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Revealing the Dopant Incorporation Mechanisms into Vapor-Liquid-Solid Grown NWs Employing Nano-Prope Scanning Auger Microscopy

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Nanowires (NWs) have been extensively studied over the last few decades for both scientific interest and technological potential. Semiconductor NWs' physical properties are profoundly dependent on their chemical composition and especially so on their dopant concentration, profiles and activity level. Controlling NWs axial and radial dopant profiles is, therefore, of utmost importance for NW-based device optimization. Over the last few years various works have shown inhomogeneous dopants profiles in many NWs systems, yet further improvement in the challenging chemical characterization of individual NW is therefore required for the identification and understanding of doping mechanisms. Recent instrumentation advances in nano-probe Field Emission Scanning Auger (npSAM), combined with low voltage sputter ion depth profiling, allows the analysis of the axial and radial elemental distributions of individual NWs. This study employed npSAM to extract the axial and radial dopant distributions of P doped SiNWs grown under various conditions and provided new insights into some of the key questions regarding the dopant incorporation mechanisms. The comparison between both axial and radial dopant profiles of SiNWs grown under different conditions assisted to quantify and distinguish between the two different dopant incorporation mechanisms (catalytic vs. side wall deposition), revealed the radially inhomogeneous catalytic doping and the self-enhancing nature of the side wall dopant incorporation, and demonstrated a surprisingly substantial reservoir effect.

The P doped SiNWs growth processes were described in detail elsewhere [1-3]. In short, all NWs produced for this study were grown in a low-pressure chemical vapor deposition setup with either 50 nm or 80 nm Au nano-particles (AuNPs) as catalysts, SiH4 and PH3 as precursor gases, and either H2 or He as carrier gases. Several different sets of growth conditions were used to fabricate axially modulation-doped (see figure 1), slightly tapered and non-tapered P-doped SiNWs. After growth, NWs were transferred from the growth substrate onto GaAs substrates or HOPG for npSAM measurements. The details of the npSAM were described elsewhere [1]. In short, the Auger data were acquired with a Physical Electronics PHI 700Xi Scanning Auger equipped with a 25 kV Schottky field emission electron gun and a coaxial Cylindrical Mirror Analyzer (CMA). Secondary electron images and Auger spectra were obtained using a 20 kV electron beam with a 5 nA incident current on the sample and a probe diameter of ~10 nm. CMA energy resolution of 0.5% was used for acquiring elemental identification spectra and for surface atomic concentrations measurements, whereas 0.1% CMA energy resolution, displayed in the N(E) mode after a polynomial background subtraction, was used for obtaining the P LMM and Si KLL peaks. Atomic concentration values were calculated using the dN(E)/dE peak to peak heights of the P LMM and Si KLL spectra and PHI supplied sensitivity factors [4]. The P detectability limit was determined by the signal-to-noise limit of the observable Auger P LMM peak and were found to be ~ 1/1250 ($4 *10^{19}$ cm^{-3}) and ~ 1/6000 ($8 *10^{18}$ cm^{-3}) for the GaAs and

HOPG substrates respectively. Depth profiling was performed using an alternating Auger data acquisition with 500 eV Argon ion sputtering.

The segmented NW's axial P profile obtained by np-SAM as measured at the NWs surface and after 3 nm etching is shown in figure 1a, while the growth schematic is presented in figure 1b. A few conclusions can be drawn from the data: (1) The segments' doping profiles enable distinctions between the contributions of different dopant incorporation mechanisms. (2) The continuously doped last 5μm and the high P concentration next to the tip imply a significant P concentration in the Au catalyst during growth (~ 1%-10%) and hence, the reservoir effect plays a key role in determining dopant incorporation. (3) Comparing between the last segment's dopant profiles before and after etching reveals that the dopant was incorporated mainly through the NW's surface, implying inhomogeneous dopant incorporation along the NW-catalyst interface. The axial and radial surface dopant profiles of the tapered SiNW are presented in figures 1c and 1d. Axial surface profiles measured at various depths (see legends) are presented in 1c, while the same data arranged as radial profiles at various distance from the NWs base, on a semi-logarithmic scale, is presented in 1d. The linear dependence of the P concentration on the NW length, and hence, on growth time, is in agreement with previous works claiming the inhomogeneous axial dopant profile is caused by sidewall deposition of the highly doped shell. Nevertheless, the surface sensitive npSAM employed in this study reveals that the P concentration of the shell is increasing with growth time along the radial direction as well. This self-enhancing increase in the radial concentration with exposure time might be the outcome of either surface segregation or self-enhancement P deposition due to modified surface chemical reactivity toward PH3 adsorption. In addition, non-tapered P doped SiNWs grown under conventional growth conditions and in an H-rich environment were also measured. An H-rich growth environment and post-growth annealing were considered to mediate the axial inhomogeneity [2]. Nevertheless, no such effect was obtained in this study, implying that the mediating effect was related to the dopant activity rather than chemical composition.

In conclusion, npSAM was found to be a useful nano-scale characterization tool with several important advantages over other techniques and helps to understand some of the key questions related to dopant incorporation into VLS grown NWs.

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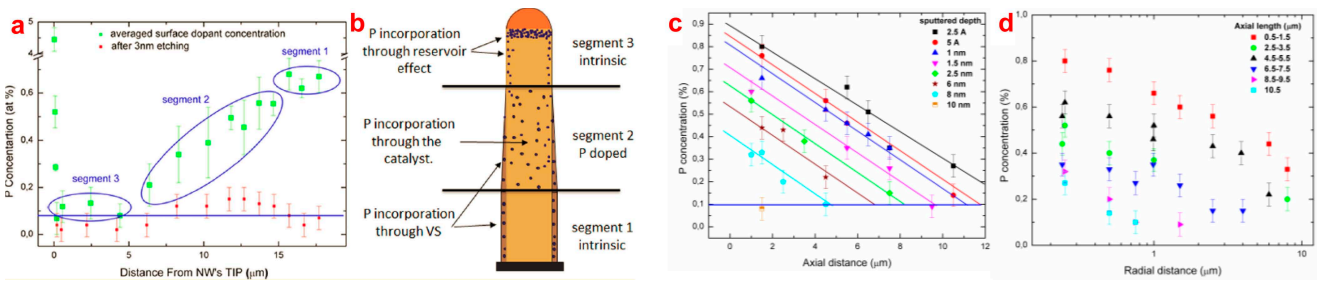

Figure 1. (a) The modulation-doped NW's P profile obtained by np-SAM and its growth schematics (b) as measured at the NWs surface and averaged over 3 NWs as grown (green) and after 3 nm etching (red). The axial surface profiles measured at various depths (c) and the same data arranged as radial profiles at various points along the NW (d) of P doped tapered SiNW.