Atomic scale dopant metrology in an individual silicon nanowire by atom probe tomography

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ABSTRACT

In this work, the p-type silicon nanowires (SiNWs) are grown by the Chemical Vapor Deposition (CVD) method using gold as catalyst droplet, silane as precursor and diborane as dopant reactant and are analyzed at the atomic scale using the three dimensional laser assisted Atom Probe Tomography (APT). This paper reports the preparation of SiNWs and their observation. A three dimensional dopant distribution and its accurate concentration are determined. The possible dopant incorporation pathway into an individual SiNW is also discussed.
Keywords: silicon nanowire, dopant, atom probe

1 INTRODUCTION

One dimensional nanostructure can play an important role for the future applications. Among them, the carbon nanotubes (CNTs) [1] and the silicon nanowires [2] attract an extreme attention because of their relative easy synthesis and potential properties. By controlling their synthesis, CNTs and SiNWs can both be candidate for ultimate nanoelectric devices. However, in comparison to CNTs, it is easier to control the electrical properties of SiNWs. Thus, a lot of efforts and progresses have been made on SiNWs in different domains in the last few years, such as electronics [3, 4], bio or molecular sensors [5, 6], modeling [7, 8] and energy devices [9, 10].

SiNWs can typically be grown by vapor liquid solid (VLS) mechanism. CVD is a the method commonly used [11]. A typical SiNW growth kinetic is schematically illustrated in Fig.1. This process is governed by three different configurations of the Si atoms: Si atom holder (Si^H, the substrate), Si atom provider (Si^P, the precursor) and Si atom receiver (Si^R, the supersaturated binary Au-Si alloys). Si^H can be chosen as Si [111], Si [110] or Ge [111] etc…; Si^P can be chosen as SiH_4, Si_2H_6 or $SiCl_4$ etc… and Si^R can be chosen as a mixing with Au, Cu or Fe etc… Before the SiNWs growth, Si^R exists on Si^H as droplets. The Si^P is then introduced into the chamber while the substrate is kept to high temperature (e.g. 500 °C). To that point, three steps are necessary for Si atoms to contribute the SiNW growth : *i)* the production of Si atoms via the decomposition of Si^P; *ii)* the incorporation of Si atoms into Si^R and *iii)* the crystallization of Si atoms at SiNW and Si^R interface.

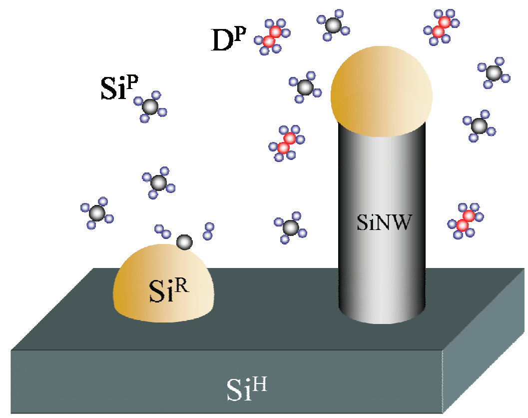

Figure 1. Schematic view of VLS mechanism system for SiNWs growth. This system includes three parts for SiNWs without dopant: Si atoms holder (Si^H), Si atoms receiver (Si^R) and Si atoms provider (Si^P). After the Si^R is deposited on Si^H as a droplet, the Si atoms coming from the decomposition of Si^P can incorporate into Si^R and then crystallize at Si^R. Crystallization at SiNW interface also occurs depending on experimental growth condition. For doped SiNWs, a fourth part, namely the dopant provider (D^P) either for p-type or n-type, should be added into the system.

The doping of SiNWs is an important issue for their electrical applications. In the CVD process, the doping process can be easily realized by the addition of dopant provider (D^P) in Si^P. For example, D^P can be chosen as B_2H_6 and PH_3 for a p-type and n-type SiNWs respectively. The different doping concentration can be realized by changing the ratio (gas pressure) between Si^P and D^P. The p-n heterostructure can also be grown by tuning the D^P level during the SiNWs growth [12]. The relation between the Si^P/D^P ratio and the accurate incorporated dopant atomic concentration should be established for having a controllable doping process. However, the control of the doping process is still very difficult because of the lack of information or measurement on dopant level in an individual SiNW. It is also very important to know through which pathway the dopant atoms can incorporate into SiNW. In this work, we use a laser assisted three-dimensional APT to characterize an individual p-type SiNW. APT is a three dimensional high resolution analytical microscope that can map the distribution of atoms in materials. The principle of the APT is based on the field evaporation of atoms. In order to realize this, an electrical potential of several kilovolts is applied to the sample, prepared in the form of a tip whose diameter should be smaller than 100 nm. Femtosecond laser pulses are superimposed to the high voltage in the case of semiconductor materials such as SiNWs. It must be noted that a SiNW is already in the form of a tip. This combination (voltage and laser pulses) gives rise to the field ionization of surface atoms. The laser pulse frequency triggers the evaporation of ions from the surface of the specimen towards a position sensitive detector. Measuring the time of flight allows the identification of the chemical nature of evaporated ions (time of flight mass spectrometry) and their impact positions on the detector allows to calculate their initial position on the surface (projection microscope). These information are used for the three dimensional reconstruction of the material at the atomic scale. The information about the concentration and distribution of dopant (e.g. B) in an individual SiNW can thus be obtained using APT.

2 EXPERIMENT

2.1 SiNWs growth

The choice of Si^R is important for the SiNWs growth. In theory, all the elements that can form eutectic liquid with Si can be used as Si^R. In this work, Au was chosen for SiNW growth because of its relatively low eutectic temperature and its easy preparation in the form of Au droplets. Several methods can be used to obtain the catalyst droplet, such as colloids [13] or evaporation [14]. The Au droplets, in our work, are growing on the Si substrate during the gold evaporation of massive Au. This method allows to control effectively and precisely the catalyst droplet number density which directly influences the SiNW surface number density. For Au droplets deposition, a 7×7 n-type doped Si (111) substrate is prepared. It should be pointed that there is a relation between the SiNWs growth direction and the Si substrate orientation. In order to facilitate the manipulation of the SiNWs, they were grown on the top surface of Si-micro-pillars. These Si-micro-pillars are prepared from Si substrate using a deep reactive ion etch process. Then the Si-micro-pillars are placed in an ultra-high vacuum chamber (10^{-10} mbar) for the Au droplets deposition. A chosen average diameter and droplet number density can be obtained by controlling, according to Ostwald ripening effect [15], the substrate temperature. In order to have a series of Si-micro-pillars with different droplet number densities, three different temperatures (400°C, 430°C and 460°C) at a fix evaporation rate (0.025 monolayer/s) were used (Fig. 2). As expected, the Au droplet number density increases with the decrease of the deposition temperature. The average diameter for 400°C, 430°C and 460°C are 40nm, 55nm and 90nm respectively. For consecutive APT analyses, a small Au droplet diameter and a weak Au droplet number density are needed. Only the Si-micro-pillars in Fig.2 (b) can be used for example.

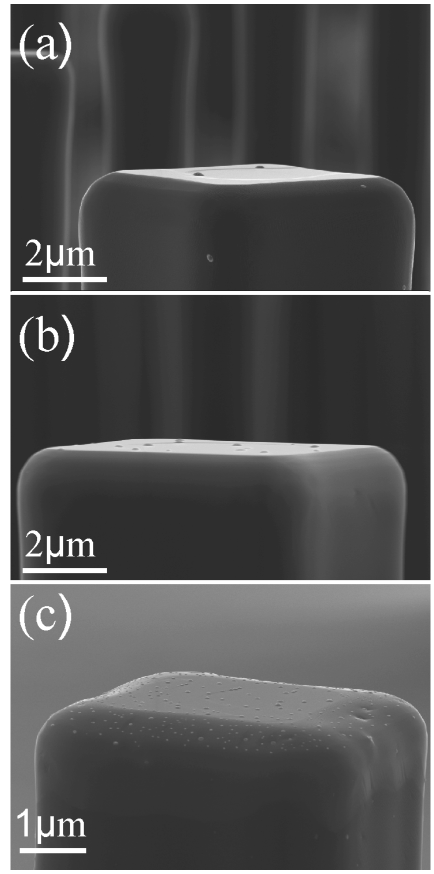

Figure 2. Three different series of Si-micro-pillars with different Au droplet number densities. The evaporation pressure is fixed at 10^{-10} mbar and temperature ranges between: (a) 460 °C; (b) 430 °C and (c) 400 °C. The Au droplet number density increases with the decrease of the deposition temperature.

The SiNWs can be grown on the Si-micro-pillars using the CVD method. In this work, SiH_4 as Si^P and B_2H_6 as p-type D^P were chosen. The carrier gas is chosen to be hydrogen which is also the by-product of SiH_4. The SiH_4 gas is diluted with H_2 in the ratio 50:49. The flow rate of SiH_4 is 50 sccm and silane partial pressure is kept at 0.4 mbar during the NWs growth. The flow rate of B_2H_6 is 1 sccm. The growth temperature and time are 500 °C and 30 min. respectively. It should be noted that this method allows SiNWs with diameter of 50-100nm to be grown perpendicularly to the Si (111) substrate, namely the SiNW growth direction is [111]. However it is shown, as reported in the literature, that when the diameter of SiNW decrease down to 20nm, the [111] growth direction may turn to [112] or [110] because of the surface energy competition between Au/SiNW interface and SiNW sidewall [16]. Taking advantage of this phenomenon, a suitable SiNW sample for APT, namely, a single SiNW perpendicular to the pillar surface, can be grown. As shown in Fig. 3, a SiNW is located vertically on the top of Si micro pillar. The top end of SiNW is illustrated in the inset part and the Au droplet can be clearly seen. A tapering of SiNW can also be seen because of the diffusion of gold atom during SiNW growth [17].

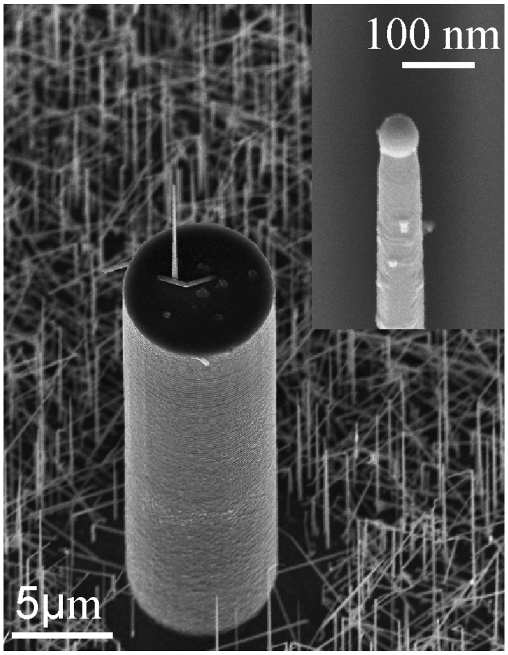

Figure 3. A p-type SiNW on a Si micro pillar fabricated by CVD method. The inset is a zoom of SiNW end and a gold droplet can be clearly seen on the top of SiNW.

2.2 APT sample preparation

For the laser assisted APT, the analyzed sample is normally connected to a W tip, it self included in a steel tube. Thus, after the growth of SiNW on Si micro pillar, an effective four-step *in-situ* process is needed to prepare the APT sample (Fig. 4 (a)).

i) Preparing a W tip using regular electro-polishing;
ii) Choosing a suitable Si micro pillar by using a micro tweezers (Kleindiek, nanotechnik, Germany);
iii) Cutting the Si pillar using a Focused Ion Beam (FIB)/Scanning Electron Microscope (SEM) dual beam system;
iv) Welding the Si pillar and W tip by using a Gas Injection System (GIS).

It should be noted here that a great attention should be paid to SiNW during the step iii) for cutting Si pillar because of the possibility of Ga atoms contamination. A Si micro pillar on a W tip can be prepared with success using this four-step process (Fig. 4 (b)).

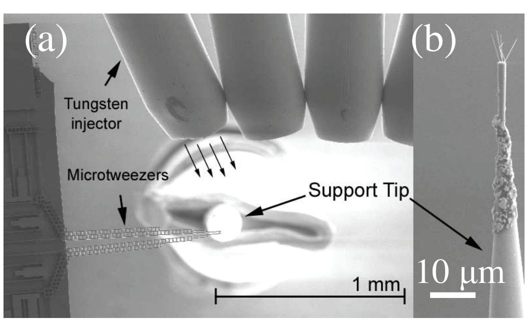

Figure 4. (a) A four-step process for transferring a Si micro pillar to a W tip.

3 RESULTS AND DISCUSSION

The result of the analysis of a p-type SiNW by APT is presented and discussed in this part. The analysis is realized in an ultra high vacuum (10^{-10} mbar) and low temperature condition (80 K). The reason to choose a low temperature is to decrease the atom vibration. The wavelength of the femtosecond laser is chosen to be green (515 nm). The laser power is chosen to be 20 mw. A high electrical potential (10kV) is also applied to the sample (tip/wire). Fig. 5 is the mass-to-charge state ratio spectrum. As indicated on Fig.5, isotopes of different elements (e.g. Si, B and H) can be clearly distinguished. Hydrogen exists in the chamber as a background gas even under ultra high vacuum. Thus, during the evaporation process, hydrogen has an opportunity to interact with the sharp tip (e.g. SiNW), and thus be detected in the spectrum. Both B isotopes are also detected. the three Si isotopes are also detected. As shown in Fig. 5 the large peak tail following the Si peaks is due to thermal effect during laser evaporation.

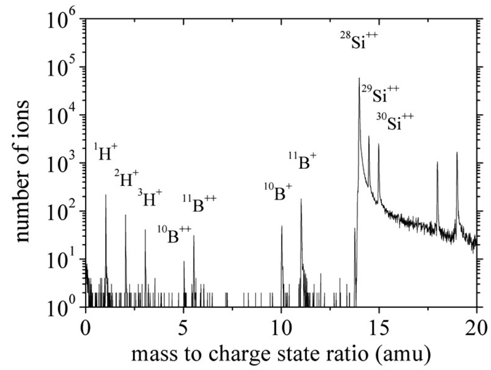

Figure 5. The mass to charge state ratio spectrum of SiNW analyzed by APT. Two types of B isotopes peaks are clearly shown in this spectrum.

The data set obtained after evaporation of an individual SiNW can be reconstructed in a three dimensional view using our APT data treatment software. One of the advantages of APT is that a combination of high spatial resolution (depth < 0.1nm and lateral < 1nm) and accurate concentration (< 100ppm) can be obtained at the same time compared to other techniques. Fig. 6 is a three dimensional reconstruction of an individual SiNW. The reconstruction volume is 16×16×58 nm^3. The matrix and dots represent individual Si and B atoms in SiNW respectively. For clarity of the image, only 20% of Si atoms have been represented in this volume. The B concentration can be calculated and is equal to 1.4×10^{20} B/cm^3 with a detection limit of 5×10^{18} at/cm^3. The B atoms are homogeneously distributed in the core of the SiNW as shown in Fig. 6. It should be noted here that the APT reconstruction volume is representative of the core of the SiNW. The information about the SiNW sidewall surface is missing during the evaporation process. The first conclusion here is that under this SiNWs' growth condition, B atoms can easily be introduced into SiNW (core). Now, the B atoms can integrate the SiNWs by two main pathways:

i) Through the Au droplet during SiNWs growth. The B atoms dissociate at the droplet interface. A complete description of this process needs to take into account the modification of the binary alloys (Au/Si) towards a ternary alloy (Si/Au/B) with different characteristic such as eutectic composition and temperature.

ii) By the lateral surface of the SiNW. Here again a complete description of the phenomena needs to consider the possible mechanisms: 1) diffusion (Fick's law) from the sidewall surface into the SiNW during growth or 2) deposition of B on the sidewall surface during the lateral growth of the SiNW. Works are in progress to work on these hypotheses.

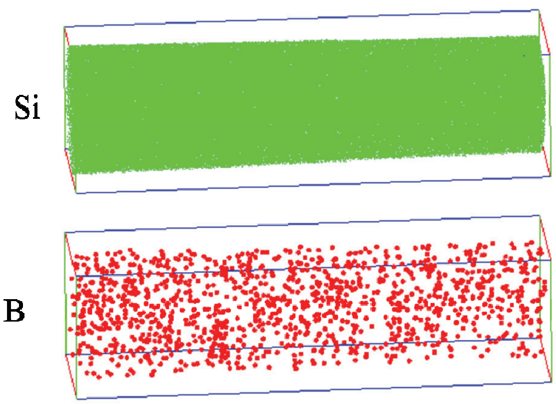

Figure 6. The three dimensional reconstruction of an individual SiNW analyzed by APT. The analyzed volume is 16×16×58 nm^3. The matrix and dots represent Si and B atoms in the SiNW respectively. Only 20% Si atoms are shown in the reconstruction for clarity. B atoms distribute uniformly in SiNW core.

To conclude, we have successfully prepared the optimized Au droplets size and number density for SiNWs growth on Si micro pillars by using an *in-situ* evaporation/deposition method. Taking advantage of this pre-growth preparation, an individual p-type SiNW is grown on a Si micro pillar by CVD method using Au, SiH_4 and B_2H_4 as Si atoms receiver, Si atoms provider and B atoms provider respectively. We have shown that B atoms can be located in SiNW core with a relatively high concentration (1.4×10^{20} B/cm^3) according to our APT results. It indicates that B atoms can effectively incorporate into SiNW following the precursor/dopant ratio. The incorporation mechanism of the dopant into the nanowire is under studies.

Acknowledgement

This work was supported partly by the DGA (Direction Générale de l'Armement) under the contract REI - N°2008.34.0031.

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