V_{sd}) of 1 V and 2 V. Three scans per measurement were performed.

In some cases, samples were annealed in a quartz tube furnace at various temperatures and atmospheres for 30 minutes.

In the following section, only results from n-type implantation with phosphorus

will be presented and discussed. FET graphs of p-type implanted nanowire mats are presented in Appendix C on page 140.

4.3 Results and discussion

Figure 4.1 shows the aluminum frame affixed to Si wafers by means of copper tape, in which were held the nanowire mats for ion implantation. This set-up was dubbed the “mask”. This system was quite effective for the goals of ion implantation and was used with only minor alterations throughout the ion-implantation experiments.

Nanowire coverage can affect the device performance. In the data presented below, all FET devices had adequate nanowire coverage, similar to those devices presented in Chapter 3. The optical micrographs have been omitted here for the sake of brevity.

4.3.1 FET Data - First Round of Ion Implantation

The first round of ion implantation was carried out on the mats shown in Figure 4.1 at a targeted doping level of 10^{17} . In most cases, the FET behavior is p-type, though the expected behavior after doping with phosphorus would be n-type.

FETs were contacted with the as-retained nanowires after ion implantation according to the procedures described in §4.2.2 on page 88. Nanowires were annealed on the FET substrates (the same FETs as the non-annealed nanowires) at 200°C under forming gas and were re-tested. They were subsequently annealed at 300°C under forming gas and were re-tested.

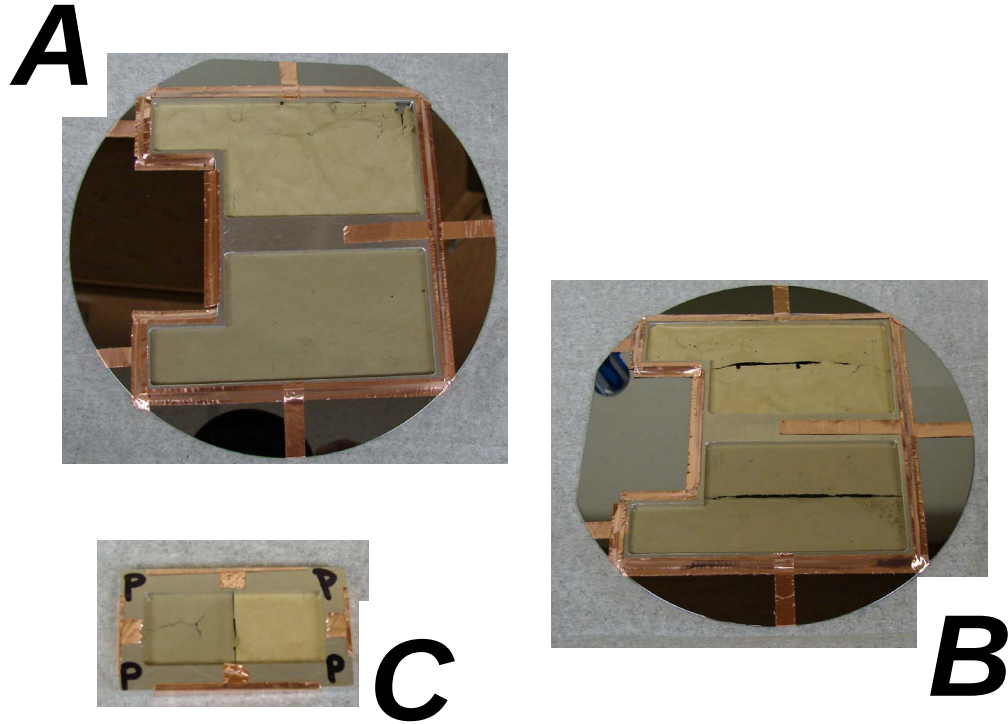


Figure 4.1: Nanowires mats in aluminum casting molds, affixed to Si wafer, prior to shipment to ion-implantation facility. Inset (A) shows the wafer containing mats subjected to ion implantation with phosphorus. Inset (B) shows the wafer containing mats subjected to ion implantation with boron. Inset (C) shows a smaller rectangular frame used for co-doping (results not presented here for the sake of brevity). Photo credit: A. Chockla.

Figure 4.2 shows the FET performance of TS nanowires ion-implanted with phosphorus (n-type) and tested as received. The device behaviors are typical of as-synthesized TS nanowires, in that they show little to no gate modulation, no hysteresis, and somewhat high currents. This device behavior can be likened to a highly conductive quasi-metallic channel and is likely an indication of the predominance of surface charges in the nanowire channels upon application of a bias voltage and gate sweep. In addition, the role of interactions between surface states on the nanowires and water bound to the surface of the silicon dioxide gate dielectric is likely a factor.

Figure 4.3 shows the FET performance of TS nanowires ion-implanted with phosphorus (n-type) and tested after annealing at 200°C in forming gas for 30 minutes. The rationale behind annealing is straightforward. In bulk silicon, ion implantation produces structural defects in the silicon crystal structure that many times are so severe that the large portions of the material no longer exhibit the high degree of crystallinity or any crystallinity at all, which is required for semiconductor device fabrication and operation, and large portion of the silicon effectively become amorphous. This process is called amorphization, and annealing allows those defect-rich portions of the silicon crystal to regain long-range periodicity and crystalline order. In the case of nanowires that were ion-implanted, the degree of structural rearrangement and amorphization was unknown *a priori*, and initial structural characterization via X-ray diffraction and TEM did not reveal any signs of widespread amorphization. So, a low-temperature anneal was applied as an initial test. Annealing in forming gas is also a technique used in industry to remove oxidation from silicon surfaces. Forming gas, also referred to as a dissociated ammonia atmosphere, is a reducing environment.

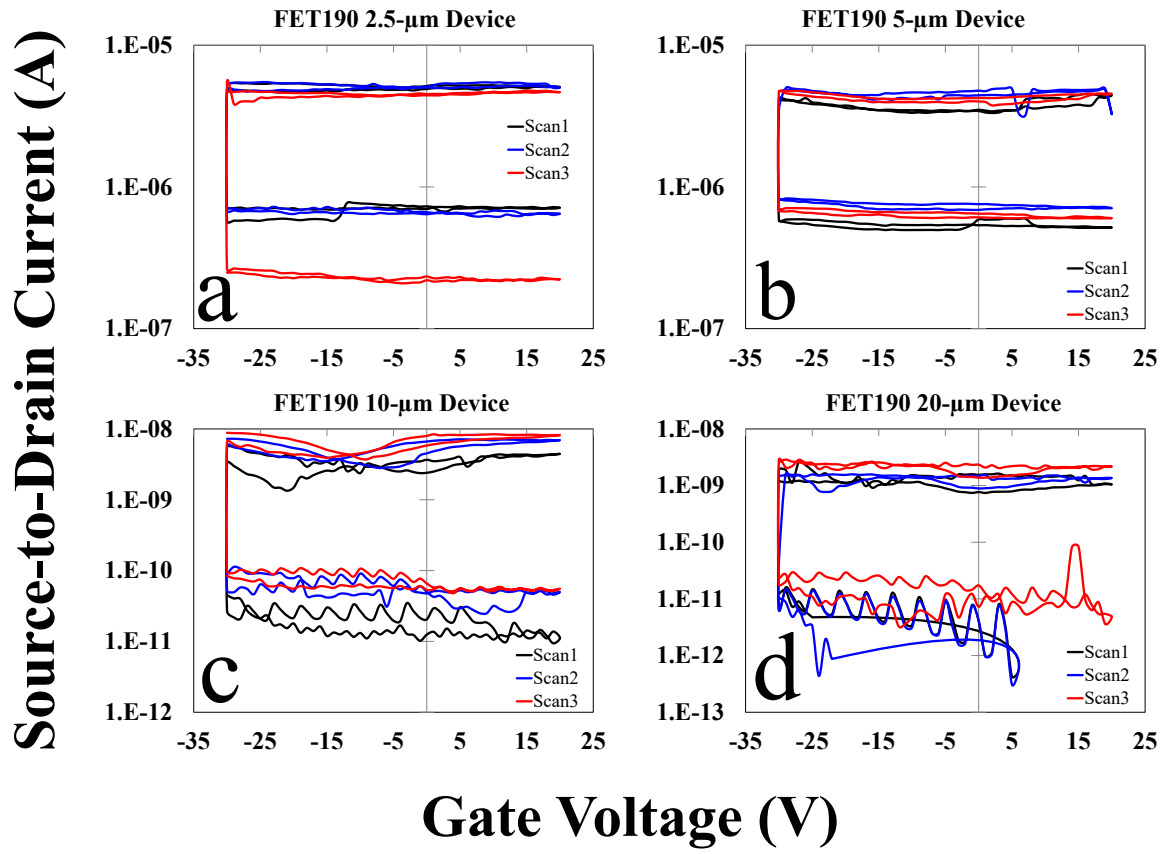


Figure 4.2: TS NWs Ion Implanted n-type — Targeted Doping of 10^{17} — As received

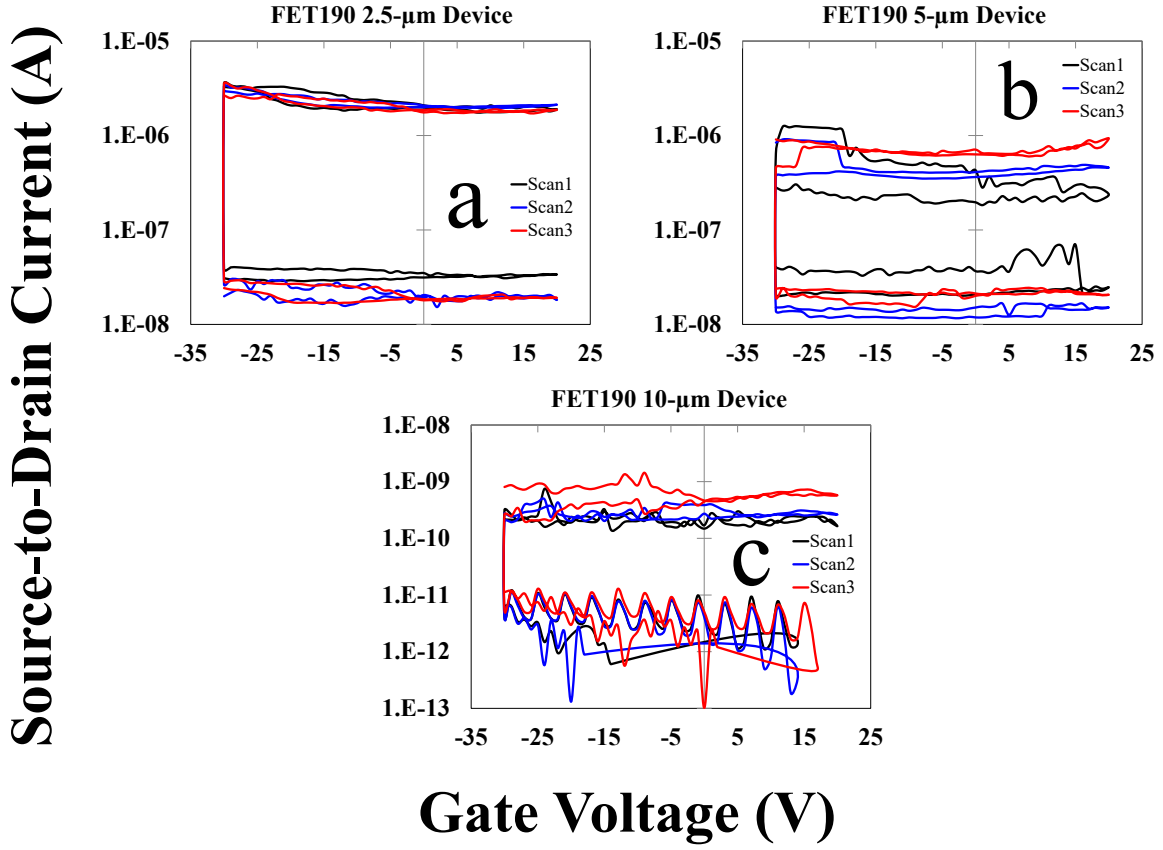


Figure 4.3: TS NWs Ion Implanted n-type - Targeted Doping of 10^{17} - Annealed at 200°C in forming gas

The hypothesis was that annealing coupled with reducing environment would eliminate the presence of surface trap states associated with amorphization and silicon dioxide. However, as can be seen in the device behavior, there is little change in the gating behavior or in the device currents, compared to Figure 4.2.

Figure 4.4 shows the FET performance of TS nanowires ion-implanted with phosphorus (n-type) and tested after annealing at 300°C in forming gas for 30 minutes. As in the case of the devices in Figures 4.3 and 4.2, the performance degrades

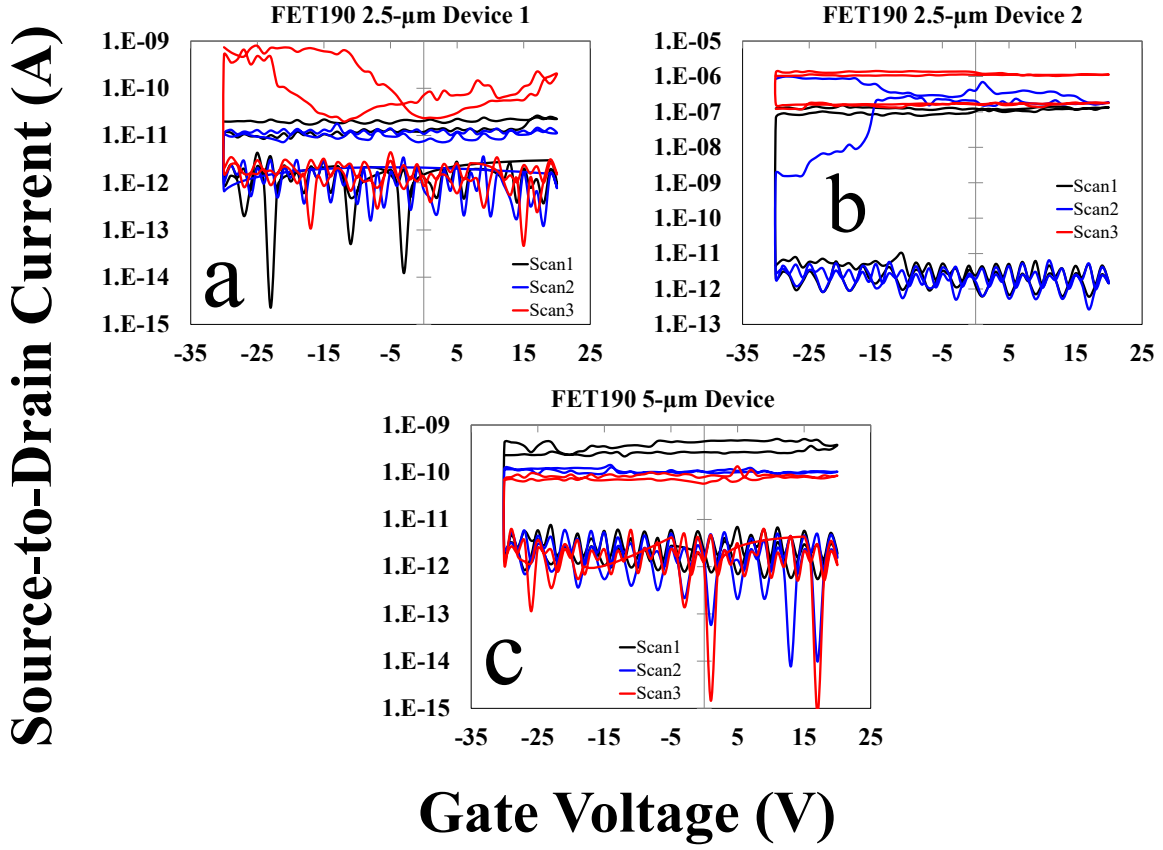


Figure 4.4: TS NWs Ion Implanted n-type - Targeted Doping of 10^{17} - Annealed at 300°C in forming gas

even further. Currents at $V_{sd} = 1\text{ V}$ (curves in the lower portion of each subfigure) are in the nanoamp range, which is of the same order of magnitude as the gate leakage currents for devices of this architecture with thermally grown silicon dioxide as the gate dielectric. These results also suggest that further annealing in forming gas eliminates to some extent the surface states that are likely responsible for the observed device currents.

Figure 4.5 shows the FET device performance of MPS nanowires that were

ion-implanted with phosphorus and tested as received. The device performances are typical of undoped, as-synthesized MPS nanowires, exhibiting large hysteresis, relatively high ON currents for the short channel devices, and large ON/OFF ratios.

Figure 4.6 shows the FET device performance of MPS nanowires that were ion-implanted with phosphorus and tested after annealing at 200°C in forming gas for 30 minutes. It is interesting to note that the trend in all devices is that of a decrease in the hysteresis as well as a decrease in the device currents. This observation is in keeping with the conjecture that surface states dominate the device behavior. In the case of MPS nanowires that exhibit an amorphous shell of polyphenylsilane and have been shown to exhibit a large degree of electrostatic surface charging in ambient conditions, the effect of low temperature annealing in a reducing atmosphere could have the effect of decrease the density of surface states that trap charges and lead to the strong hysteresis in as-synthesized MPS nanowires.

Figure 4.7 shows the FET device performance of MPS nanowires that were ion-implanted with phosphorus and tested after annealing at 300°C in forming gas for 30 minutes. As in the case of the devices in Figure 4.6, the trend is toward decreasing hysteresis and decreasing currents, further serving as a suggestive indication of the role of surface charges in the device performance.

4.3.2 FET Data - Second Round of Ion Implantation

After the first round of ion implantation, some calculations were performed to determine the doping distribution and penetration depth of the ions. As a result, the decision was made to increase the doping target to 10^{19} and decrease the fabric

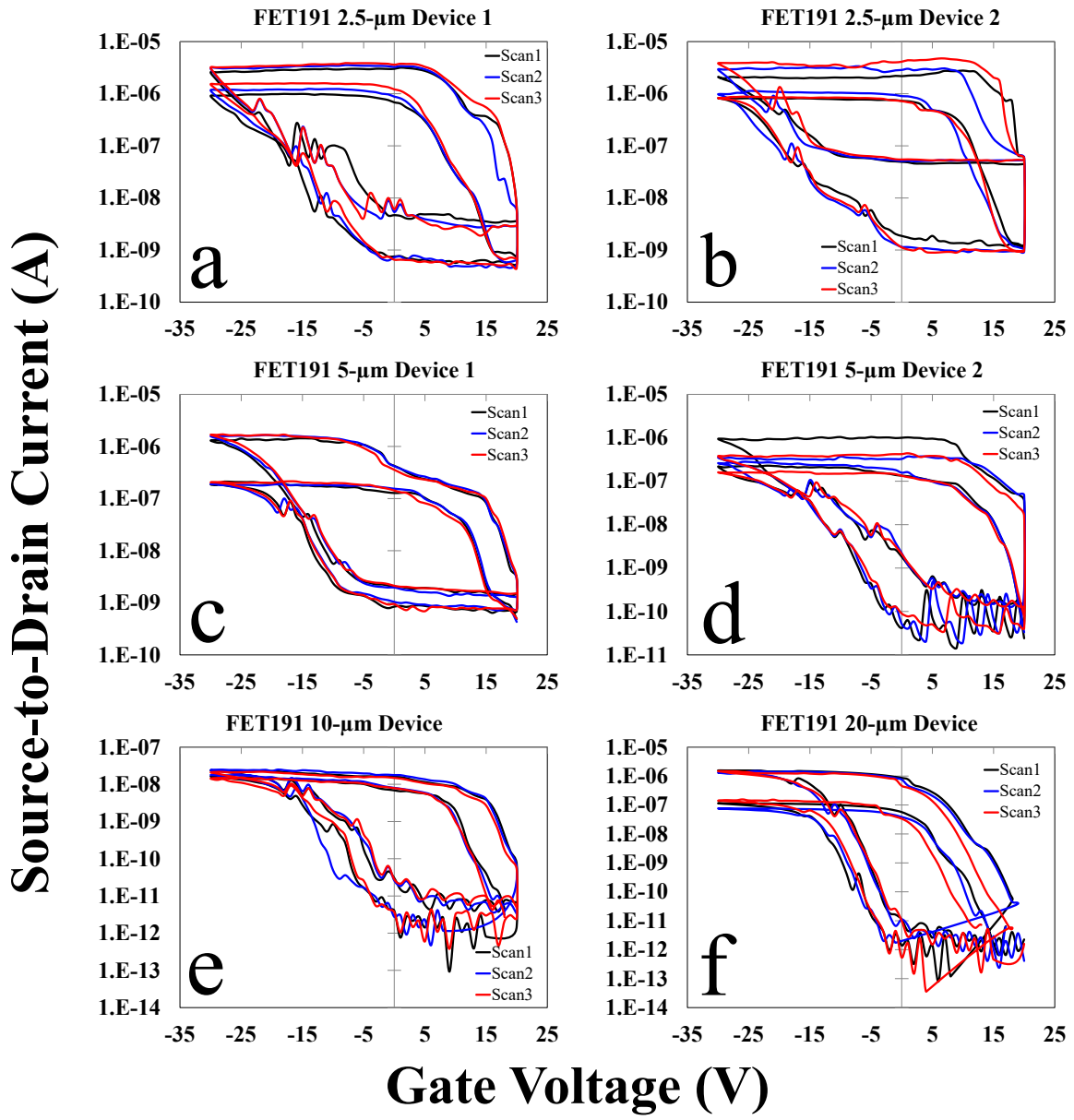


Figure 4.5: MPS NWs Ion Implanted n-type - Targeted Doping of 10^{17}

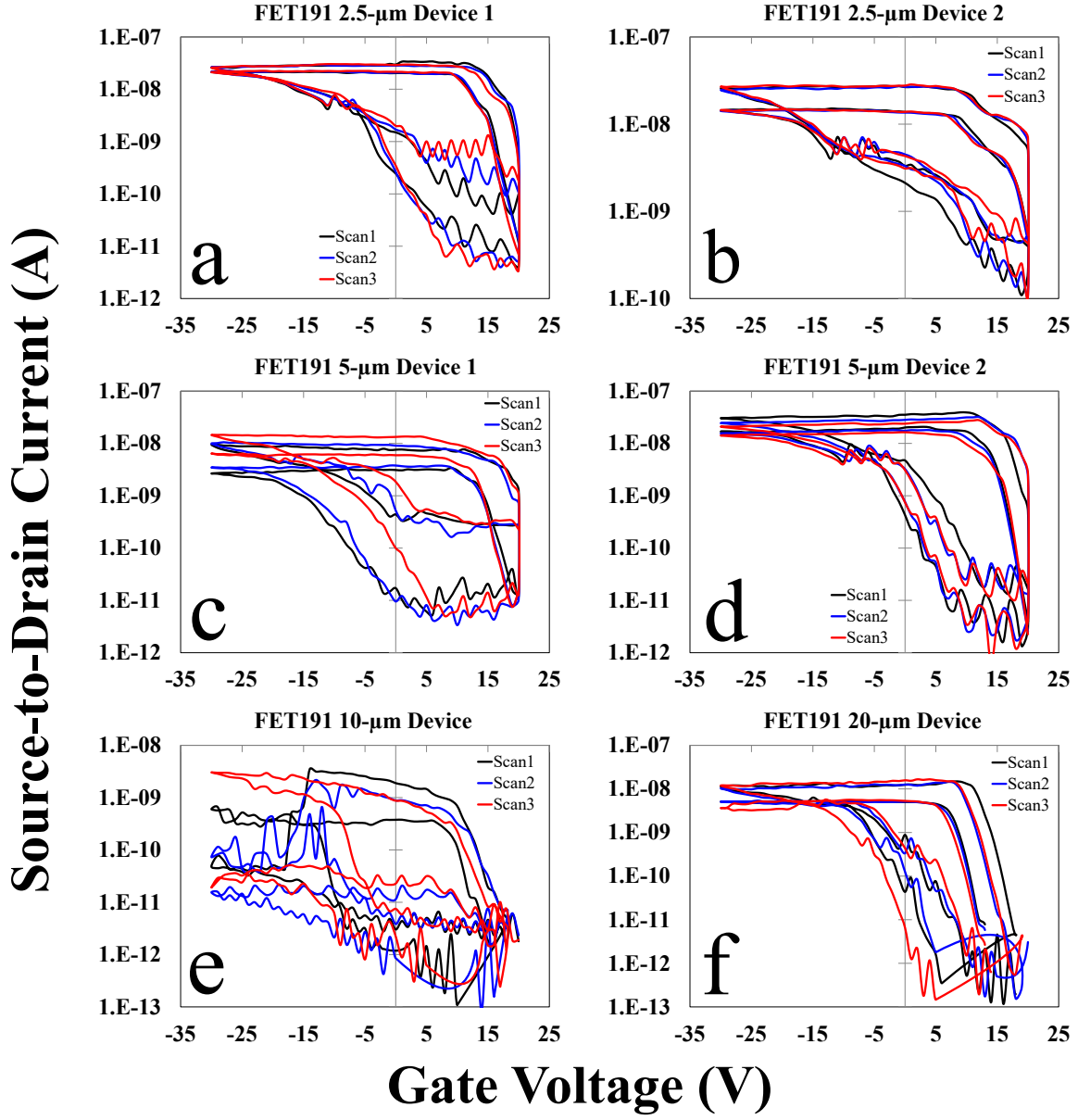


Figure 4.6: MPS NWs Ion Implanted n-type - Targeted Doping of 10^{17} - Annealed at 200°C in forming gas

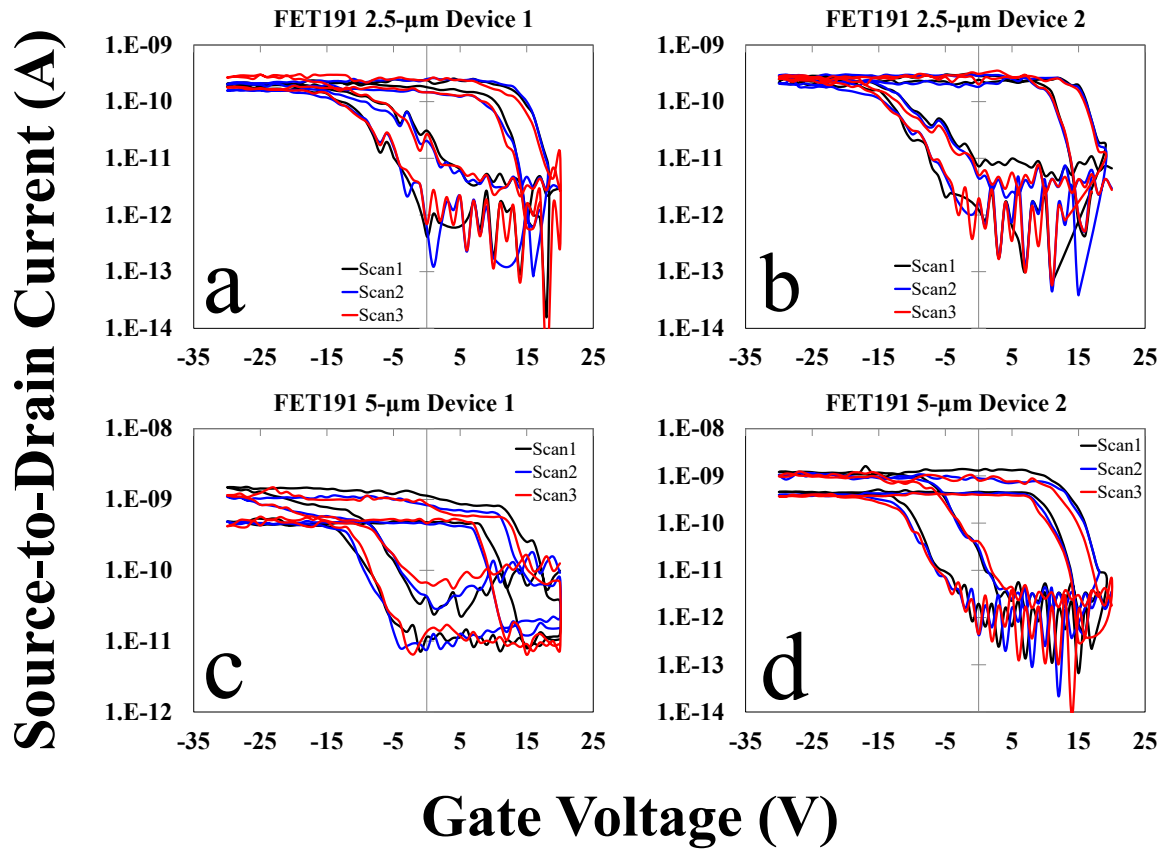


Figure 4.7: MPS NWs Ion Implanted n-type - Targeted Doping of 10^{17} - Annealed at 300°C in forming gas

thickness down to c. $10\ \mu\text{m}$. Separate FETs were made from nanowires ‘as returned’ and after annealing.

Figure 4.8 shows the FET performance of as-received TS nanowires ion implanted with phosphorus at a targeted doping level of 10^{19} . The performance is typical of as-synthesized TS nanowires and very similar to that of the devices shown in Figure 4.2. No appreciable gate modulation is observed and while device currents are relatively high, there is a great deal of noise in the curves, which could suggest poor nanowire quality or structural changes after implantation that give rise to inhomogeneous surface properties.

Figure 4.9 shows the FET performance of TS nanowires ion implanted with phosphorus at a targeted doping level of 10^{19} and annealed in forming gas at 300°C for 30 minutes. The performance of these devices stands in stark contrast to that of the other devices in Figure 4.8. Ambipolar behavior, which arises from conduction of both negative and positive charge carriers that are present at comparable populations, is seen in the $2.5\text{-}\mu\text{m}$ devices (a) and (b). This behavior could be a result of the electron conduction from the presence of charge carriers from the activated phosphorus dopant in addition the conduction of holes as a result of surface states that arise from annealing in the reducing atmosphere of the forming and that also are induced by the gate field, as in the case of other devices.

Figure 4.10 shows the FET performance of MPS nanowires ion implanted with phosphorus at a targeted doping level of 10^{19} . These devices exhibit a broad range of behaviors, with only one $2.5\text{-}\mu\text{m}$ device in (a) displaying the performance anticipated for MPS nanowires, even after ion implantation, as evidenced by devices in insets (a)

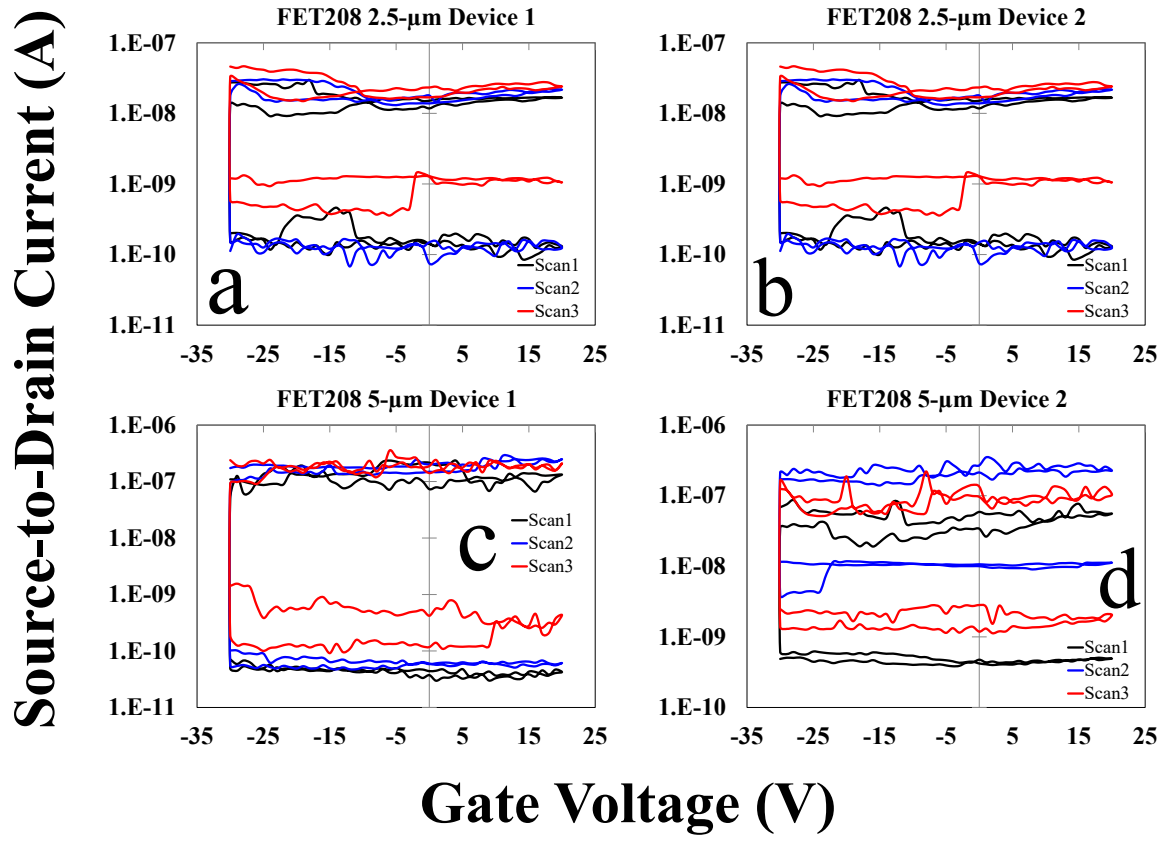


Figure 4.8: TS NWs Ion Implanted n-type - Targeted Doping of 10^{19} - As received

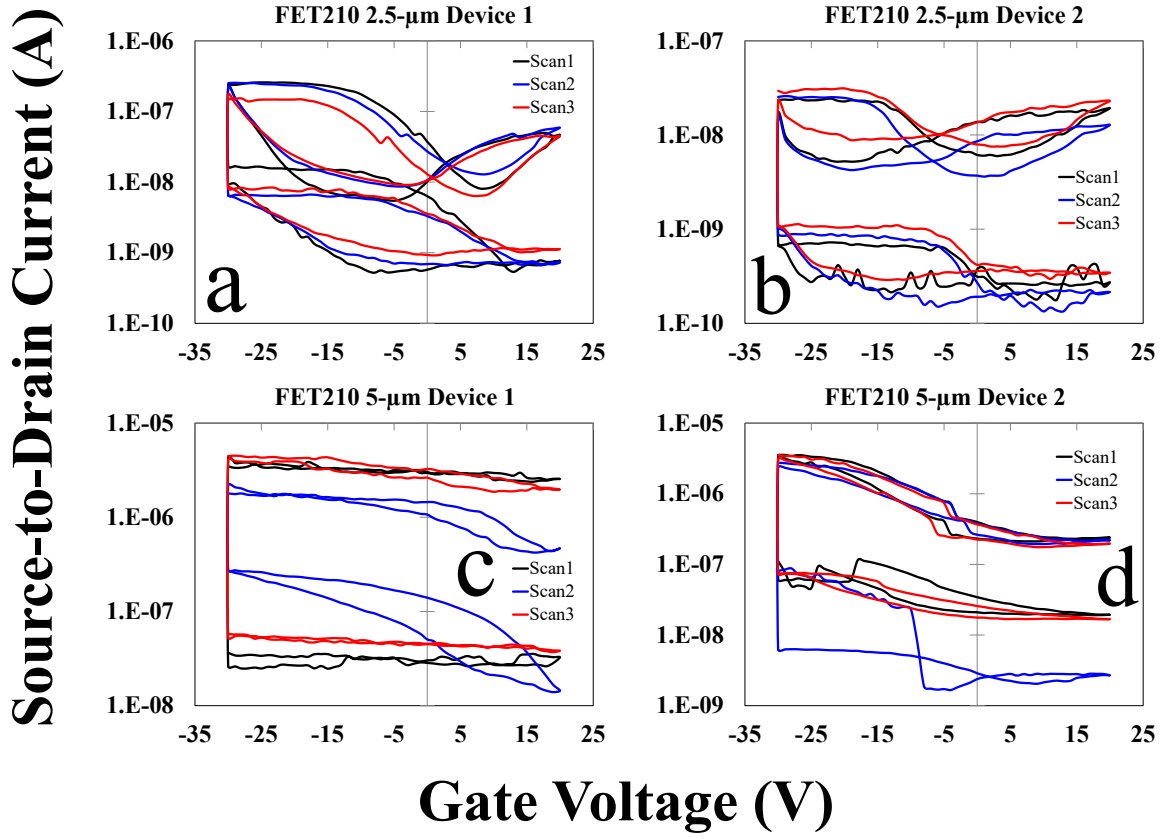


Figure 4.9: TS NWs Ion Implanted n-type - Targeted Doping of 10^{19} - Annealed at 300°C in forming gas

and (b) of FET 191 in Figure 4.5 on page 96.

Figure 4.11 shows the FET performance of MPS nanowires ion implanted with phosphorus at a targeted doping level of 10^{19} and annealed at 300°C in forming gas. Again, it is seen that the device behaviors are disparate and do not show a clear trend, with some device exhibiting gate modulation with hysteresis, (a) and (c), and others are show no gating and have relatively large currents.

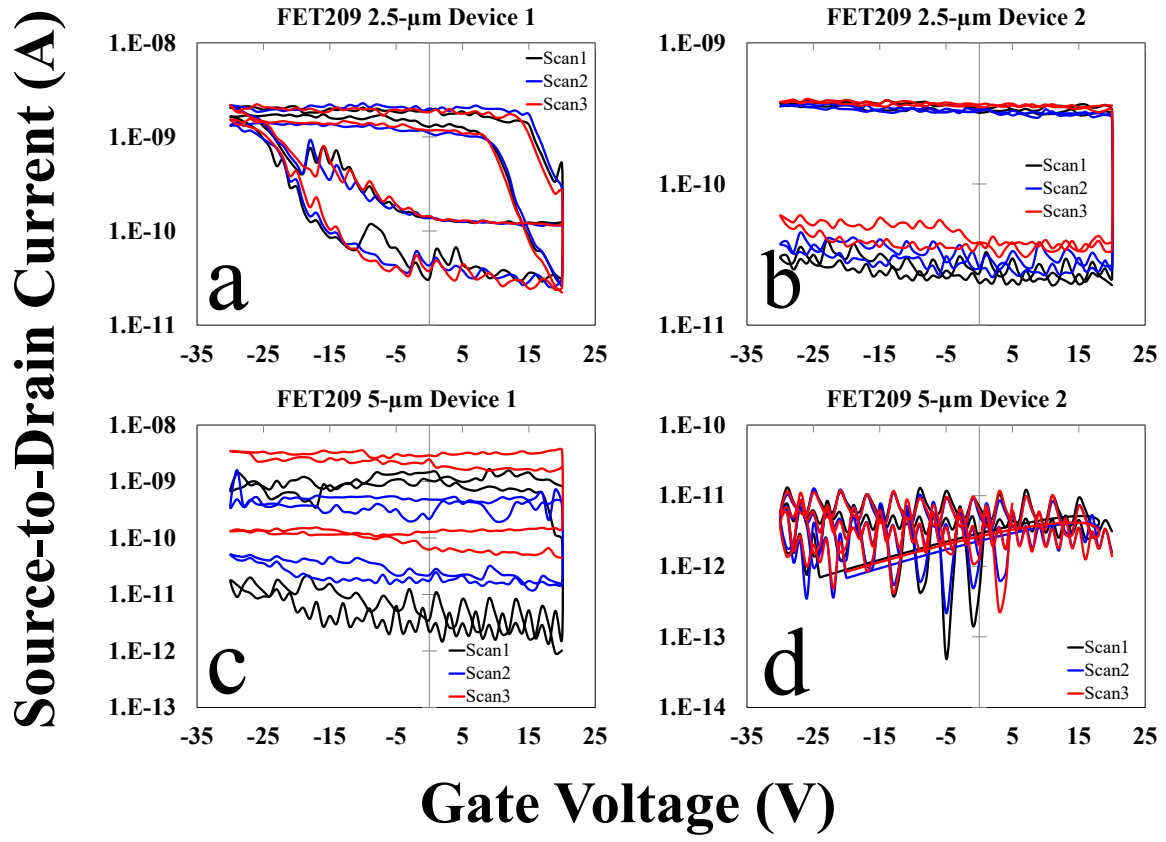


Figure 4.10: MPS NWs Ion Implanted n-type - Targeted Doping of 10^{19}

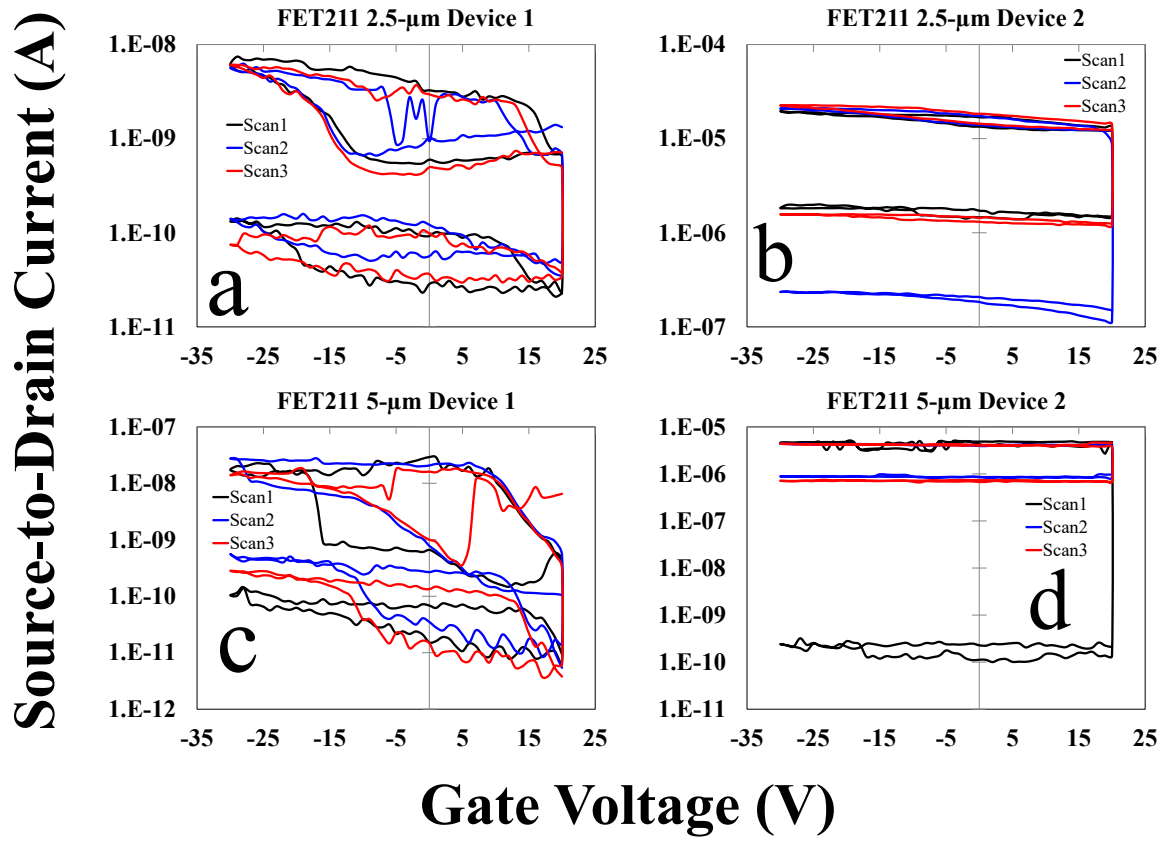


Figure 4.11: MPS NWs Ion Implanted n-type - Targeted Doping of 10^{19} - Annealed at 300°C in forming gas

4.3.3 FET Data - Third Round of Ion Implantation

Following some deliberation after the second round of ion implantation, the decision was made to focus only on the MPS SiNWs. An in-depth study of the FET performance under various annealing conditions was performed.

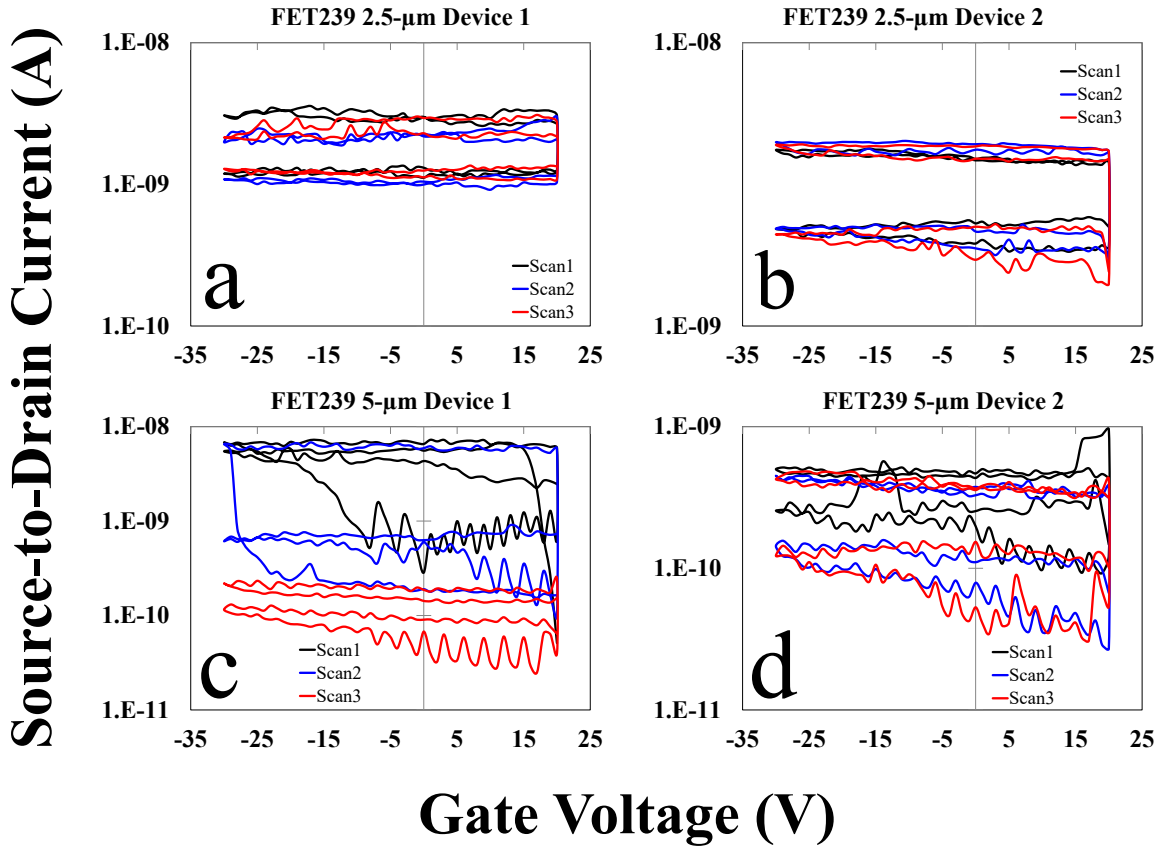


Figure 4.12: MPS NWs Ion Implanted n-type - Targeted Doping of 10^{19}

Figure 4.12 shows the FET performance of MPS nanowires ion implanted with phosphorus at a targeted doping level of 10^{19} . Once again, anomalous and disparate device performances are observed with little correlation or trend among

devices. Currents are relatively low, and the devices mostly show no gate response.

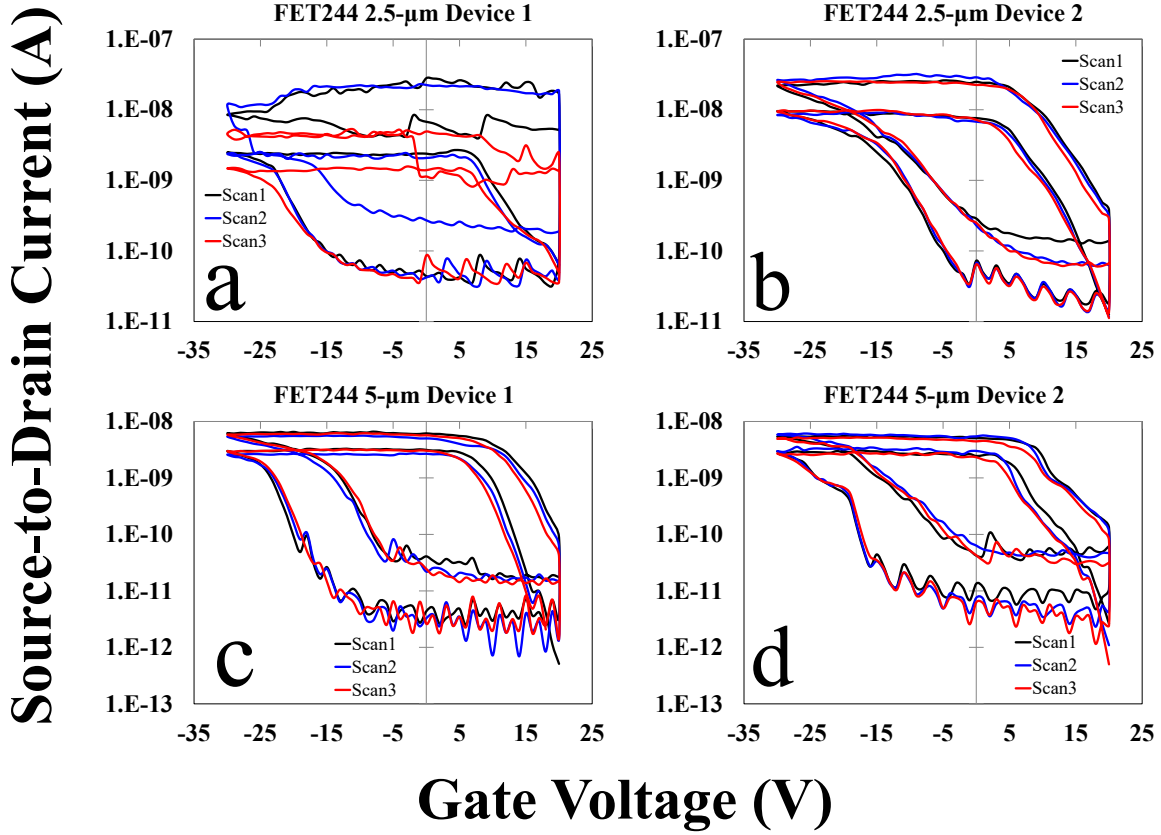


Figure 4.13: MPS NWs Ion Implanted n-type - Targeted Doping 10^{19} - Annealed at 500°C in forming gas

Figure 4.13 shows the FET performance of MPS nanowires ion implanted with phosphorus at a targeted doping level of 10^{19} that were subsequently annealed at 500°C in forming gas. These devices in contrast display behaviors that are akin to as-synthesized MPS nanowires, in which broad hysteresis is observed. However, in contrast to as-synthesized MPS nanowires, these devices present relatively low currents in the nanoamp range. One possible explanation for this behavior is that

higher temperature annealing in the reducing atmosphere eliminates some of the surface defects that are present after implantation but also reduces the number of sites that give rise to charging and are responsible for the hysteresis observed in as-synthesized MPS nanowires, thus reducing the device current while still displaying hysteresis.

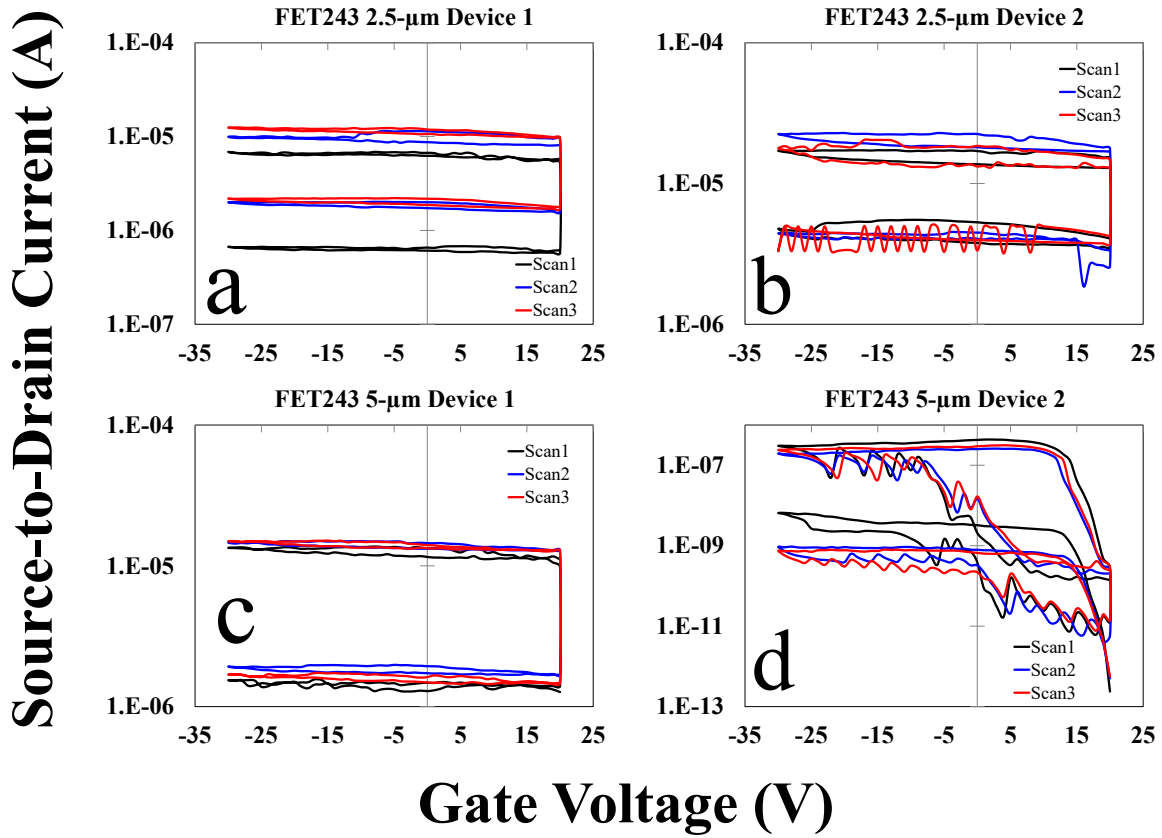


Figure 4.14: MPS NWs Ion Implanted **n-type** - Targeted Doping 10^{19} - Annealed at 500°C in nitrogen

Figure 4.13 shows the FET performance of MPS nanowires ion implanted with phosphorus at a targeted doping level of 10^{19} that were subsequently annealed

at 500°C in high-purity nitrogen. In this case, device currents are quite high in the microamp range, but no gate modulation is observed nor is there hysteresis. This evidence is again suggestive that annealing has a strong effect on the surface properties of the nanowires. It is possible that, if any dopant effects are present, they result in quasi-metallic conductivity, as might be the case for *in-situ* doped nanowires at high dopant concentrations. However, this is only a conjecture based on inferences from the data presented here and in Chapter 3.

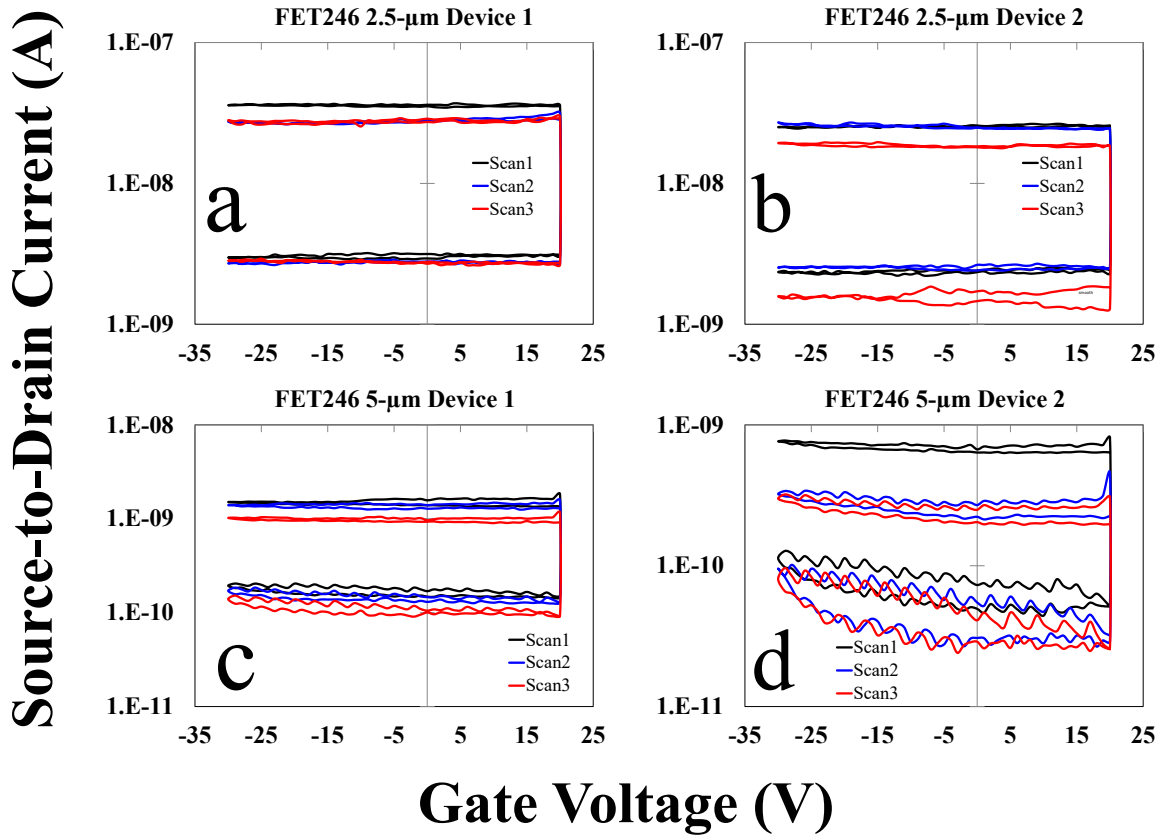


Figure 4.15: MPS NWs Ion Implanted **n-type** - Targeted Doping 10^{19} - Annealed at 500°C in air

Figure 4.15 shows the FET performance of MPS nanowires ion implanted with phosphorus at a targeted doping level of 10^{19} that were subsequently annealed at 500°C in air. These device characteristics are similar to those in Figure 4.13, with the exception that device currents that are somewhat lower no gate modulation is observed nor is there hysteresis.

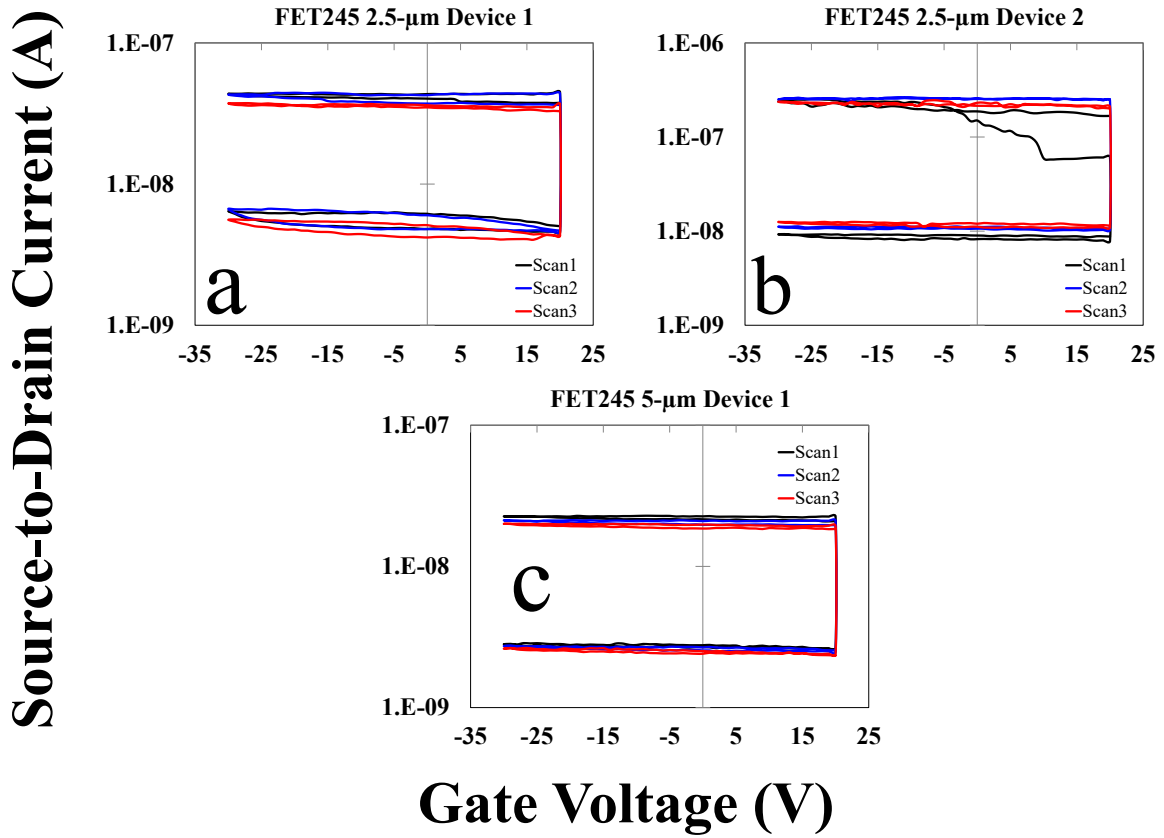


Figure 4.16: MPS NWs Ion Implanted n-type - Targeted Doping 10^{19} - Annealed at 800°C in forming gas

Figure 4.16 shows the FET performance of MPS nanowires ion implanted with phosphorus at a targeted doping level of 10^{19} that were subsequently annealed at

800°C in forming gas. Again, these devices show no hysteresis and no gate modulation, and device currents are low but comparable to those in the previous device.

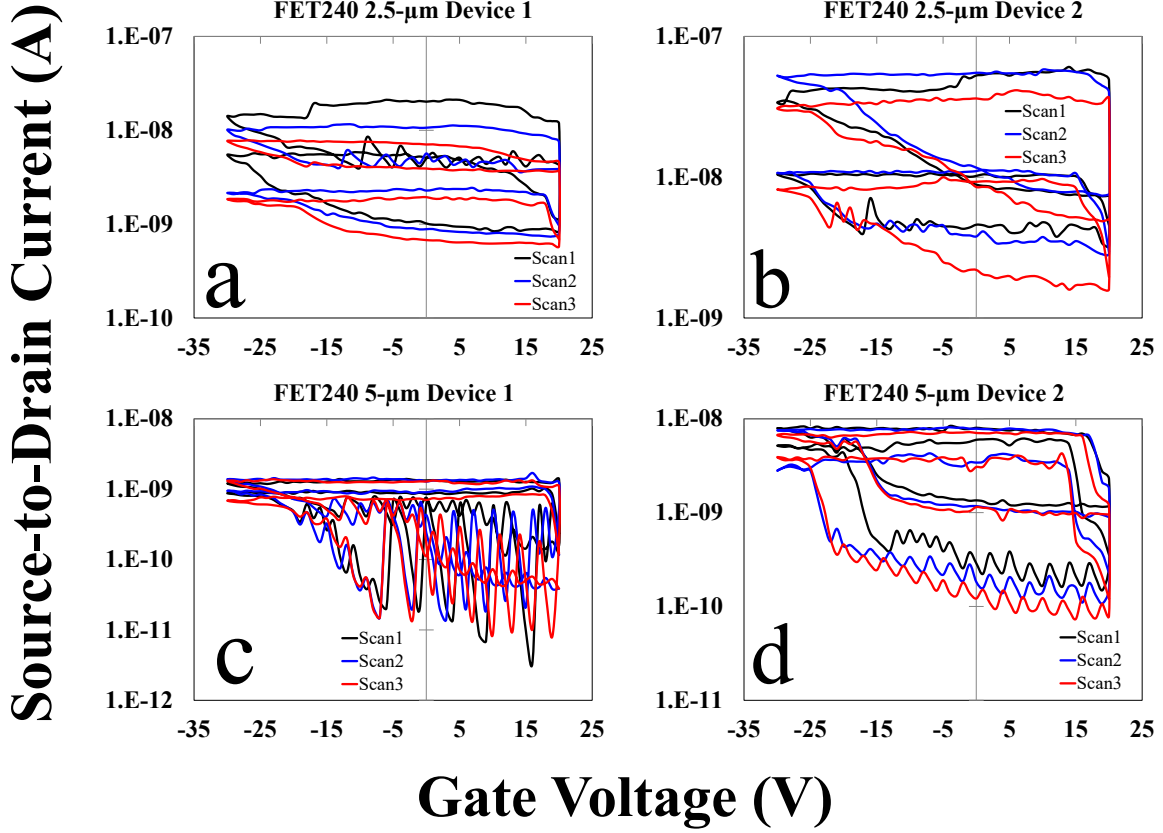


Figure 4.17: MPS NWs Ion Implanted **n-type** - Targeted Doping 10^{19} - Etched in *aqua regia*

Lastly, Figure 4.17 shows the FET performance of MPS nanowires ion implanted with phosphorus at a targeted doping level of 10^{19} that were subsequently etched in *aqua regia*. The effect of etching is to oxidize the surfaces of the nanowires and to remove the Au seeds, which can lead to trap states in the bandgap of Si. In this case, the effect of etching is produce hysteresis in the devices, but no effect is

seen on device currents compared to as-received implanted nanowires.

Discussion In general, the device behaviors are quite anomalous, and there exists a great deal of variance among devices, even those located on the same chip and made with the same portion of nanowires subjected to the same processing. A potential explanation for this seemingly anomalous behavior and broad variance among similar devices made from the same batch of implanted nanowires, is that implantation does not affect the nanowires uniformly and the thickness of the mat shields a great deal of the mats volume from ion bombardment. Thus, nanowires located nearest to the surface of the mat received a comparatively strong dosage of ions and thus the concentration will be higher. The depth penetration profile [121] has a long decaying tail, but at the implantation conditions — namely accelerating voltage of 200 keV and dosage of approximately 1.9×10^{16} ions cm^{-2} — the dopant concentration is extremely low even at 1 μm from the surface¹⁰, approximately 9.89×10^{-1} atoms cm^{-3} .

In addition, the damage suffered by the nanowires that are near the surface of the mats should also be comparatively more severe than that suffered by the nanowires that are near the wafer interface.

However, when FET devices are confected, nanowires are drawn from a portion of the mat and dispersed together in solution, and it is not possible to isolate nanowires

¹⁰For the purposes of calculation, because the mats are approximately 90% void space, and whereas the ion implantation calculations [121] use models that were developed for bulk silicon, the target thickness used for the calculation was 1 μm , rather than the 10 μm thickness of the mats used during this round of ion implantation

are any particular depth in the mate. This would be extremely impractical, even if such a procedure were possible. And the fact that implantation effects vary with surface depth is one of the key conceptual failings of ion implantation on nanowire mats, given that fact that the mats are randomly oriented networks of nanowires that themselves can vary in nanowire density within the same mat.

Therefore, when attempting to compare the FET performance of similar devices confected with the same batch of nanowires on the same device wafer, very broad variances occur, and anomalous effects should be expected.

4.3.4 EPR characterization

EPR results from ion implanted MPS nanowires show no sign of conduction electrons (i.e., no clear peak is present at $g = 1.998$). Subsequent annealing of the ion-implanted nanowires had little effect on the EPR signal vis-à-vis conduction electrons, but the spectra do appear show changes in the surface defects of the nanowires after annealing, perhaps as a results of rearrangement of surface atoms and the formation of oxide (annealing in air) and the elimination of Si dangling bonds at the surface (passivation with hydrogen via annealing in forming gas) that lead to a difference in the relative numbers of paramagnetic centers associated with the Si nanowire surface, i.e., P_B and E -type defect centers, such as the E' and EX centers [68, 69, 122–126]. Some supplementary figures are included in Appendix B beginning on page 134.

In Figure 4.18, a composite of several spectra are shown. At the bottom in the subfigure labeled “As-received”, a broad peak is seen centered at approximately 3333 G. This peak corresponds to a g-factor of approximately $g = 2.006$, attributed to

P_B centers, or Si dangling bonds. The peak is of extremely high intensity compared to as-synthesized nanowires, those peak intensity is not always attributable to spin concentrations alone. The breadth and intensity of the peak related to Si dangling bonds is likely an indication of damage to the nanowires suffered as a result of ion implantation.

Furthermore, the effect of annealing is to shift the peak toward a position more closely centered around a g-factor of $g = 2.002 - 2.000$, which is indicative of the formation of centers related to silicon dioxide defects and highly localized Si dangling bonds in bulk silicon. These paramagnetic defects are related to silicon vacancies in SiO_2 that has an excess of oxygen [127]. In addition, E' centers are also related to defects arising in Si/SiO_x systems.

Annealing in air appears to strongly favor formation of oxide related defects as observed by the strong shift in the subfigure located second from the top labeled “500°C in air”.

Annealing in forming gas (H_2/N_2) also results in a shift away from the spectrum centered around Si dangling bonds, however there is stronger asymmetry in the signal, which might be a result of contributions from Si dangling bonds not located at the nanowire surfaces (i.e., a convolution of resonance signals). The same is true of the spectrum collected from MPS nanowires after annealing in high-purity nitrogen gas.

The top spectrum shows the signal acquired from nanowires after annealing at 800°C in forming gas. The peak does not exhibit strong asymmetry, which might

indicate resonance signals from closely related defects centers. It has been reported that high temperature annealing in hydrogen passivated P_B dangling bond centers [127]. Thus, it is likely that these annealing conditions dramatically reduce the density of P_B . In addition, the reducing atmosphere of formation gas may diminish the presence of oxide-related surface defects. The observed resonances would then only be attributed to defect centers in the core of the nanowires or interfacial phenomena that are unaffected by annealing. If there is a contribution from P donor states, the spin density is not sufficiently high enough to be visible, given the strong resonance intensities resulting from other high-density spins.

Furthermore, the EPR samples suffer from the same inability to isolate nanowires that have received a uniform dosage, as in the argument made for the inhomogeneities observed in FET data. Not all the nanowires in the mat received a uniform ion implantation dosage, but it is not possible to isolate nanowires from the top surface of the mats, which likely have received closer to a uniform dosage, than the nanowires at the bottom of the mat.

Lastly, TEM characterization of samples taken from the MPS and TS nanowire mats after implantation at a target doping level 10^{19} do not show signs of amorphization and have the appearance of as-synthesized nanowires¹¹. This fact is further indication that the effects of ion implantation are subtle, though from EPR characterization the effects on nanowire surfaces are quite widespread. This stands to reason, given that nanowires have a high surface area-to-volume ratio. Alterations

¹¹ *Vide* Appendix A on page 122

to the surfaces of the nanowires would not necessarily be apparent in TEM, which is more adept at characterizing volumes of materials via electron interactions as they pass through, albeit very small volumes, of material.

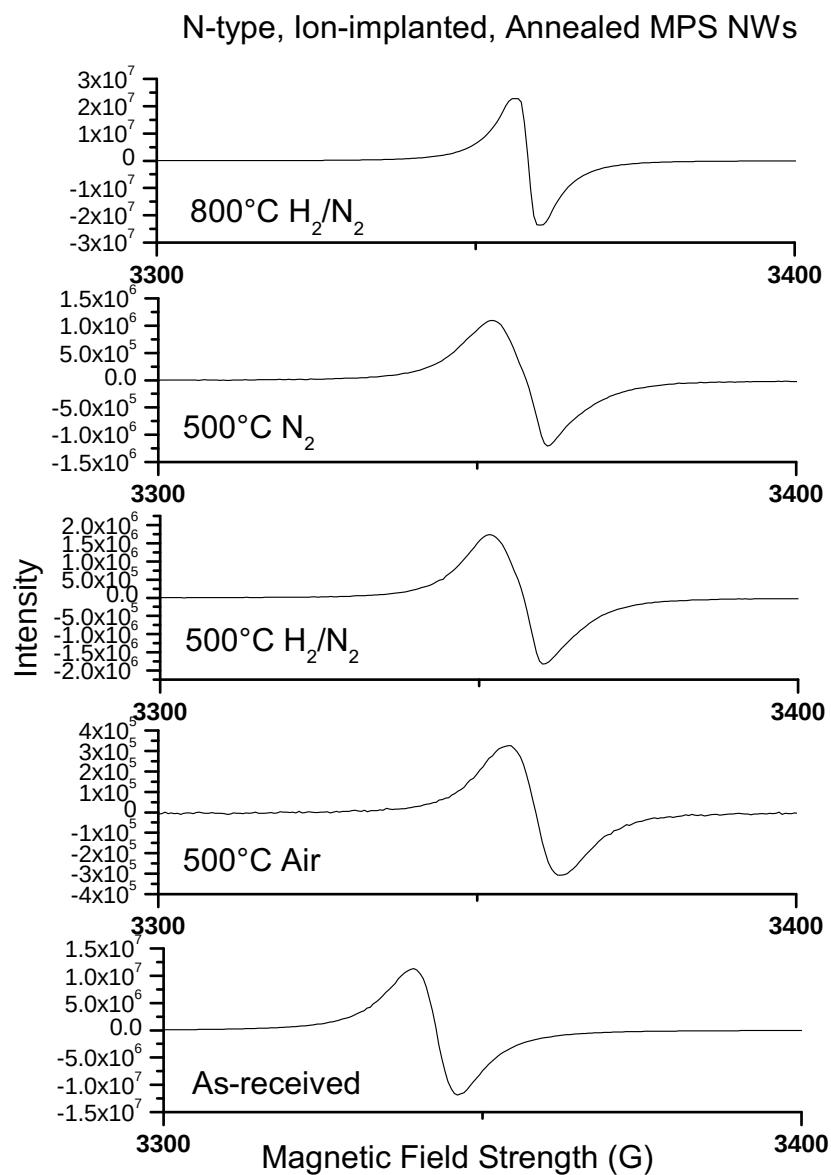


Figure 4.18: Composite figure of EPR spectra from ion-implanted MPS nanowires as received and after annealing at different temperatures and atmospheres, as noted in each subfigure.

4.4 Conclusions

Ion implantation was performed on nanowire mats in an attempt to incorporate phosphorus doping. A series of FET devices were made to characterize the transfer properties of these materials, both as-received and after annealing. The device performances were disparate, and few trends could be discerned. Because the FET behavior of nanowires is strongly associated with the presence of surface states and defects, it is likely that ion implantation generates these defects, which can be altered through annealing, but without the emergence of desired n-type FET behavior.

EPR characterization tells a related story about the emergence and evolution of surface and bulk defects in silicon and, likely, defective silicon oxide, as observed through the detection of broad, high-intensity, resonance peaks that appear to shift as a result of annealing at different temperatures and in different atmospheres. The effects of annealing alter the number and distribution of these paramagnetic defects. P donor states, though, are not observed, as they would be too low in spin concentration, if present, to make an appreciable contribution to the resonance spectrum.

Further work must be done to thoroughly characterize the nature of the changes. Ion-implanted nanowire mats are perhaps not the best medium for the study of the effects of ion irradiation of silicon nanowires. A better method to isolate the changes concomitant with ion implantation of nanowires would be to implant a single layer of nanowires on a substrate, or nanowires individually isolated, say from a dilute dispersion, such that a more uniform implantation profile can be achieved. The effects on ensembles of nanowires that have received a uniform dosage, could

more precisely reveal the evolution of the defect centers observed here.

4.5 Acknowledgements

This work was a team effort by the Korgel nanowire team. The author wishes to acknowledge and thank Drs. Aaron Chockla and Timothy Bogart for designing the frame the frame for ion implantation and Jim Smitherman and Butch Cunningham in the machine shop for constructing the frame, as well as Catherine Shipman, Alejandro Maurer, and Alex Eukel for assisting in the synthesis of large quantities of nanowires for elaboration of the mats. Dr. Chockla was also the main point of contact with Core Systems. Dr. Vince Holmberg is also acknowledged for his insights and discussions in adjusting the annealing conditions.

Chapter 5

Conclusions

“The scientific man does not aim at an immediate result. He does not expect that his advanced ideas will be readily taken up. His work is like that of the planter — for the future. His duty is to lay the foundation for those who are to come, and point the way. He lives and labors and hopes.”

— Nikola Tesla, “Radio Power Will Revolutionize the World” in *Modern Mechanics and Inventions* (July 1934)

In many ways, silicon nanowires are mostly surface. Some describe these materials as one-dimensional (in the sense of a 1D nanostructure), but the studies presented herein show that silicon nanowires are indeed multi-dimensional.

These studies have shown that it is possible to dope silicon nanowires *in-situ* with phosphorus by simple addition of a phosphorus precursor into the reaction solution used for SFLS growth of nanowires.

EPR studies reveal that P donor states are incorporated into the silicon nanowires, but FET studies do not present a clear picture of n-type behavior, and many features are observed in the transfer curves that cannot be accounted for entirely. Rather, inferences can be made regarding the surface properties of the silicon

nanowires and the effects that surface states might have on the FET characteristics, based on studies conducted in the literature.

Ion implantation also reveals a wide breadth of phenomena related to surface defects. FET studies demonstrate a wide range of variability in the behaviors. Furthermore, widespread amorphization of the nanowires is not observed, yet EPR reveals the presence of defects related to oxides and a high density of dangling bond centers.

In the research presented here, the reader should come away with a glimpse of silicon nanowires as a very complex system that is worthy of study, especially where surface phenomena are concerned.

Future studies could focus on the determination of the exact nature of the surface defects present in silicon nanowires doped *in-situ* using surface sensitive techniques such as X-ray photoelectron spectroscopy to reveal the state of oxidation of these silicon nanowires or scanning probe microscopy of single nanowires in order to pin point with great spatial resolution the differences in nanowire conductivity. In addition, ion implantation should not be abandoned as a means to dope nanowires, but a better understanding must be gained of the evolution of surface defects. This understanding might be achievable through more rigorous EPR studies on small ensembles of isolated nanowires on a substrate, rather than through the use of mats that are non-uniformly implanted.

In addition, this research provides even more fodder for the development of solution-based processing of silicon nanowires for their eventual incorporation of

solution-processable displays and large-area devices. Thin-film devices containing *in-situ* doped silicon nanowires could some day be used in developing sensors embedded into textiles or fabrics, given that even at lab scale as has been shown here, doped nanowire mats can be produced with relative ease.

Appendices

Appendix A

Supplementary electron microscopy data

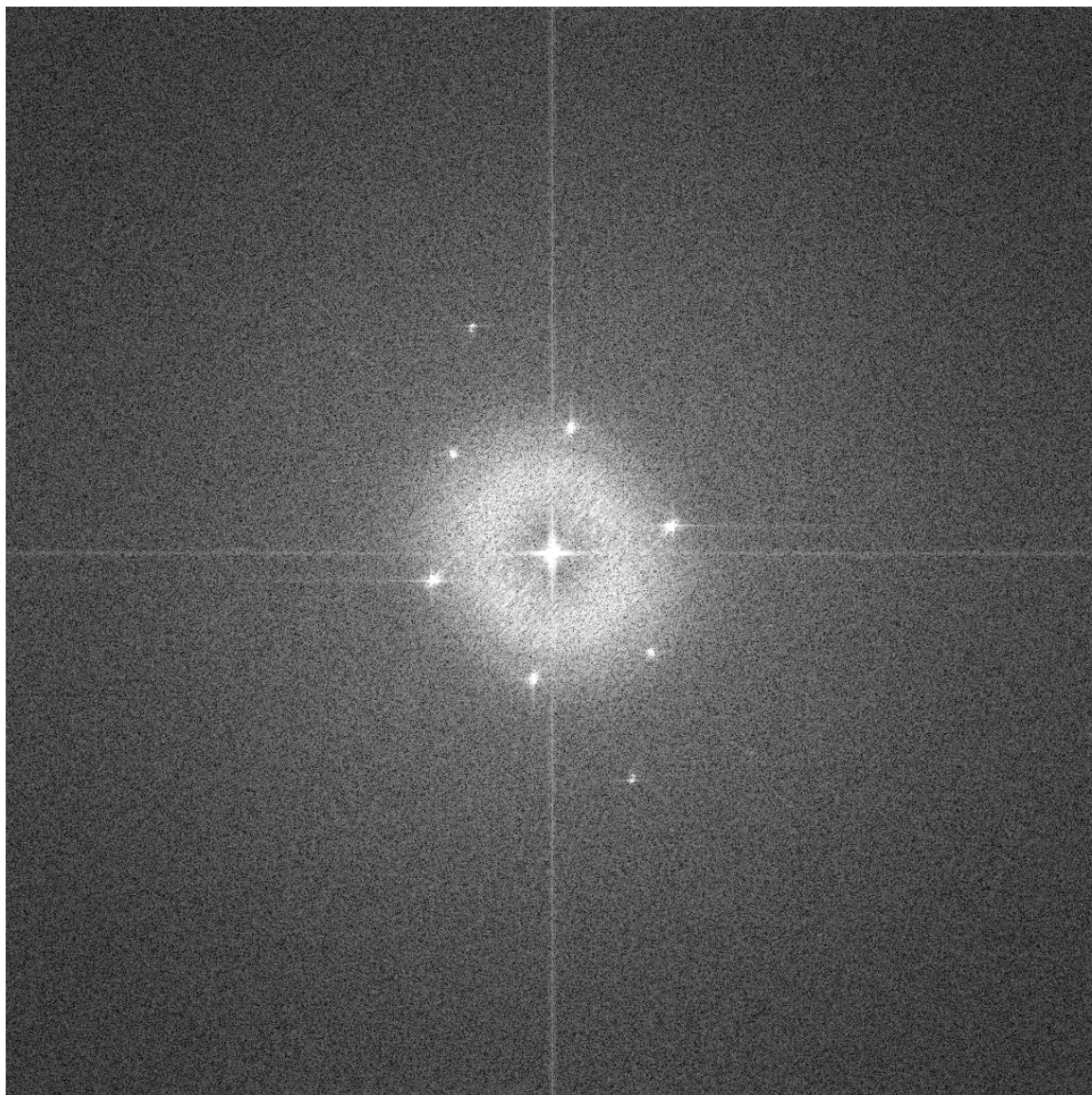


Figure A.1: Fast Fourier Transform (FFT) of the HRTEM image in Figure 2.7 located in Chapter 2 on page 35

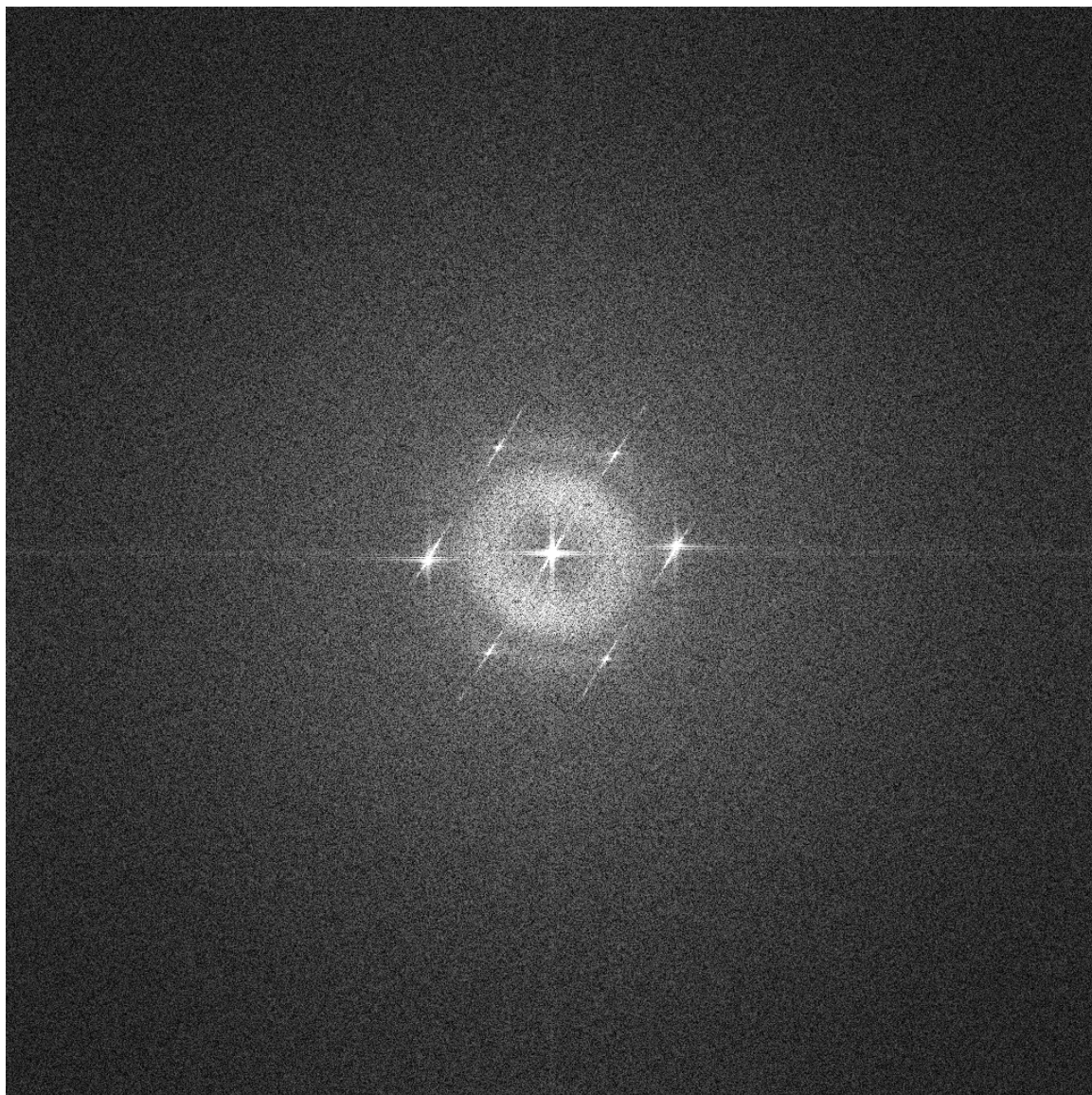


Figure A.2: Fast Fourier Transform (FFT) of the HRTEM image in Figure 2.9 located in Chapter 2 on page 37.

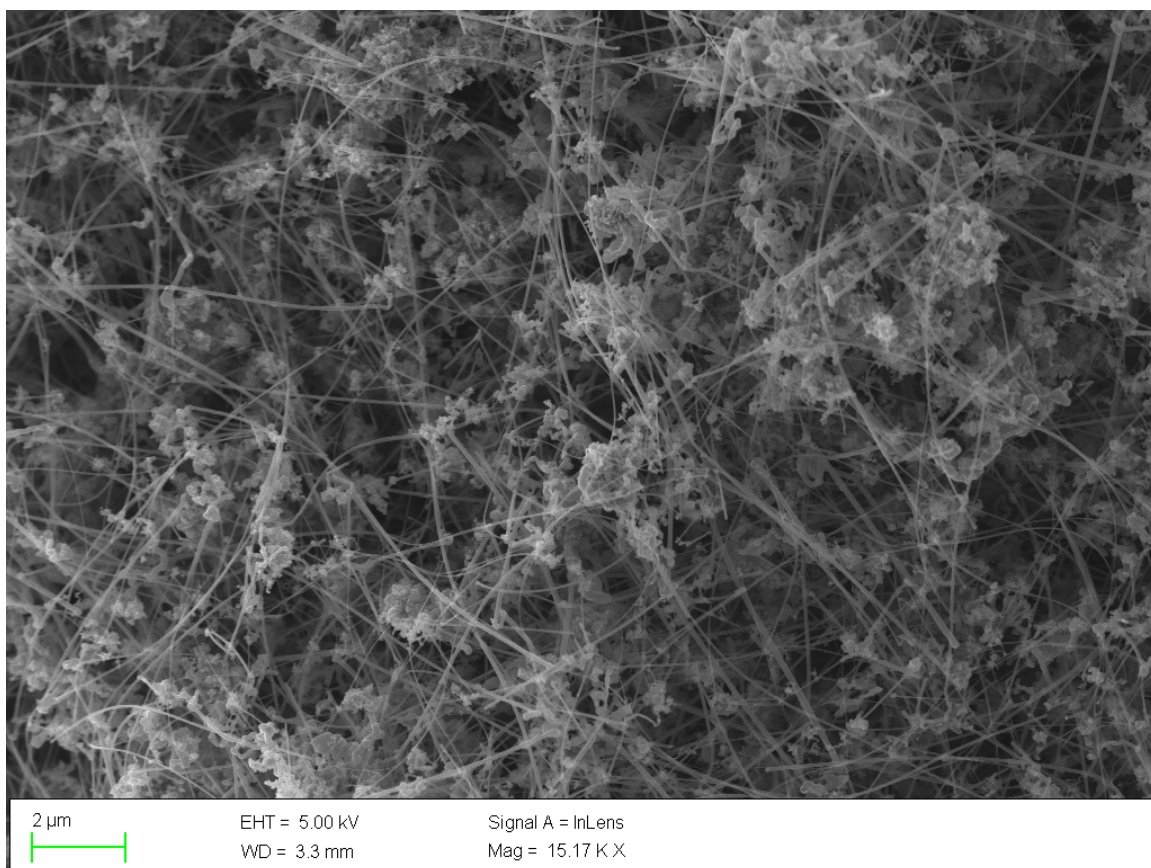


Figure A.3: SEM micrograph of TS nanowires doped with $\text{P}(\text{SiMe}_3)_3$ at a Si:P mole ratio of 5.5×10^3 .

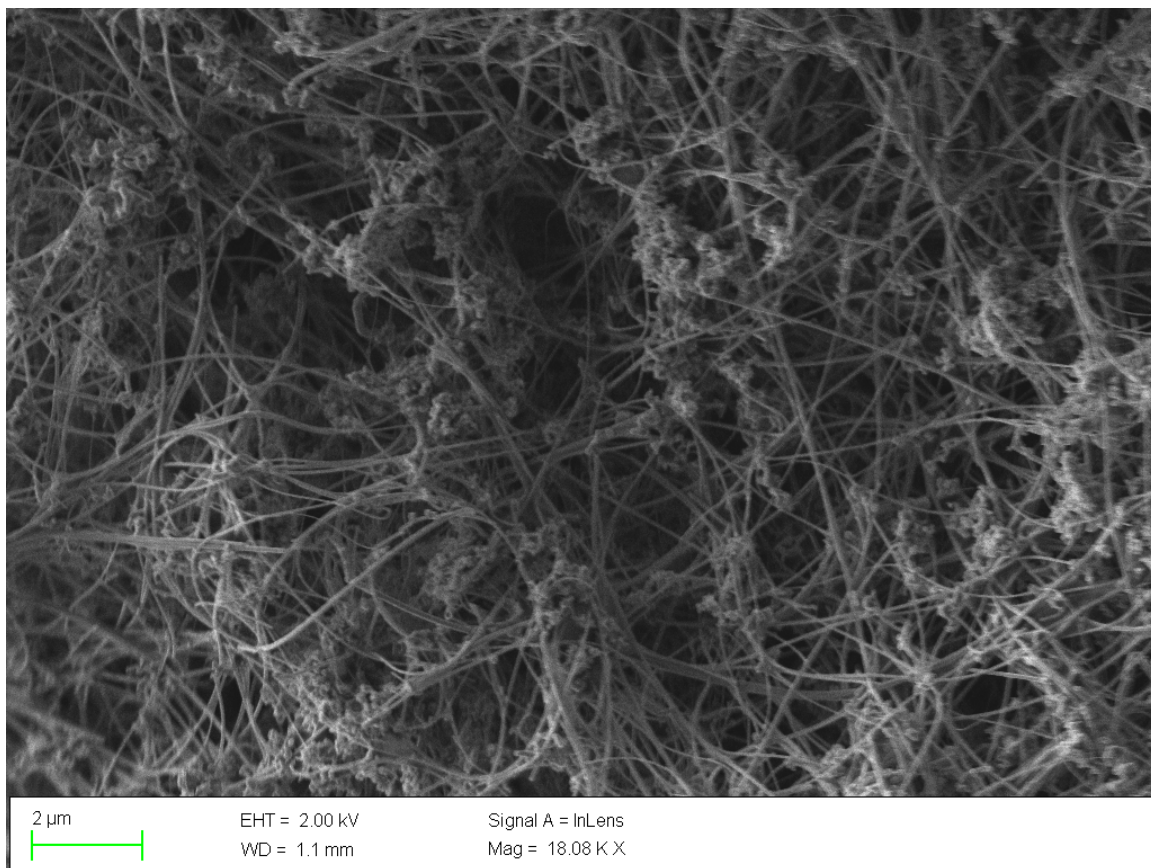


Figure A.4: SEM micrograph of TS nanowires doped with $\text{P}(\text{SiMe}_3)_3$ at a Si:P mole ratio of 5.5×10^4 .

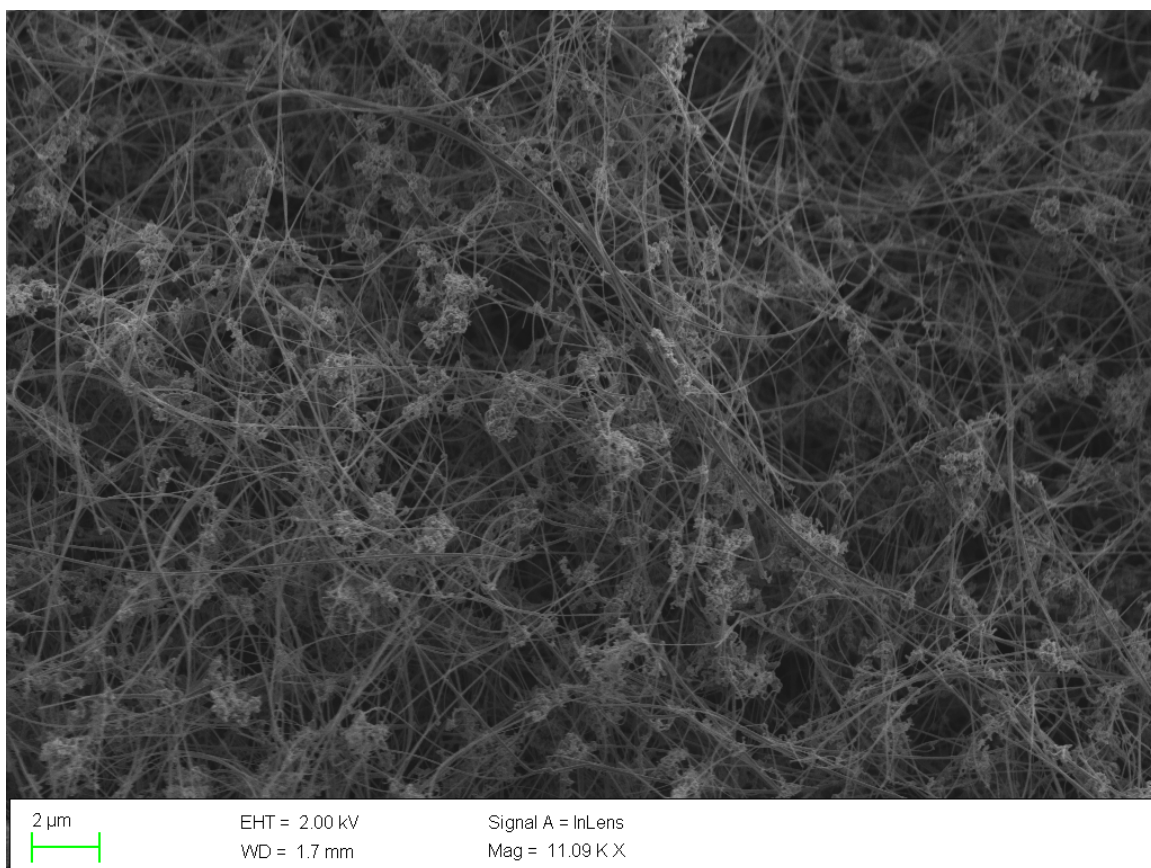


Figure A.5: SEM micrograph of TS nanowires doped with $\text{P}(\text{SiMe}_3)_3$ at a Si:P mole ratio of 5.5×10^5 .

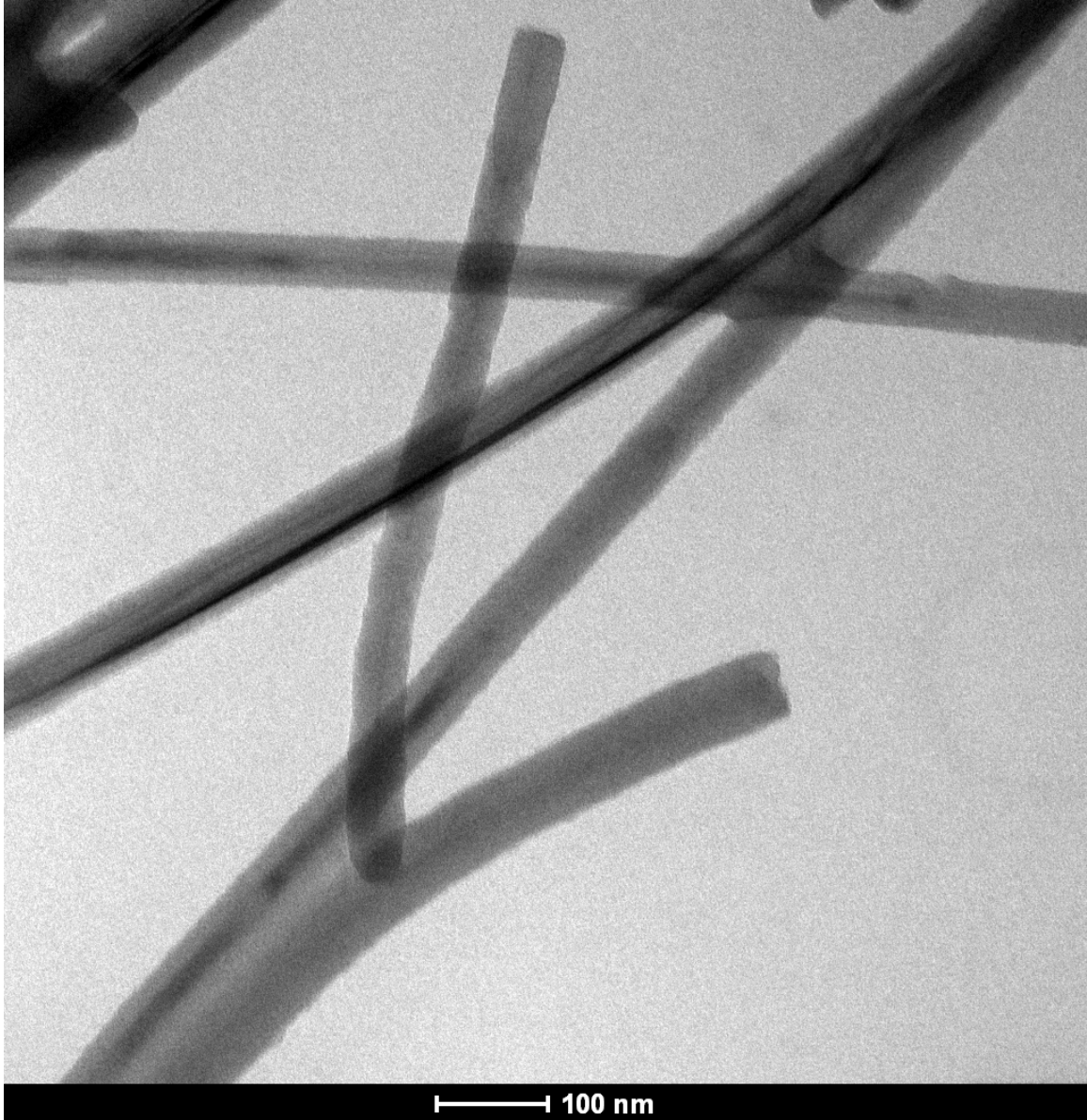


Figure A.6: TEM micrograph of MPS nanowires ion implanted at a targeted doping concentration of 10^{19} atoms cm^{-3} .

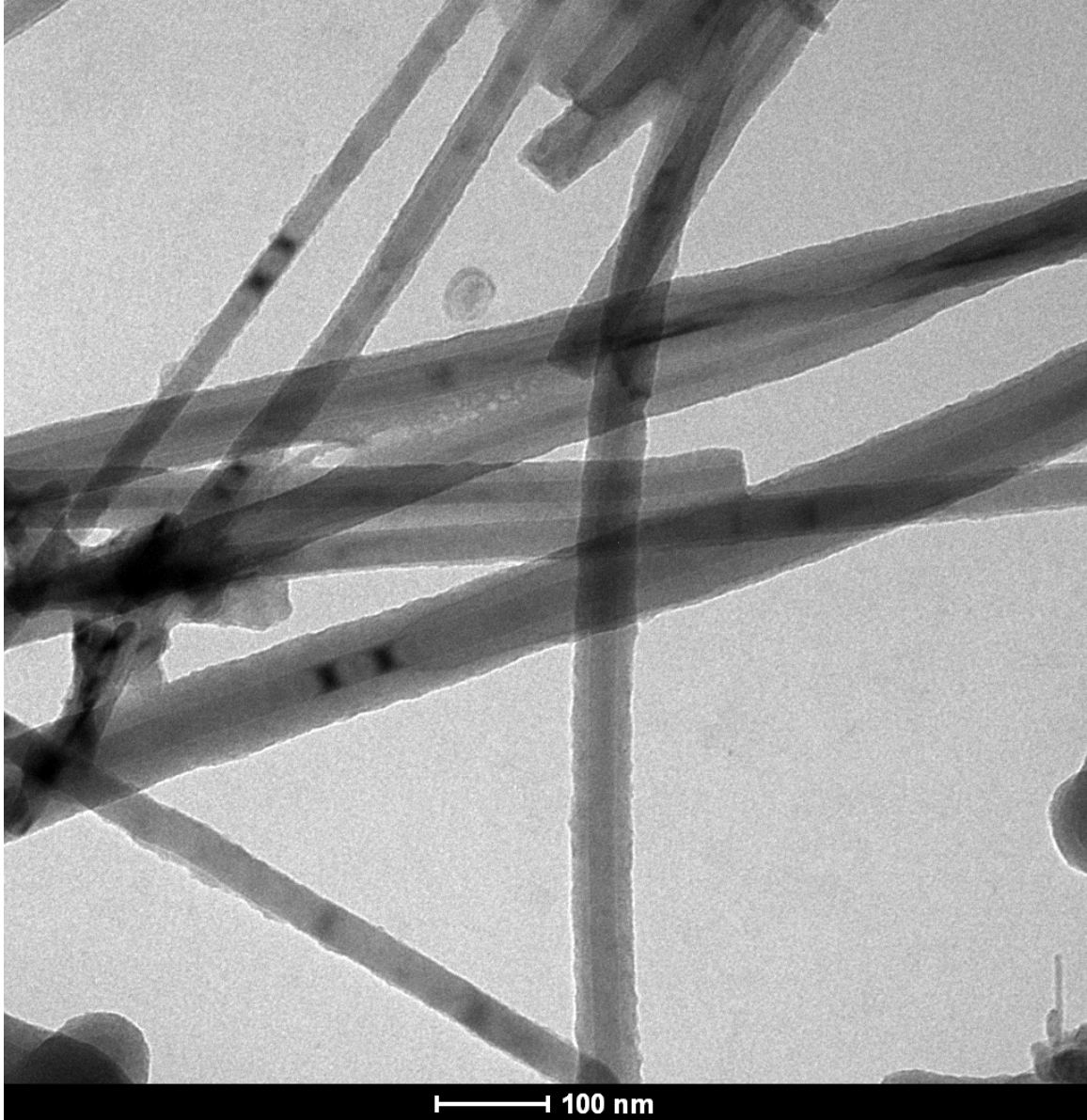


Figure A.7: TEM micrograph of MPS nanowires ion implanted at a targeted doping concentration of 10^{19} atoms cm^{-3} .

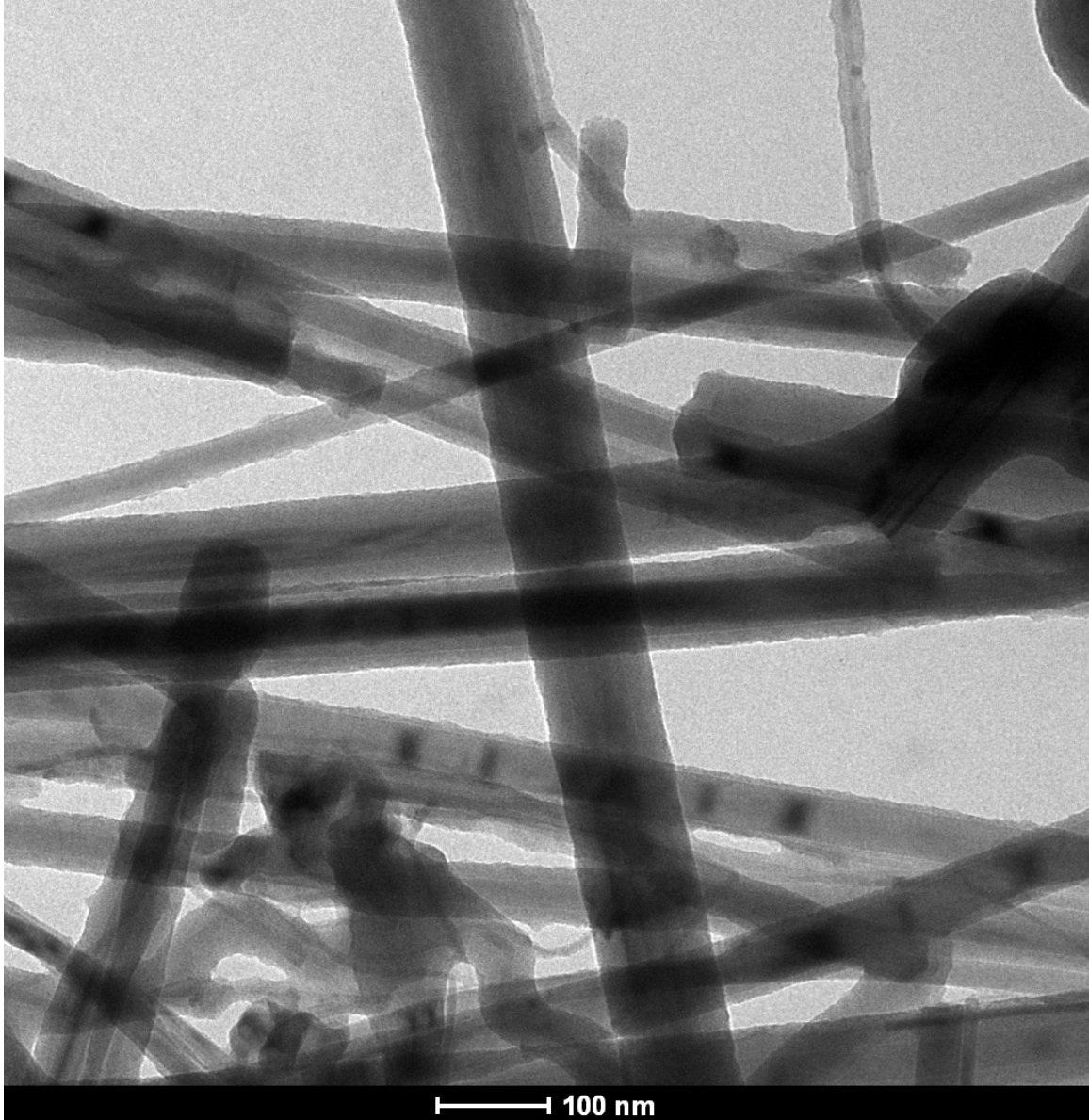


Figure A.8: TEM micrograph of MPS nanowires ion implanted at a targeted doping concentration of 10^{19} atoms cm^{-3} .

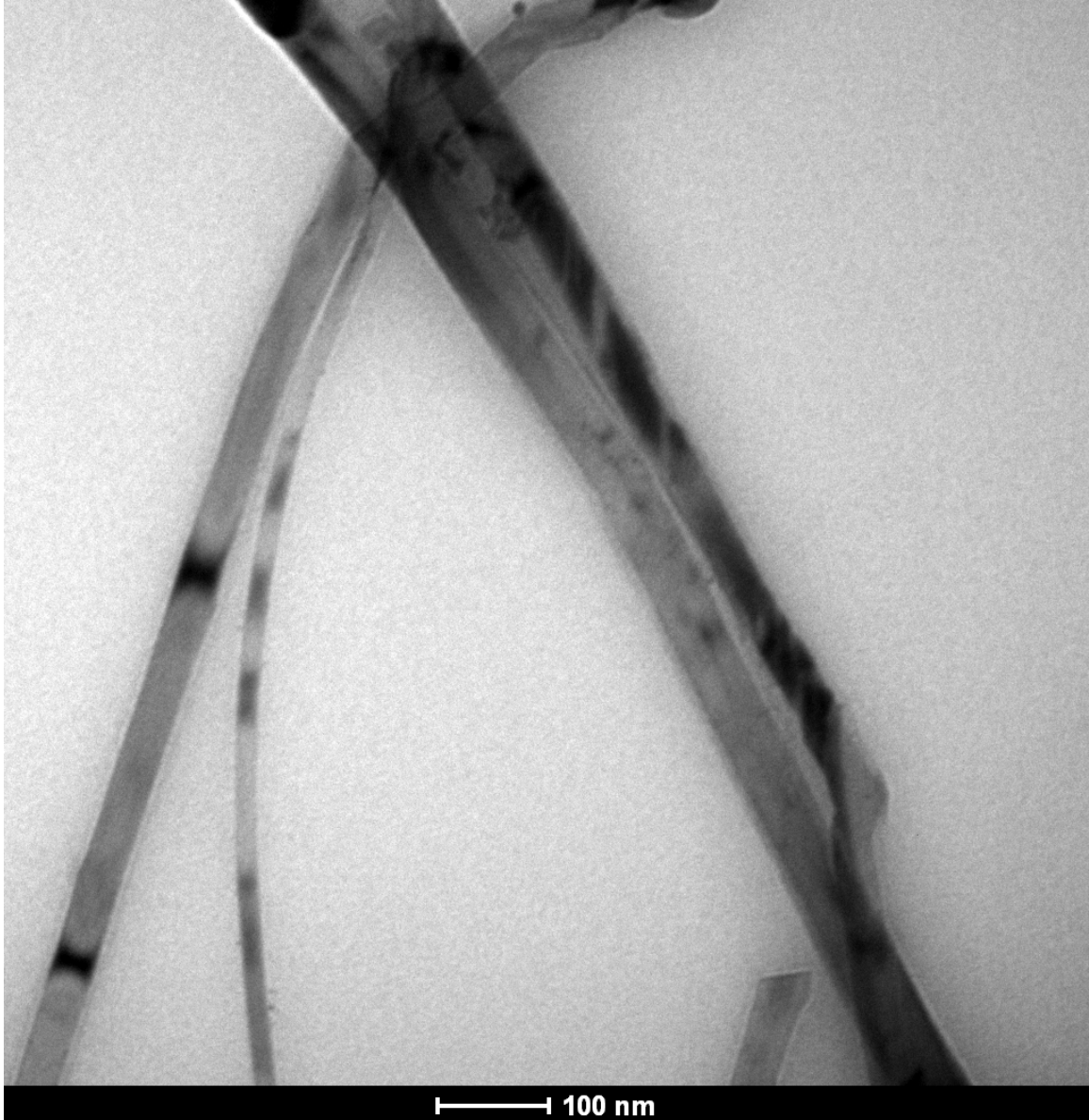


Figure A.9: TEM micrograph of TS nanowires ion implanted at a targeted doping concentration of 10^{19} atoms cm^{-3} .

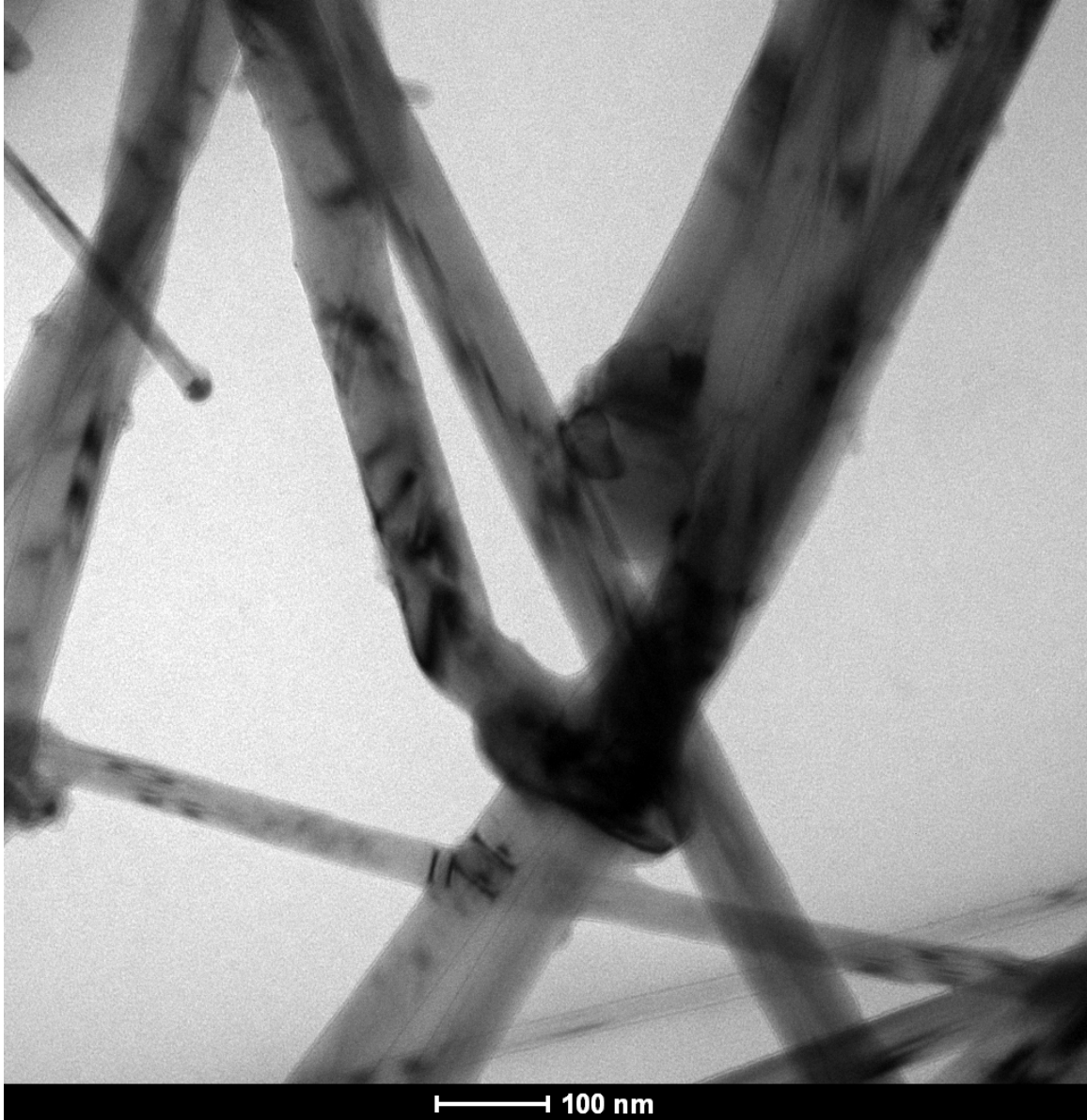


Figure A.10: TEM micrograph of TS nanowires ion implanted at a targeted doping concentration of 10^{19} atoms cm^{-3} .

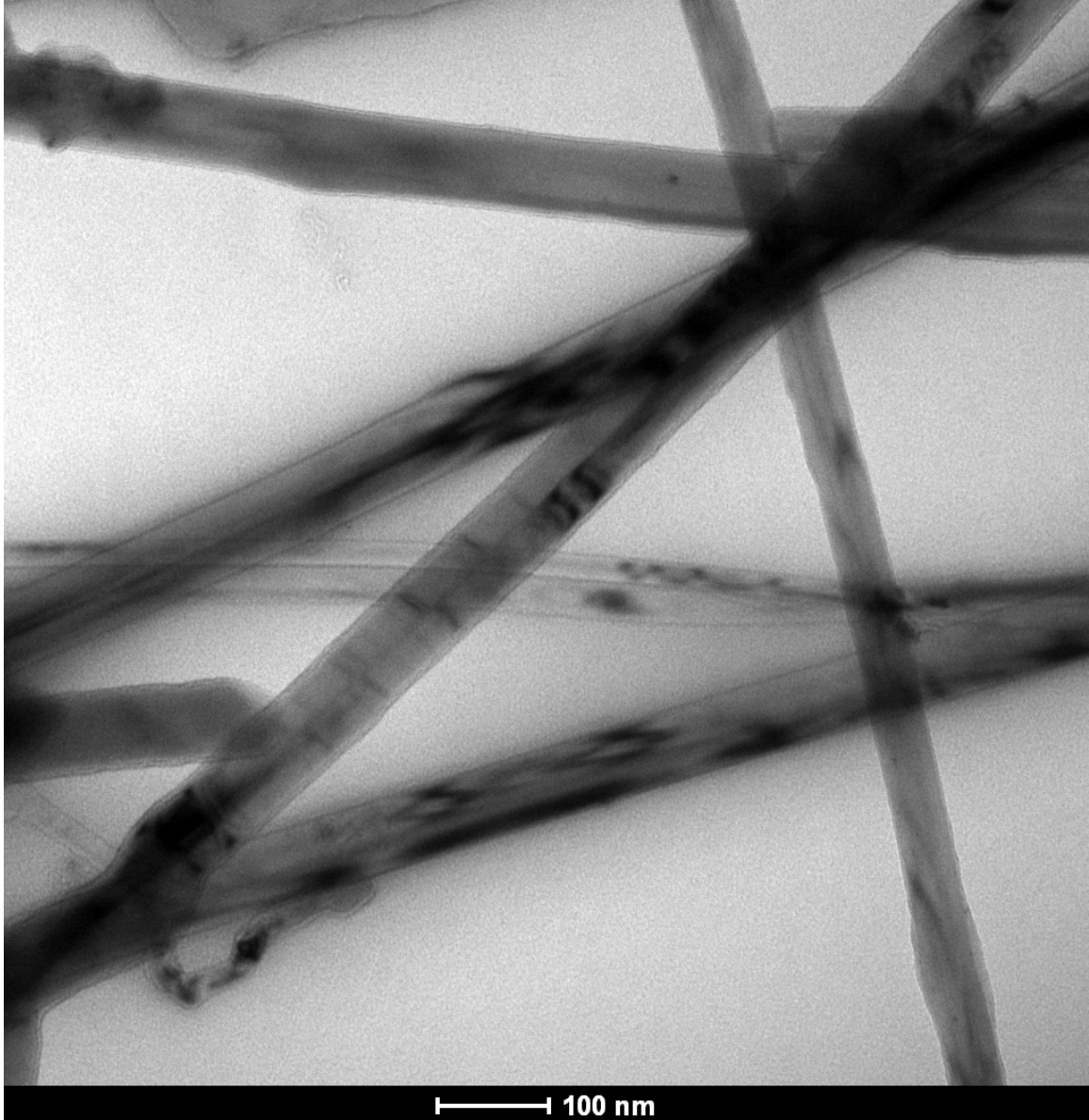


Figure A.11: TEM micrograph of TS nanowires ion implanted at a targeted doping concentration of 10^{19} atoms cm^{-3} .

Appendix B

Supplementary EPR data

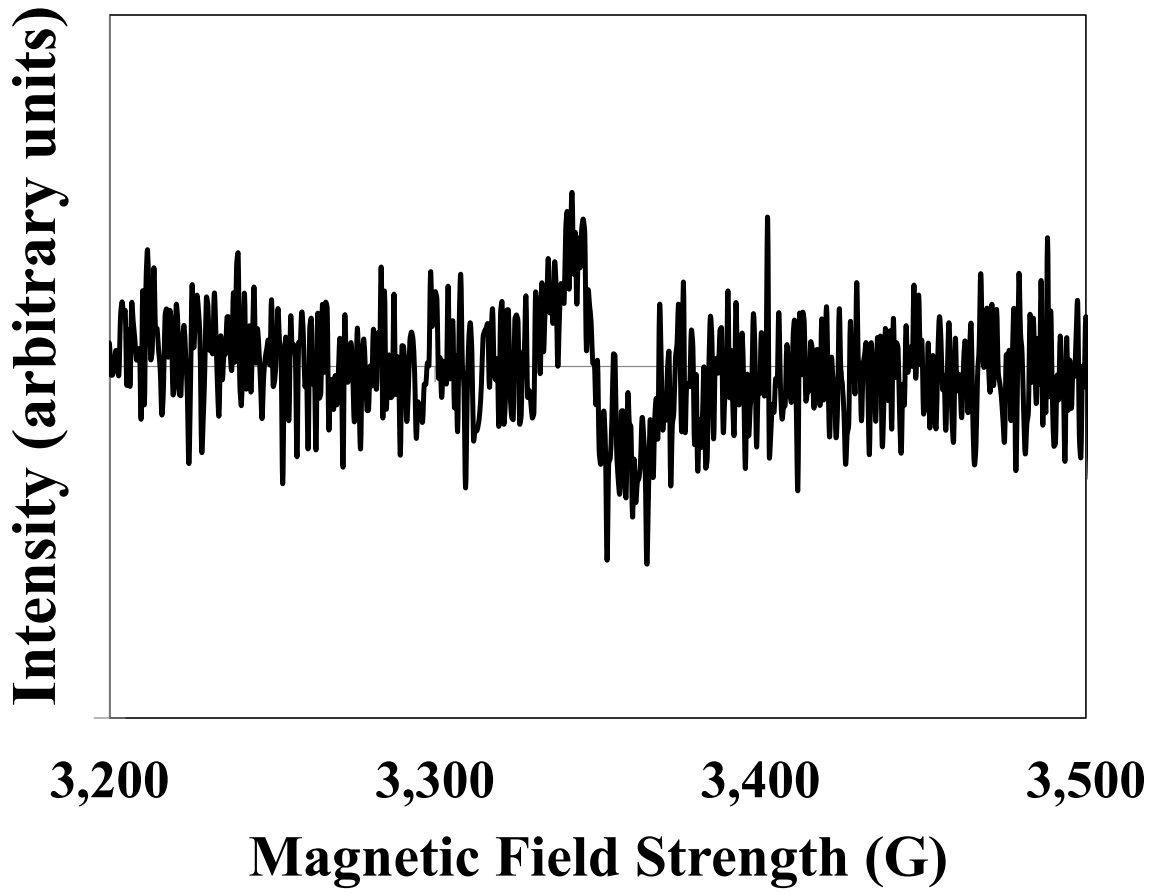


Figure B.1: EPR spectrum of MPS Si nanowires *in-situ* -doped with DPP at a Si:P mole ratio of 10^3 . The nanowire quality is so degraded that the surface states are barely detectable, and the signal-to-noise ratio is quite low. This result indicates that the *in-situ* -doping at this high level with DPP for MPW nanowires is not recommended.

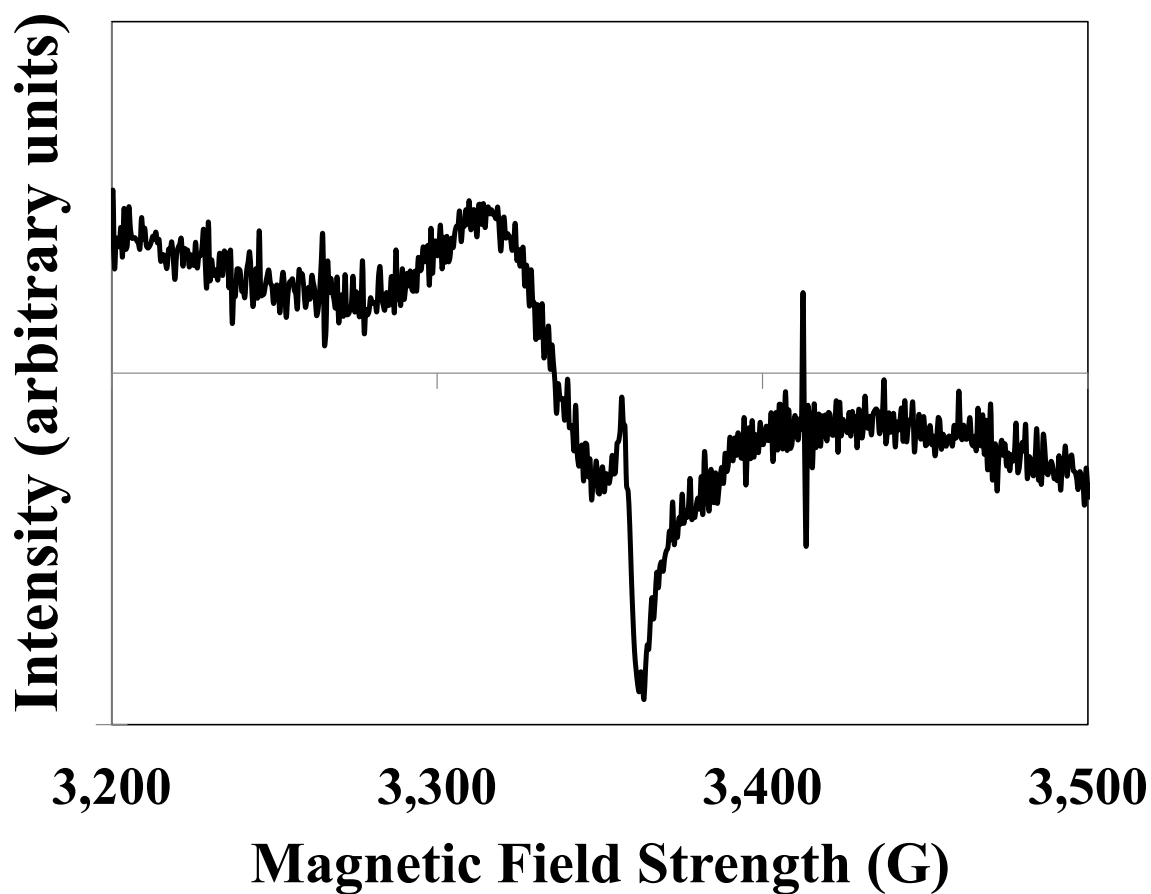


Figure B.2: EPR spectrum of TS Si nanowires *in-situ* -doped with $\text{P}(\text{SiMe}_3)_3$ at a Si:P mole ratio of 10^3 . The nanowire quality is quite poor as well, but there is a sufficiently large signal in the EPR spectrum to conclude the presence of P donor states. Moreover, the broad hump adjacent to the donor peak indicates that Si surface states are also affected at this high doping level. This result is further indication that *in-situ* -doping at high levels is not recommended.

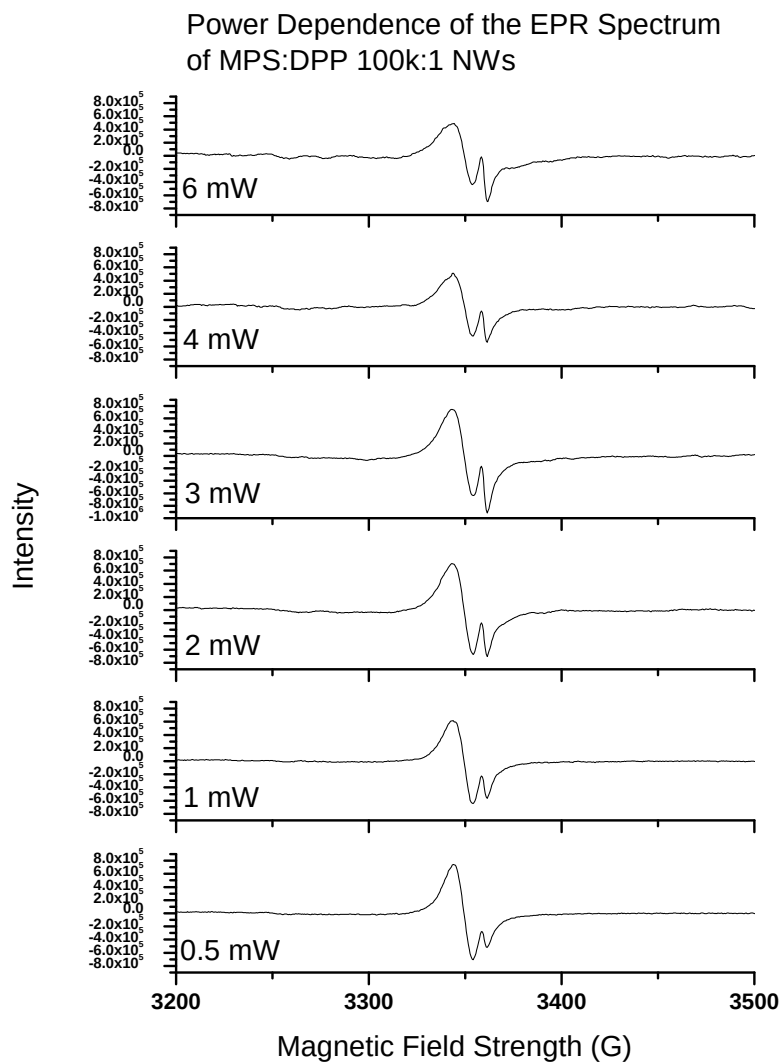


Figure B.3: EPR spectrum of DPP *in-situ* doped MPS silicon nanowires at a Si:P mole ratio of 10^5 , for multiple levels of microwave power – The power saturation behavior of the spin resonance signals was determined by varying the microwave power level while keeping other acquisition parameters, such as field modulation, constant. As can be seen from the figure, signal distortions can be observed for the P donor peak beginning at a microwave power of 3 mW. The signal intensity decreases as the microwave power increase, which is typical of resonance signals in which spin-relaxation phenomena are predominant.

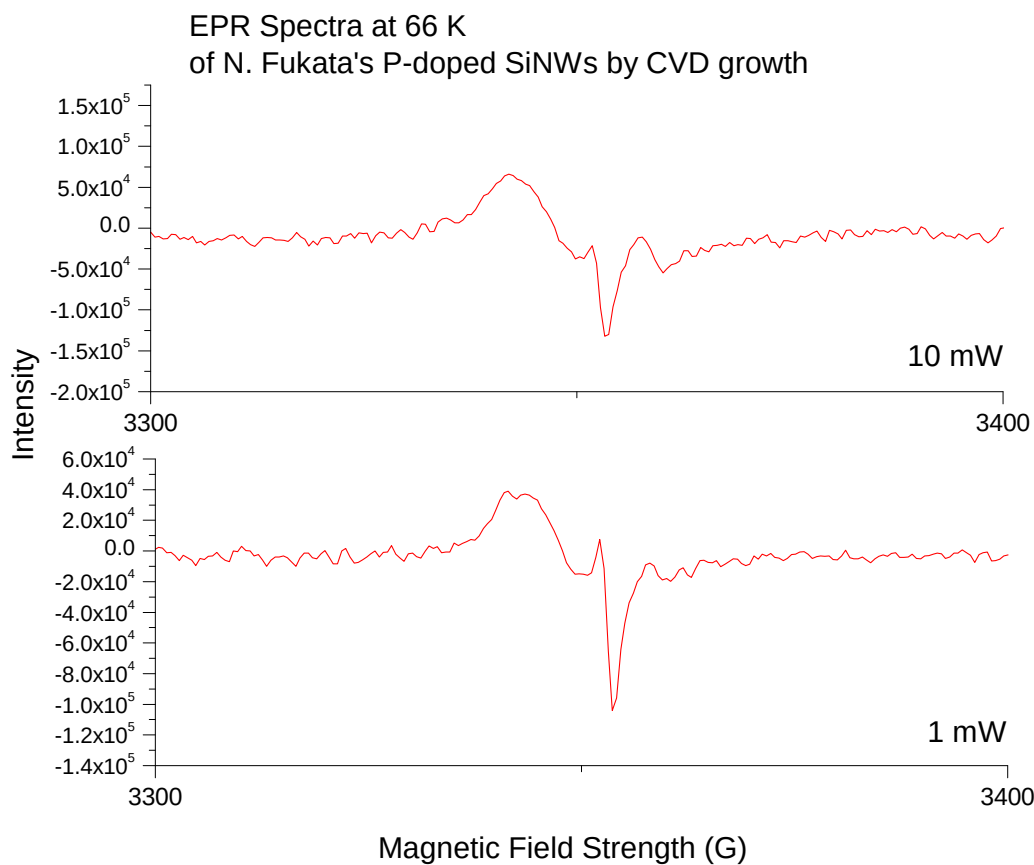


Figure B.4: EPR spectra of *in-situ* phosphorus-doped silicon nanowires grown by CVD in the laboratory of N. Fukata of Tsukuba University, Tsukuba, Japan. Both spectra are from the same sample, and differ only in the microwave power utilized here to observe the resonance saturation behavior of the spin system. Both spectra display two primary resonance peaks, one arising from Si dangling bonds and another arising from P donor states in Si, immediately adjacent and to the right of the Si peak. The spectra were acquired at a temperature of 66 K.

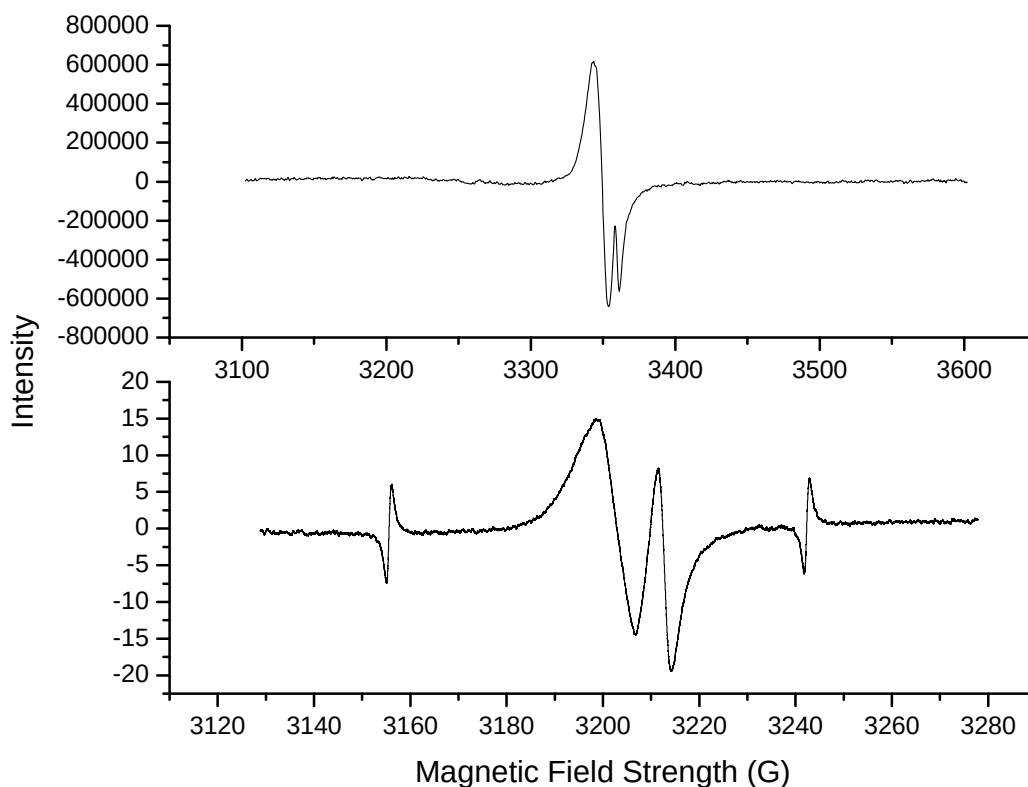


Figure B.5: EPR spectra of (Top) *in-situ* doped TS nanowires at a Si:P mole ratio of 10^5 and (Bottom) *in-situ* phosphorus-doped silicon nanowires grown by CVD in the laboratory of N. Fukata of Tsukuba University, Tsukuba, Japan. Both spectra display two primary resonance peaks, one arising from Si dangling bonds and another arising from P donor states in Si, immediately adjacent and to the right of the Si peak. The bottom spectrum contains to small satellite peaks that are due to the presence of manganese in solution, which are added to provide a known spin concentration for the purposes of spin quantitation. The spectra were acquired at a temperature of 4.2 K.

Appendix C

Supplementary FET device data

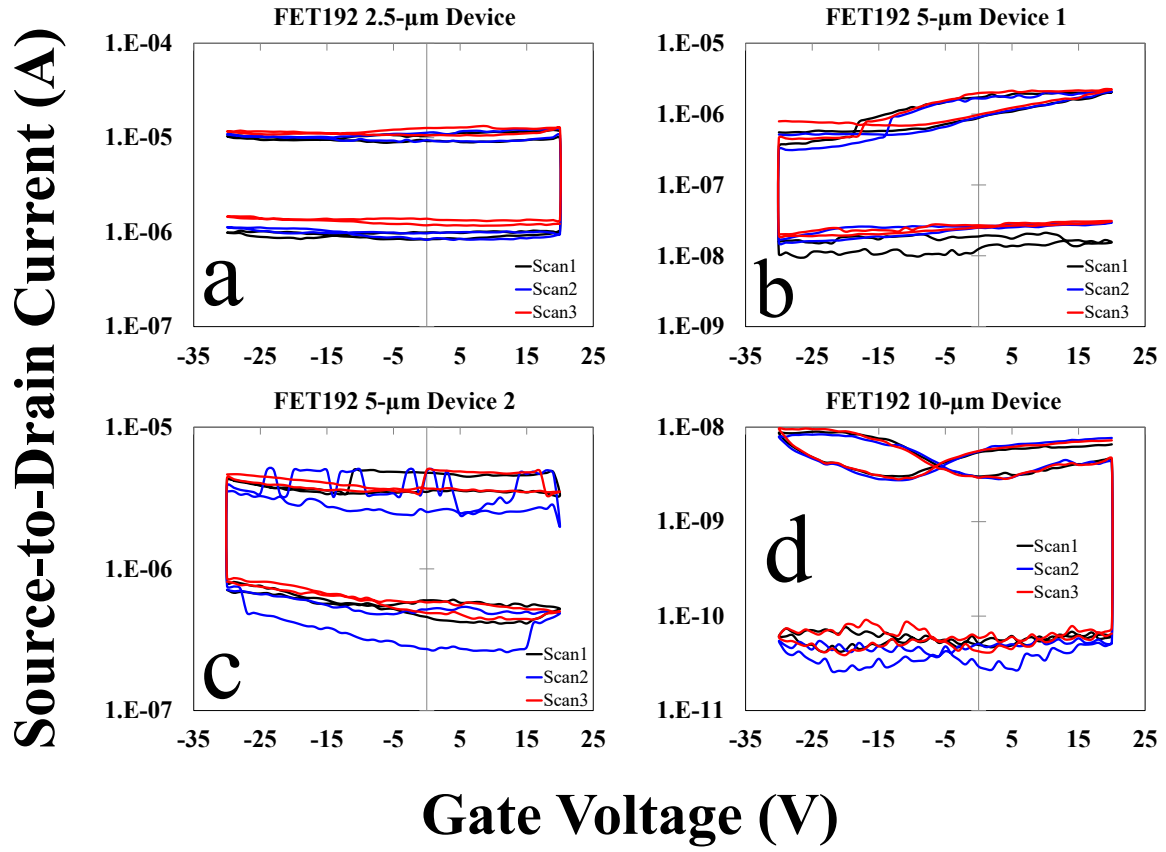


Figure C.1: TS NWs Ion Implanted **p-type** - Targeted Doping of 10^{17}

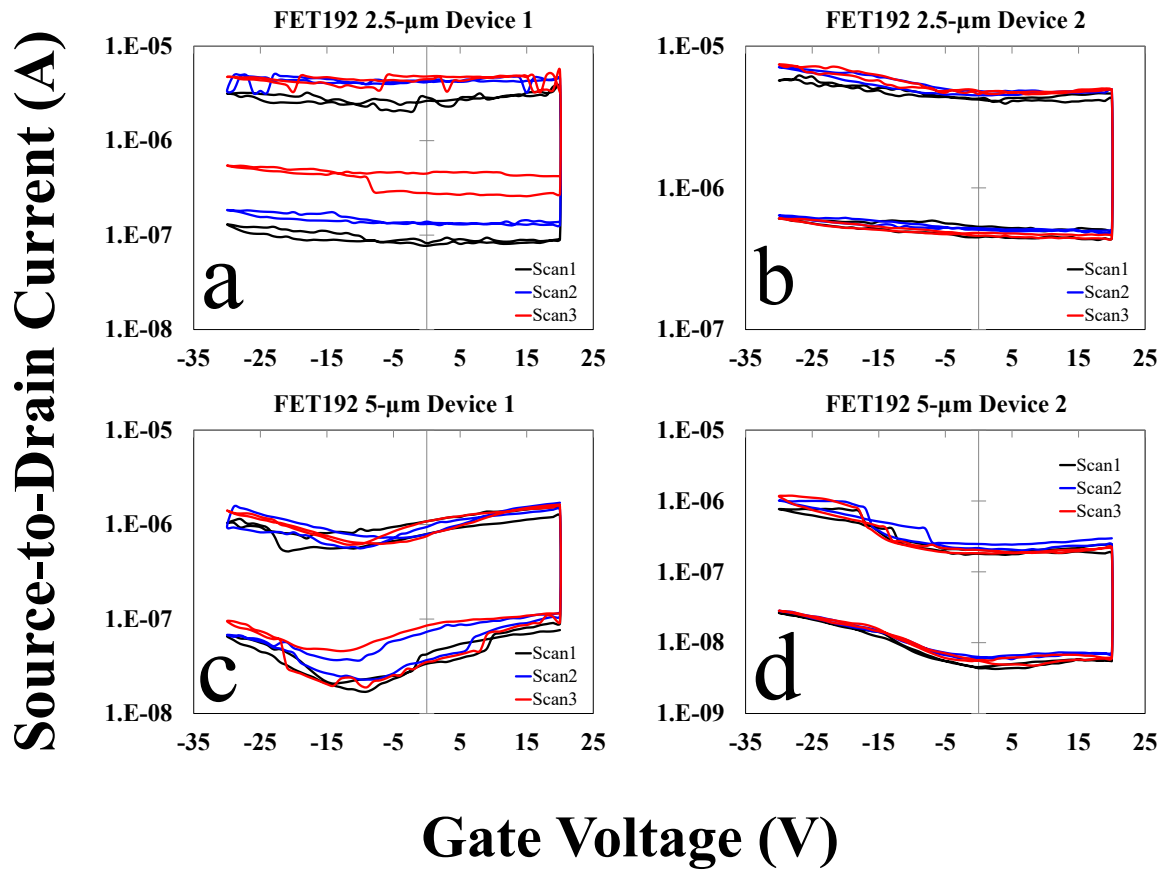


Figure C.2: TS NWs Ion Implanted **p-type** - Targeted Doping of 10^{17} - Annealed at 200°C in forming gas

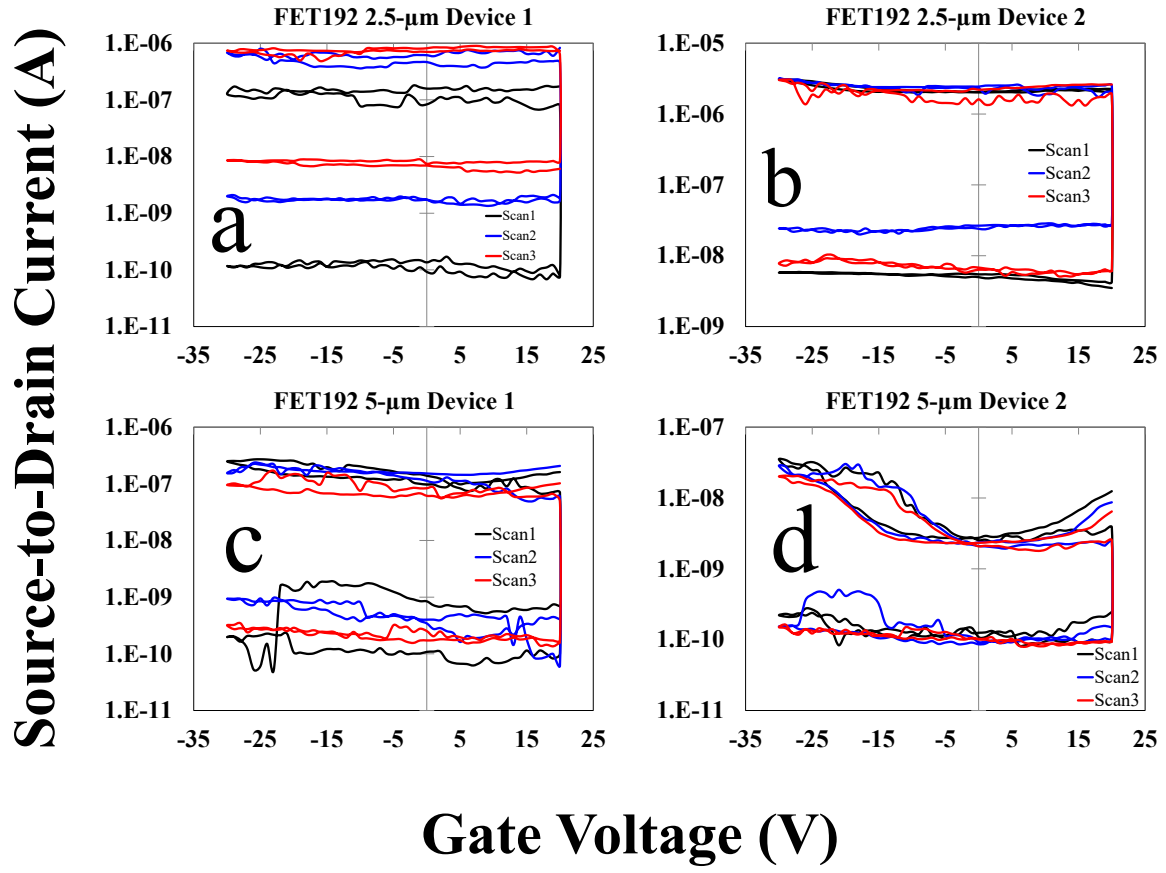


Figure C.3: TS NWs Ion Implanted **p-type** - Targeted Doping of 10^{17} - Annealed at 300°C in forming gas

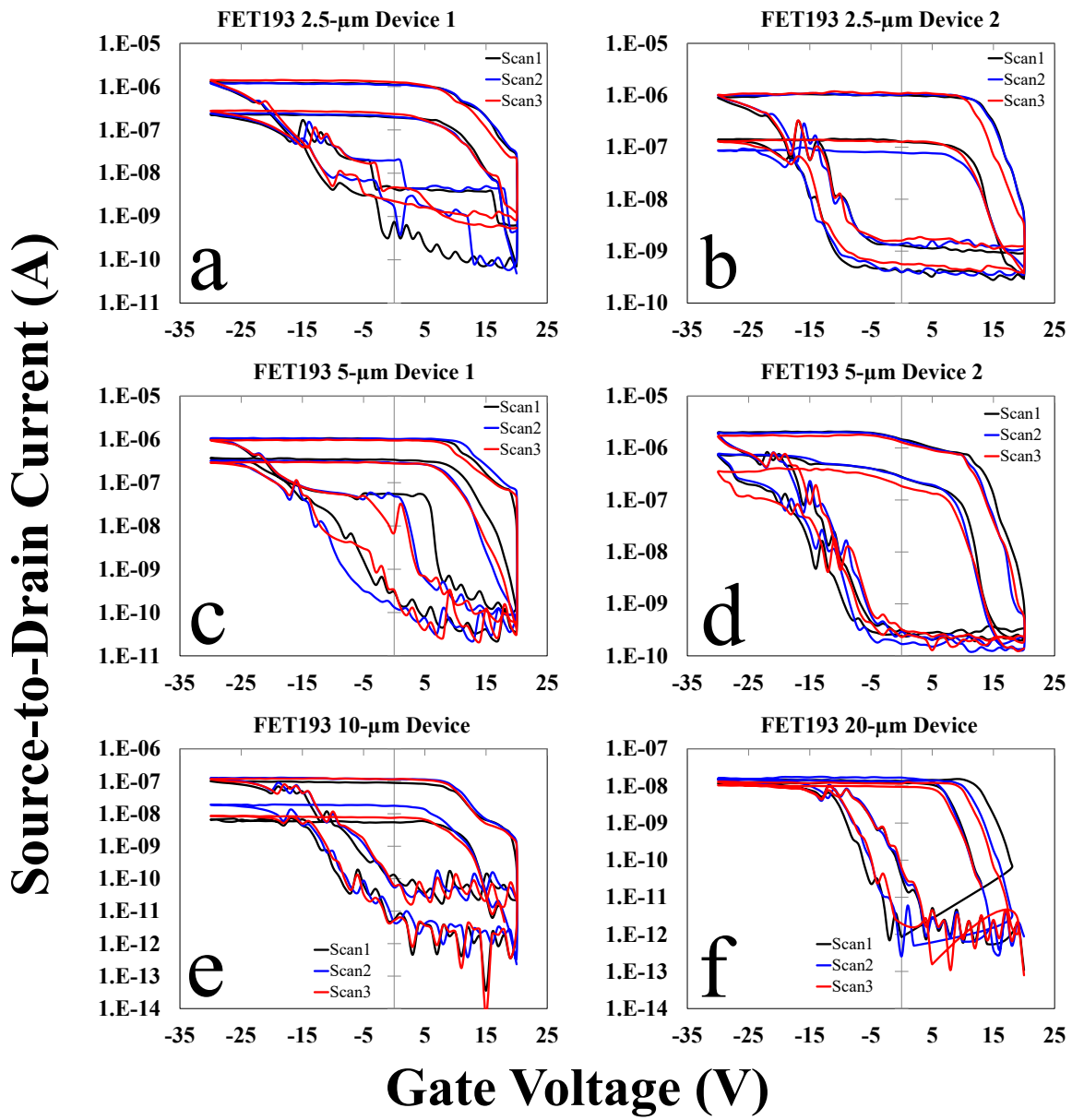


Figure C.4: MPS NWs Ion Implanted **p-type** - Targeted Doping of 10^{17}

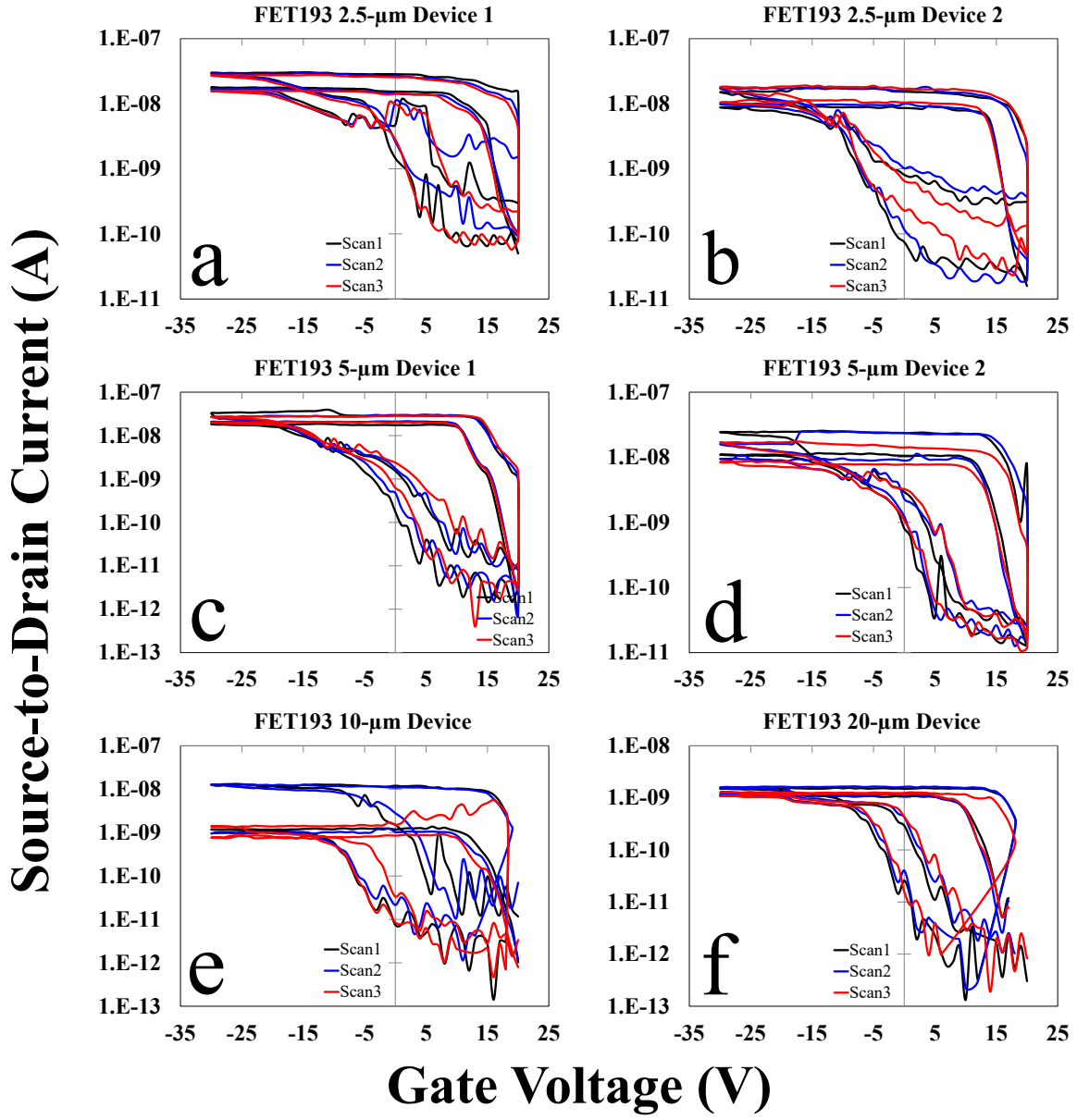


Figure C.5: MPS NWs Ion Implanted **p-type** - Targeted Doping of 10^{17} - Annealed at 200°C in forming gas

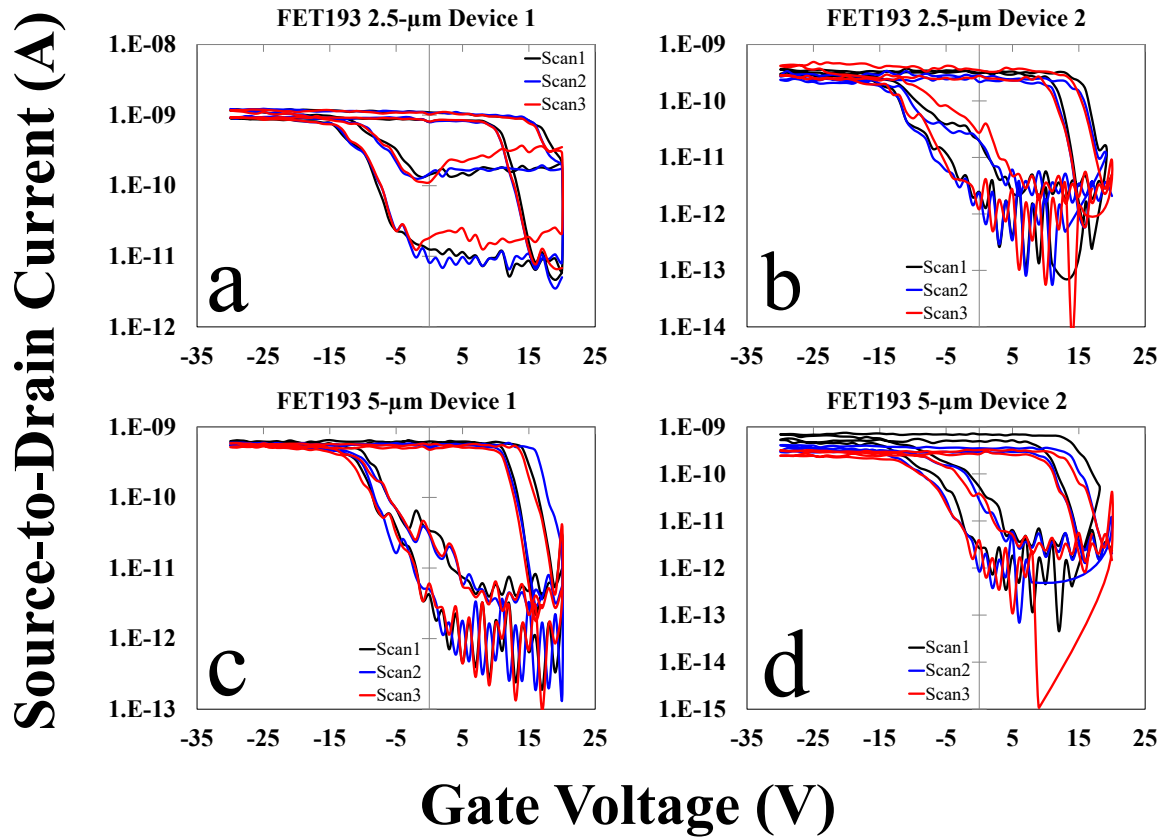


Figure C.6: MPS NWs Ion Implanted **p-type** - Targeted Doping of 10^{17} - Annealed at 300°C in forming gas

Table C.1: **FET 154** – Average Values of the Transfer Characteristics – Undoped Si Nanowires as synthesized from MPS – Curves are plotted in Fig. 3.1 found in Chapter 2 on page 53.

FET 154					
Device	V_{sd}	I_{ON} (A)	I_{OFF} (A)	ON/OFF Ratio	Hysteresis (V)
2.5 μm	1 V	3.168×10^{-6}	7.699×10^{-8}	41	37
	2 V	6.388×10^{-6}	2.233×10^{-7}	29	12
5 μm	1 V	7.099×10^{-7}	4.803×10^{-1}	1479	26
	2 V	3.208×10^{-6}	4.103×10^{-9}	782	33
10 μm	1 V	3.903×10^{-7}	9.43×10^{-10}	414	32
	2 V	1.345×10^{-6}	2.904×10^{-9}	463	30
20 μm	1 V	7.285×10^{-9}	1.682×10^{-11}	433	31
	2 V	1.439×10^{-7}	3.288×10^{-12}	4.38×10^4	30

The above values are the average of three measurements at each of the bias voltages.

Table C.2: **FET 149** – Average Values of the Transfer Characteristics – *In-situ* DPP-doped SiNWs synthesized from MPS precursor at a Si:P ratio of 10^3 and etched in aqua regia – Curves are plotted in Figs. 3.10 and 3.12 found in Chapter 2 on pages 64 and 66.

FET 149					
Device	V_{sd}	I_{ON} (A)	I_{OFF} (A)	ON/OFF Ratio	Hysteresis (V)
2.5 μm - 1	1 V	5.917×10^{-8}	1.835×10^{-7}	0.32	10.3
	2 V	7.284×10^{-8}	4.450×10^{-7}	0.16	13.3
2.5 μm - 2	1 V	6.528×10^{-10}	5.517×10^{-10}	1.18	3.66
	2 V	1.540×10^{-8}	1.179×10^{-8}	1.31	21.6
5 μm - 1	1 V	1.805×10^{-10}	5.424×10^{-11}	3.33	27
	2 V	2.017×10^{-9}	1.763×10^{-9}	1.14	13.0
5 μm - 2	1 V	7.907×10^{-11}	1.228×10^{-11}	6.44	4.33
	2 V	6.138×10^{-10}	6.738×10^{-10}	0.91	5.67
10 μm - 1	1 V	2.112×10^{-10}	9.844×10^{-11}	2.14	1.00
	2 V	3.144×10^{-9}	2.913×10^{-9}	1.08	11.2
10 μm - 2	1 V	1.379×10^{-10}	4.765×10^{-12}	28.9	16.3
	2 V	6.422×10^{-10}	5.768×10^{-10}	1.11	16.5
20 μm	1 V	1.244×10^{-10}	3.414×10^{-11}	3.64	1.00
	2 V	3.616×10^{-10}	3.011×10^{-10}	1.20	20.3

The above values are the average of three measurements at each of the bias voltages.

Source-to-Drain Current (A)

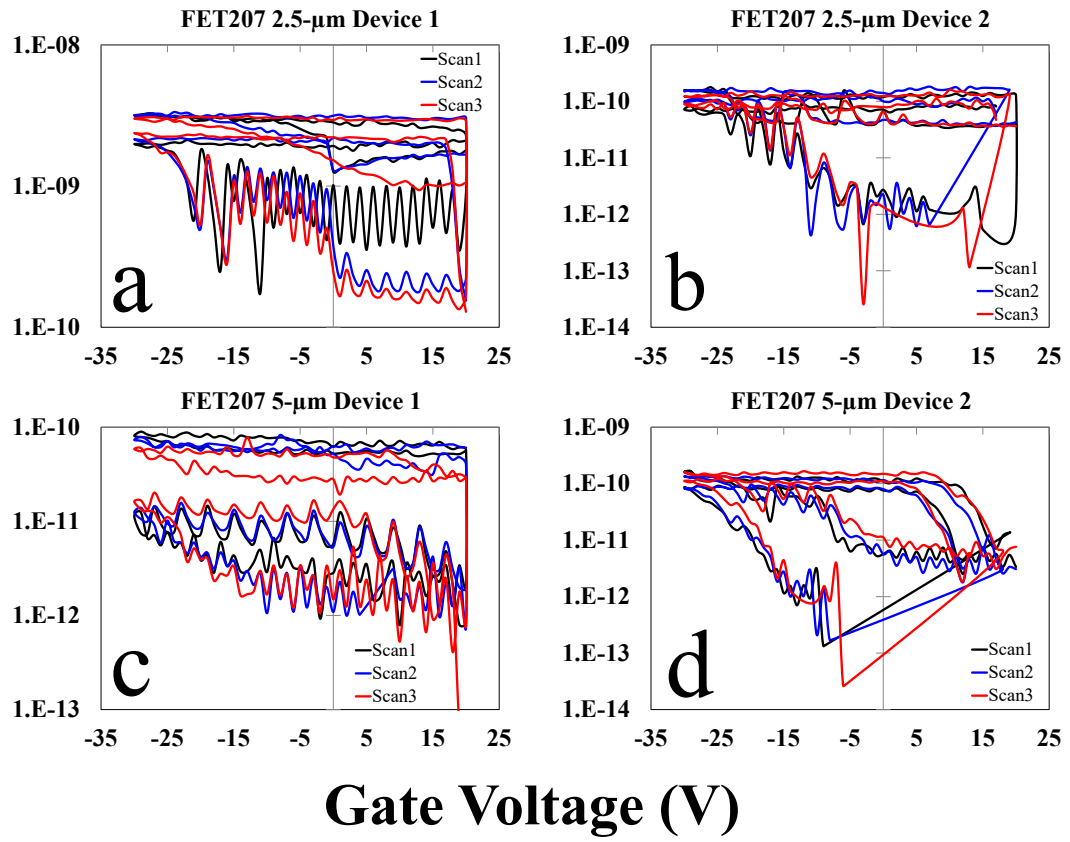


Figure C.7: MPS NWs Ion Implanted **p-type** - Targeted Doping of 10^{19}

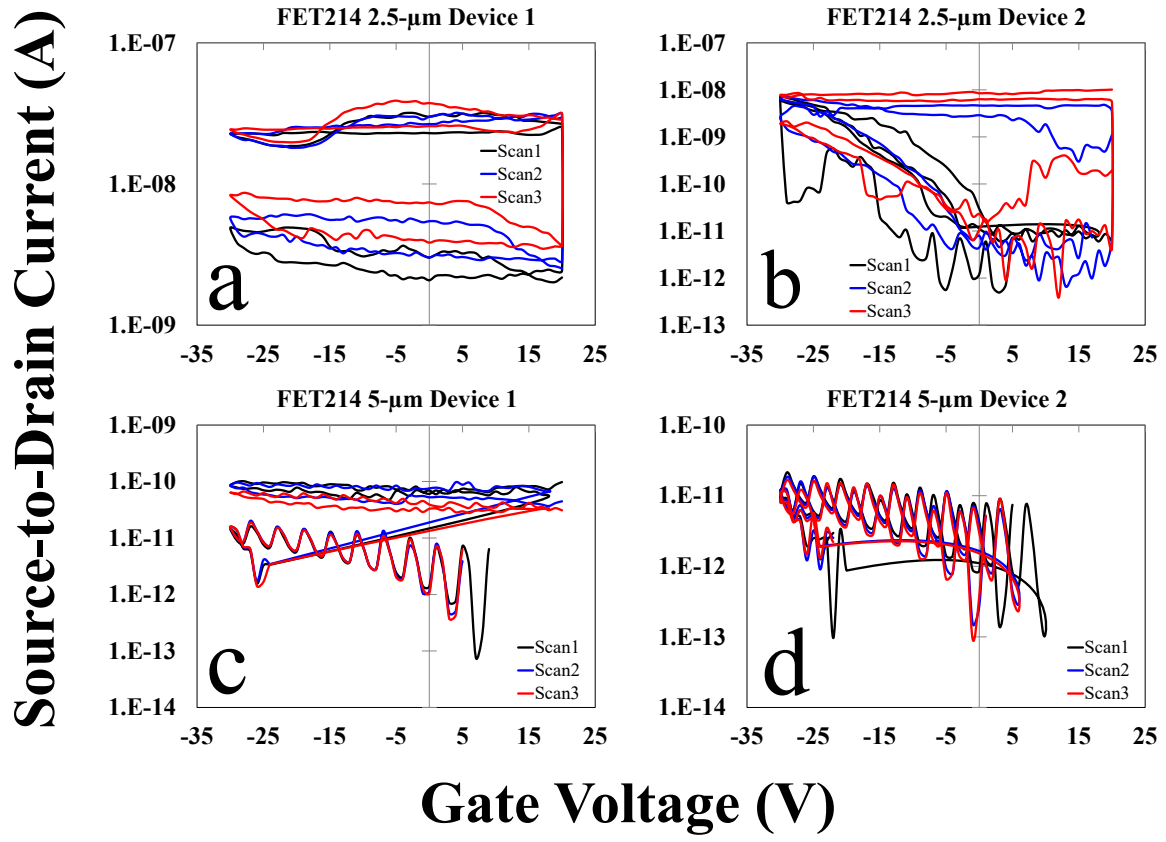


Figure C.8: TS NWs Ion Implanted **p-type** - Targeted Doping of 10^{19}

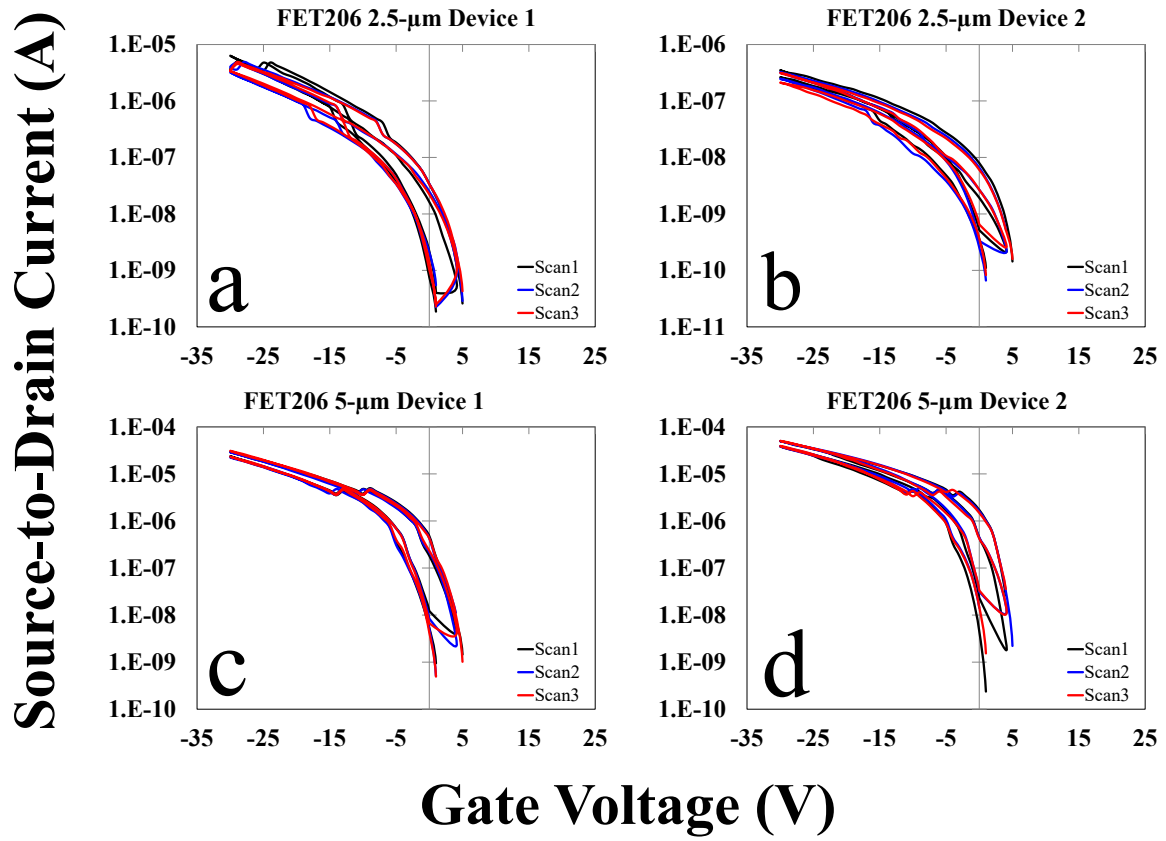


Figure C.9: TS NWs Ion Implanted **p-type** - Targeted Doping of 10^{19} - Annealed at 300°C in forming gas

Appendix D

Ion implantation calculations for a model based on bulk silicon

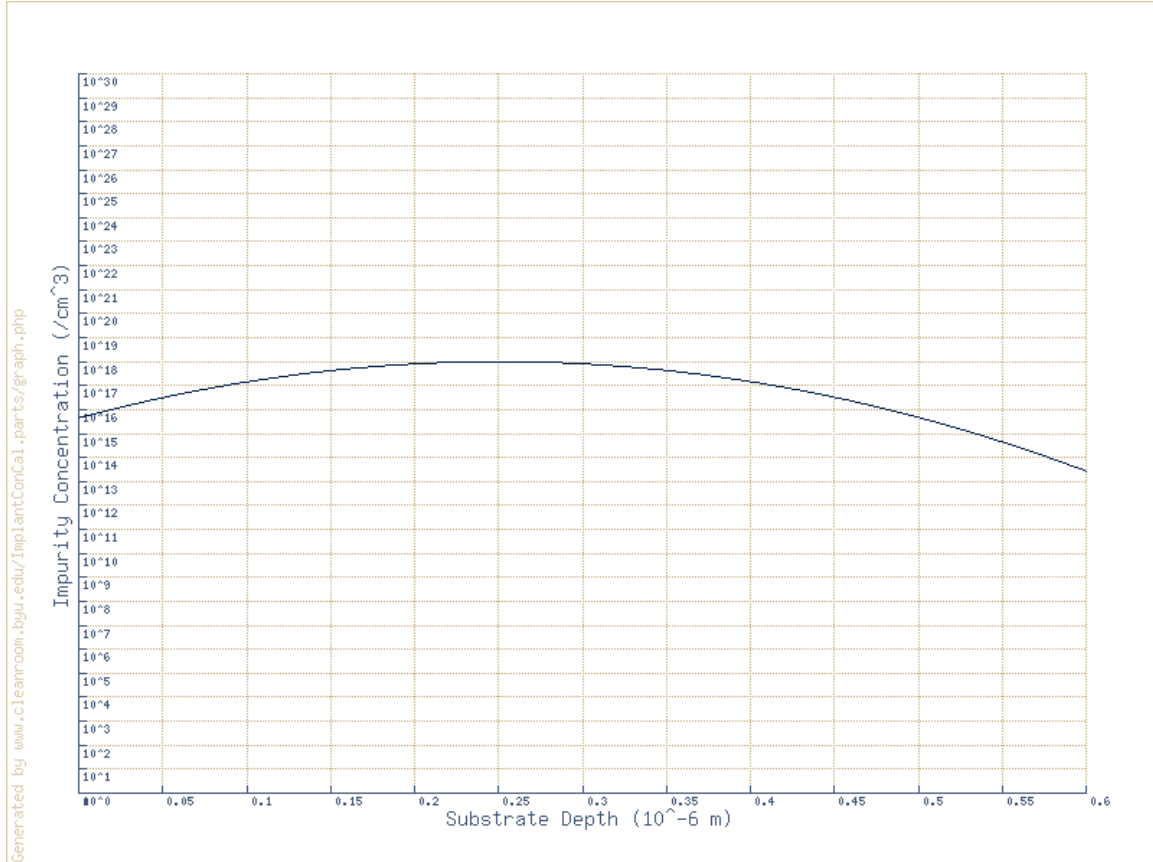


Figure D.1: Calculation of the ion concentration as a function of penetration depth through bulk Si. The substrate material is monocrystalline silicon, the dopant is phosphorus, the ion energy is 200 keV, the ion dose is 1.9×10^{13} ions cm², and the substrate depth is 1 μ m. The graph was generated by means of an online calculator in the form of a webapplet that is available free of charge via the World Wide Web at <http://www.cleanroom.byu.edu/ImplantConCal.phtml>.

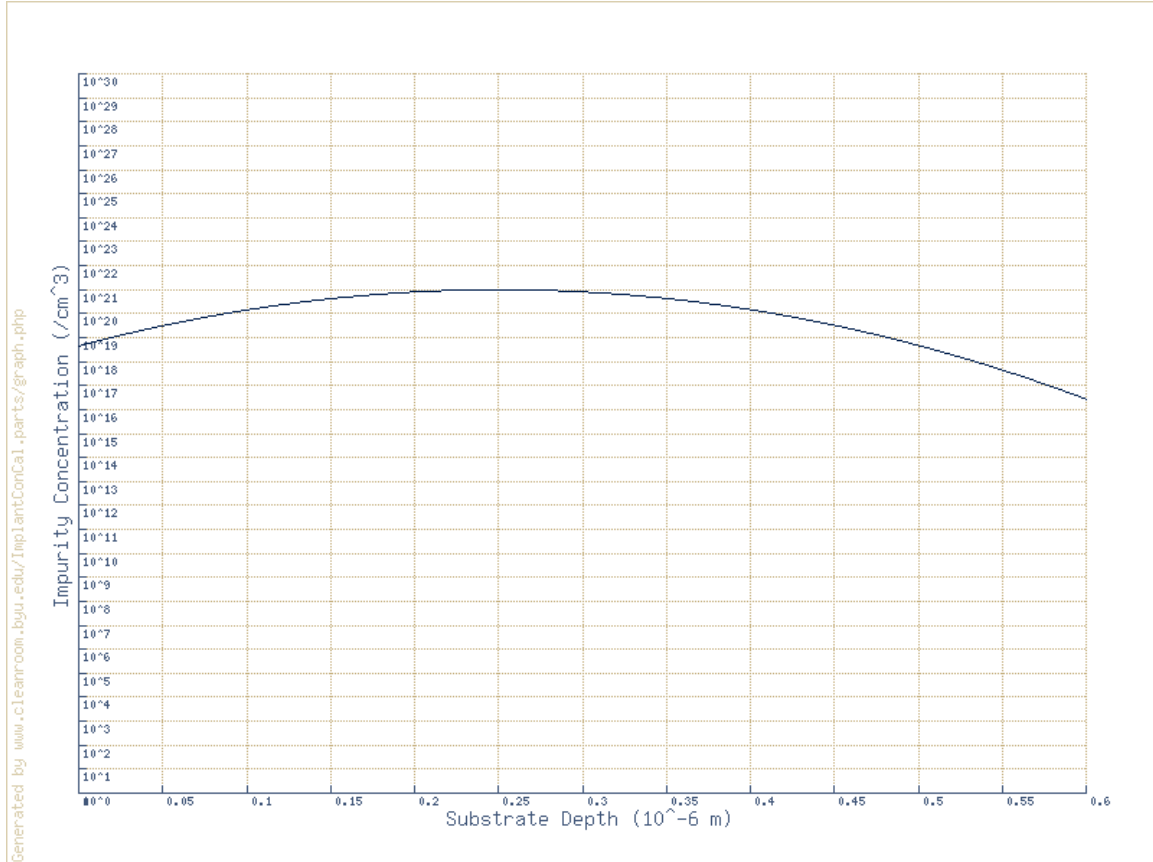


Figure D.2: Calculation of the ion concentration as a function of penetration depth through bulk Si. The substrate material is monocrystalline silicon, the dopant is phosphorus, the ion energy is 200 keV, the ion dose is 1.9×10^{16} ions cm^2 , and the substrate depth is 1 μm . The graph was generated by means of an online calculator in the form of a webapplet that is available free of charge via the World Wide Web at <http://www.cleanroom.byu.edu/ImplantConCal.phtml>.

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Vita

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