

Analysis of Nanowire Dopant Incorporation and Distribution with Atom Probe Tomography and Nano Probe Scanning Auger Microscopy

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1. Introduction

In parallel with the remarkably successful scaling of CMOS over the last decade, many bottom-up approaches to nanoscale semiconductor devices have been investigated. Catalyst mediated semiconductor nanowires (NWs) in particular have been the focus of substantial research efforts [1]. The potential to develop tunnel field effect transistors for low power logic are an especially compelling advantage for catalyst mediated NWs [2]. It remains a challenge, however, to establish the dopant concentration and identify any gradients that may exist.

Atom probe tomography (APT) has proven to be an effective, and thus far unique, tool with which to quantitatively analyze the dopant distribution in semiconductor NWs [3,4]. APT has also provided unique insights into dopant re-distribution in CMOS structures [5]. Scanning Auger Microscopy (SAM) is less recognized as an analytical tool for dopant distribution analysis, but recent advances in instrumentation have improved sensitivity and resolution, enabling new applications [6].

Here we describe recent advances in the APT and nano probe SAM (npSAM) analysis of semiconductor NWs. We focus on the influence of the vapor-liquid-solid (VLS) growth mechanism, described below, on the dopant distribution, and the possible identification of a new source of doping anisotropy for NWs doped through the catalyst, *in situ*, during growth.

2. Nanowire doping processes

We briefly review two mechanisms of *in situ* doping, beginning with catalyst-mediated doping. In the VLS growth process, a metal seed particle forms a liquid alloy with the semiconductor species of interest following exposure to a precursor source vapor. The supersaturation of the eutectic liquid leads to the nucleation of solid semiconductor nanoparticle, which in turn leads to NW formation if the precursor supply is continued and the droplet can form stable interface with the growing NW. If a dopant precursor is introduced, it too may decompose on the surface of the catalyst particle and become incorporated in the semicon-

ductor. *p-n* junctions can be formed by switching the dopant precursor [7], with the junction abruptness limited by the amount of dopant dissolved in the catalyst particle. Such through-catalyst doping enables the fabrication of tunnel diode structures that show negative differential resistance without the complications of post-growth masking and implantation [2]. For the present study, Si and Ge NWs were grown using colloidal Au nanocatalysts in a hot-wall chemical vapor deposition system. SiH₄ and GeH₄ were used as semiconductor precursors, and PH₃ and B₂H₆ as dopant precursors, as described previously [3,4].

In the context of VLS growth, it is important to bear in mind the possibility of surface doping, which results from non-selective decomposition of the dopant precursor on the NW sidewalls. There have been many examples thus far of hydride-based growth of Si and Ge NWs in which surface doping of the NW has occurred [8]. Recently, we showed that surface doping could be mitigated through the modification of the growth environment so as to suppress the chemical reactions that produce active surface dopants [9]. Here we present evidence that through-catalyst mediated doping may also result in surface enrichment.

3. P doped Ge nanowires analyzed by APT

We first describe APT studies of P-doped Ge NWs, followed by SAM studies of P-doped Si NWs grown in a similar process. The focus of this report is the radial non-uniformity of the dopant distribution. To avoid the potentially confounding effects of surface deposition, the PH₃ gas flow was turned off and the reactor evacuated prior to growth of the segment of NW that was analyzed by APT. All the P atoms incorporated into the NW were therefore dissolved in the droplet prior to termination of the PH₃ flow. Due to non-selective growth on the NW sidewalls, the Ge NWs are tapered, and a thin shell of intrinsic homoepitaxial material surrounds the core defined by the VLS growth.

APT analysis was conducted with a LEAP 4000Si at 40 K with 6-12 pJ laser pulses at 200 kHz, and reconstructions were performed with IVAS software. Figure 1 shows the P concentration in a Ge NW that was doped from the

catalyst reservoir in the absence of PH_3 flow. The extent of the reconstructed volume clearly lies outside the region of P enrichment, indicating that: (1) the NW surface is doped by a reactor memory effect; (2) there is selective precipitation of P at the VLS triple junction during growth; or (3) APT analysis conditions have led to an artifact either by inducing P diffusion or selective evaporation. We do not expect that (3) is the case as a similar P distribution was seen in three NWs under multiple run conditions. To completely rule out the possibility, additional studies on uniformly doped bulk samples will be necessary.

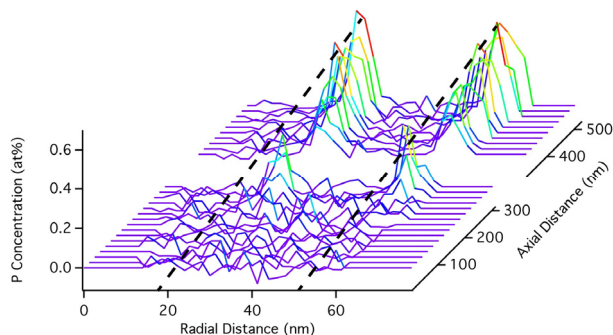


Fig. 1 Radial concentration of P in Ge NW, with the right axis split to correspond with the location where PH_3 flow was terminated. The approximate position of the VLS-triple junction during growth, and therefore VLS-grown material, is indicated by the dashed line. Due to taper, intrinsic shell material is seen outside the doped region for larger axial distances (away from the growth tip).

Explanation (1) is unlikely given that the reactor was evacuated completely prior to resumption of growth, with P concentration prior to PH_3 termination greater than that following PH_3 flow termination. Therefore, we hypothesize that P is selectively deposited at the triple junction. This effect may reflect an enrichment of P at the surface of the Au-Ge eutectic, an enhanced solubility near the Ge solid-vapor interface, or a reduced kinetic barrier at the triple junction with respect to Ge.

3. P doped Si nanowires analyzed by npSAM

Similar APT studies were conducted in P doped Si NWs, but the proximity of the P (mass 31) and Si isotopes (masses 28, 29, 30) has precluded a dopant mapping of comparable resolution thus far. Instead, we used scanning Auger microscopy to map the P distribution along a Si NW in which the PH_3 flow had been modulated from off to on to off. SAM is a surface selective technique, enabling limited depth profiling by successive sputtering of the analyzed surface. Figure 2 shows the surface doping concentration versus NW position, with the catalyst tip to the left. The rightmost nominally intrinsic portion has been surface doped during growth [10] of the middle doped portion. The left-most portion has been doped by P remaining in the catalyst after the PH_3 flow was turned off. Significantly, depth profiling (red dots) shows that the P is concentrated near the surface even for the left-most portion of the NW,

consistent with the picture presented for P-doped Ge.

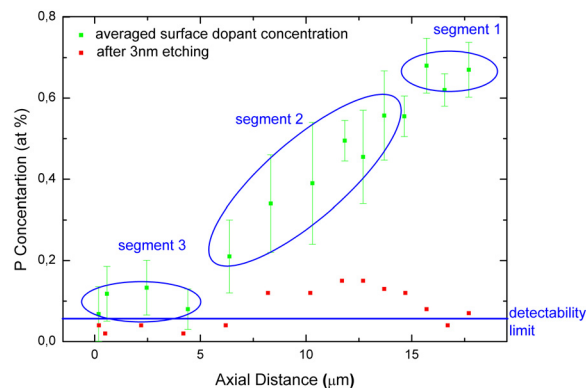


Fig. 2 Axial distribution of P dopants in SiNW before (green) and after (red) 3 nm etching. The NW was grown from right to left.

5. Conclusions

We described preliminary studies of the radial distribution of P dopant atoms in Si and Ge NWs grown using a Au-catalyzed VLS process. Evidence is presented of near-surface dopant enrichment even when doping through the catalyst. These findings have important implications for the understanding and control of doping in VLS-grown NWs and devices.

Acknowledgements

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