Physica B 439 (2014) 41–45

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Properties of Si nanowires as a function of their growth conditions

Anna Cavallini [a,*], Stefania Carapezzi [a], Antonio Castaldini [a], Alessia Irrera [b,c]

[a] Department of Physics and Astronomy, University of Bologna, Viale Berti Pichat 6/2, Bologna I 40127, Italy
[b] IPCF CNR, Viale Stagno D'Alcontres, n. 37-98158 Messina, Italy
[c] MATIS IMM CNR, Viale Santa Sofia, n. 64 95123 Catania, Italy

ARTICLE INFO

Available online 18 November 2013

Keywords:
Silicon nanowires
Shallow levels
Deep levels
Gold incorporation
Bundling

ABSTRACT

Silicon nanowires physical properties strongly depend on their growth conditions, as already assessed. We report on the electrical properties of nanowires (NWs) grown by the vapor–liquid–solid (VLS) mechanism, one of the most established for NW growth, and by the more recent metal-assisted wet chemical etching (MaCE). Wet etching growth process promises to be an industrial advantageous way for growing Si NWs, because of its cheapness, fastness, relative easiness. The electronic level scheme in VLS grown, boron (B)- and phosphorus (P)-doped NWs has been experimentally investigated. We have demonstrated that the doping impurities induce the same shallow levels as in bulk silicon. The presence of two donor levels in the lower half-bandgap is also revealed, which has been successfully related to VLS growth details.

We report, also, on the first results on the physical properties of Si NW arrays grown by MaCE, and compare them to those of VLS grown Si NWs.

1. Introduction

Semiconductor nanowires (NWs) are the most promising candidates to enable the operating of Moore's law for the coming years [1]. Their size may allow overcoming the approaching physical limit of the lithography, to the downscaling of Integrated Circuits (ICs). Additionally, their double nature of interconnection and active devices opens to new possibilities for the clever realization of ICs, with a higher (3D) degree of integration. Technological applications of these 1D nanostructures range in every field of microelectronics: electronic devices [2], logical gates [3], nonvolatile memories [4], photovoltaics [5], photonics [6], and biological sensors [7].

The possibility of availing of the silicon technology, together with the best capability to interface with it, makes the silicon (Si) NWs a truly appealing choice. In view of actual manufacturing of Si NWs-based devices, key issues are the crystal structure of the NWs, their alignment with the substrate, their dopant concentrations and impurity levels. All these issues are directly related to the NW growth methods.

Various techniques and mechanisms have been devised [8], starting from the early sixties of last century [9], to control Si NW growth, diameter, and morphology. The VLS mechanism is the most consolidated [9–11]. Metal-catalyst, usually gold (Au), particles are dispersed over a Si substrate (Fig. 1a). Above the Au–Si eutectic temperature (360 °C), Si dissolves in Au to form Au–Si alloy droplets (Fig. 1b). These latter supersaturate, by collecting Si from the surrounding Si gas precursors and the Si NWs begin to grow at the liquid-solid interface of the droplets (Fig. 1c) [12]. The VLS mechanism is widely employed for Si NWs production, because it allows a precise control of NW morphology, together with the possibility of direct incorporation and compositional control of p- and n-type dopant atoms [13,14], essential to the realization of p–n junctions.

An alternative Si NW fabrication method, which is gaining ever more attention, is the MaCE one [15,16]. This is a wet, electroless, anisotropic etch technique. Typically, Au is deposited as unpatterned, discontinuous layer over a Si substrate, which works as local cathode where the reduction of oxidants, H_2O_2, occurs. The holes generated, h^+, allow the oxidation of silicon at the local anode and give rise to the ionic form, Si^{4+}, soluble in acidic solution, HF. Under controlled conditions, the redox reactions occur only at the Au–Si interface. The result is a Si–etching underneath the Au islands, hence the consequent formation of Si NWs in the Au–uncovered spots of the Si substrate (Fig. 2). MaCE is a simple, low temperature and low-cost way to grow Si NWs, which duplicates the semiconductor and crystallographic features of the source substrate. In principle, these NW arrays are ordered and densely packed, made of high aspect-ratio single crystal Si NWs [17].

In view of the Si NWs exploitation as active layers in actual devices, it is of major importance to know how their synthesis

* Corresponding author. Tel.: +39 51 2095108.
E-mail addresses: anna.cavallini@bo.infn.it, anna.cavallini@unibo.it (A. Cavallini), stefania.carapezzi2@unibo.it (S. Carapezzi), castaldini@bo.infn.it (A. Castaldini), irrera@its.me.cnr.it (A. Irrera).

0921-4526/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.physb.2013.11.021

conditions induce the formation of deep levels in their bandgap as well as the possible diffusion of the metal-catalyst [18]. Another important issue is the modeling of NW doping incorporation that implies, of course, the knowledge of the bandgap shallow levels related to the dopant species. For bulk semiconductors, the defect level characterization methods are consolidated. As regards the NWs, they are, instead, only at the earliest stage [19,20] and there is an impelling necessity of adapting the theoretical and technical basics of the established, experimental techniques to meet the challenge of probing these new, exciting systems.

In the following we report on the experimental evidence of bandgap levels in VLS grown, Au-catalyzed, B- and P-doped Si NW arrays. Their presence has been detected by means of Deep Level Transient Spectroscopy (DLTS) [21,22] and Photo-Induced Current Transient Spectroscopy (PICTS) [22,23] measurements. First, by means of cross-reference of our experimental results with theoretical studies [24], the defect level structure in Si NW bandgap has been analyzed. Second, the shallow and deep levels experimentally found have been interpreted in the light of NW growth details, like the doping procedure and the possible Au contamination, gaining much insight about the detrimental processes occurring during NW synthesis.

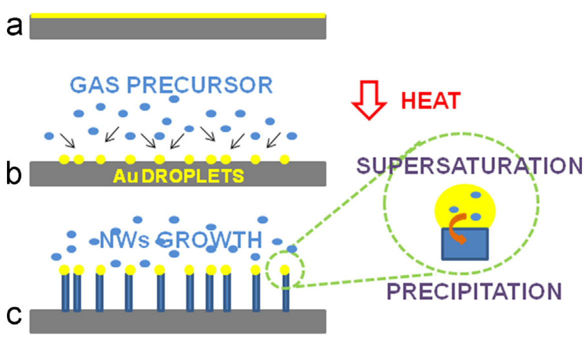

Fig. 1. (a)–(c) Growth of 1D structures by VLS mechanism.

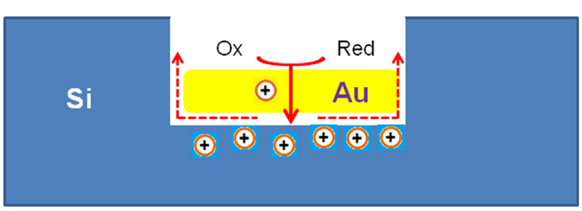

Fig. 2. Scheme of processes involved in the MaCE technique.

Furthermore, preliminary results of DLTS characterization of MaCE fabricated, P-doped Si NWs are reported. We advance some hypotheses to analyze our results into the framework of the previously illustrated MaCE and VLS growth mechanisms.

2. Material and methods

2.1. Si NWs grown by VLS

The growth substrates are n-doped, Czochralski-Si wafers, with carrier concentrations ranging from 3×10^{15} to $1\times10^{16}\ \mathrm{cm}^{-3}$. They have been thermally oxidized in order to create a superficial SiO_2 layer of 200 nm. To catalyze the NWs growth, Au particles with a diameter of about 3 nm have been dispersed over these substrates. The Si NWs have been synthesized via VLS mechanism into a Chemical Vapor Deposition (CVD) chamber at the temperature of 600 °C, in flowing silane as Si gas precursor. The doping procedure has been performed during the NW growth using diborane and phosphine as p-type and n-type dopant precursors, respectively. The carrier gas was nitrogen. The dopant concentration, N_A, in B-doped Si NWs ranges from 10^{18} to $10^{19}\ \mathrm{cm}^{-3}$, while N_D, in P-doped Si NWs is in the order of $10^{18}\ \mathrm{cm}^{-3}$.

Scanning electron microscopy (SEM) has been used to perform the morphological characterization of the NW arrays. Both B- (Fig. 3a)) and P-doped (Fig. 3b)) NWs show a cylindrical shape. The average diameter values have been determined through statistical analysis of SEM micrographs. The B-doped NWs show an average diameter of 300–380 nm, while the P-doped ones show an average diameter of 20–26 nm. Because of these sizes, no quantum confinement effects are expected. The differences in the average diameter values between B- and P-doped Si NWs are most likely related to surface doping during the NWs synthesis [25–27].

2.2. Si NWs grown by MaCE

The source substrate is n-type (P concentration of $10^{16}\ \mathrm{cm}^{-3}$) single crystal, (1 0 0)-oriented Si wafer. First, the surface has been cleaned to remove native oxide by UV oxidizing and dipping it in 5% HF. Afterwards, a 2 nm-thick Au layer has been deposited on the Si substrate by electron beam evaporation. Finally, the NWs fabrication has been performed by etching the sample, in an aqueous solution of HF and H_2O_2. The whole growth process has occurred at room temperature.

The structural characterization of the (1 0 0)-oriented NW arrays has been performed by SEM (micrographs obtained both

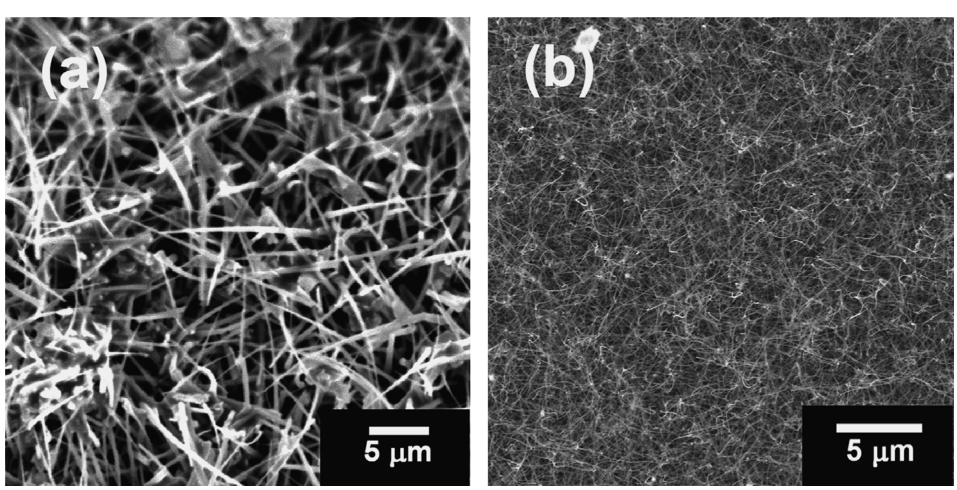

Fig. 3. SEM planar view (beam voltage $E_b=10$ kV) of VLS grown (a) B-doped and (b) P-doped Si NWs.