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Growth parameters and shape specific synthesis of silicon nanowires by the VLS method

Laurence Latu-Romain, Céline Mouchet, Cyril Cayron, Emmanuelle Rouviere, Jean-Pierre Simonato

Abstract In this paper the effect of varying temperature, pressure and chemical precursors on the vapour–liquid–solid (VLS) growth of silicon nanowires (Si NWs) have been investigated. Some aspects of nucleation and growth mechanisms are discussed. Control on Si NW morphology by varying the choice of gaseous precursor (silane or dichlorosilane) at elevated temperatures is reported.

Keywords Silicon nanowires · Growth parameters · Gas precursor · Shape control · Synthesis · Surrounding environment

Introduction

Semiconductor nanowires have attracted a lot of attention in recent years due to their fascinating intrinsic properties and their potential applications in emerging nanoelectronics (Li et al. 2006; Lieber et al. 2007). Specifically, silicon nanowires (Si NWs)

have been particularly studied due to the importance of silicon to the microelectronics industry. These nanowires have been employed as fundamental building blocks in various micro and nanoelectronics experimental devices and are expected to play a major role in the development of future electronics (Mc Alpine et al. 2007; Yu et al. 2007; Verplanck et al. 2007; Yang et al. 2006).

To date, a variety of methods have been employed for the synthesis of Si NWs. The most popular approach, vapour–liquid–solid (VLS) growth mechanism first reported 40 years ago by Wagner and Ellis (1964) requires the use of catalytic nanoparticles and a Si-containing gas precursor. Gold is the most commonly employed catalyst although other systems have proven to be effective (Kamins et al. 2001; Baron et al. 2006). Catalytic gold nanoparticles are generally obtained by two routes: dewetting of a gold thin film from a surface (Kwak et al. 2007) or deposition of colloidal gold (Cui et al. 2001). When the gold nanoparticles are present on the growth substrate, the VLS process proceeds in three main steps. Firstly, the alloying process consists of the formation of liquid droplet containing the metal catalyst and dissolved Si. For gold, the eutectic composition is obtained at 363 °C. Secondly, when the silicon concentration reaches the upper solubility limit, nanowire nucleation commences. At this stage, a three phase biphasic system (SiH₄ gas, Au/Si alloy and Si solid) may be attained, the Au/Si liquid droplet being intercalated between the gaseous and the solid

L. Latu-Romain · C. Mouchet · E. Rouviere · J.-P. Simonato (✉)
CEA-Grenoble, LITEN/DTNM/LCH, 17, rue des Martyrs,
38054 Grenoble Cedex 9, France
e-mail: jean-pierre.simonato@cea.fr

C. Cayron
CEA-Grenoble, LITEN/DTH/Grenoble Electron
Microscopy-Minatec, 17, rue des Martyrs,
38054 Grenoble Cedex 9, France

phases. Thirdly, the axial growth arising from further dissolution of Si into the liquid phase and simultaneous crystal packing at the bottom leads to a forward push of the catalytic phase to form a nanowire. On completion of the nanowire growth phase, the gold catalyst is observed at the nanowire tips.

This process strongly dependant on growth conditions (e.g. temperature, pressure or gas precursors) may lead to formation of Si NWs with significant different morphologies. In this paper, we report the effects of varying temperature, pressure and chemical precursor on Si NWs growth, and we present specific conditions necessary to obtain non-symmetrical nanowires.

Experiments

Thin gold films of 10 nm were deposited on $\langle 111 \rangle$ oriented Si substrates in a PVD reactor. Dewetting was then performed at 550 °C for 10 min under dihydrogen atmosphere. Catalytic growth of Si NWs was performed in a 200 mm CVD Centura reactor, using either silane (SiH_4) or dichlorosilane (SiH_2Cl_2), diluted in H_2 , as precursors. The impacts of varying temperature, pressure and gas precursors were studied independently. The growth temperature was varied from 500 °C to 850 °C and the precursor gas flow rate varied from 20 sccm to 150 sccm at pressures ranging from 10 to 80 Torr (1.33×10^3 – 1.07×10^4 Pa). A flow of H_2 was kept constant during the experiment at 10 slm. The diameters of the nanowires ranged from 50 nm to 100 nm at 500 °C, and from 400 nm to 1 μm at 850 °C. Scanning Electron Microscopy observations were performed using a SEM-FEG (Leo 1530).

Results and discussion

Effect of temperature

The thermal activation parameter was monitored through an Arrhenius diagram which plots the logarithm of the growth rate as a function of the inverse of temperature (Fig. 1). Two kinetic regimes were observed. At high temperature, i.e. above 700 °C, a deviation from the linear behaviour was observed in the Arrhenius plot. The growth rate did

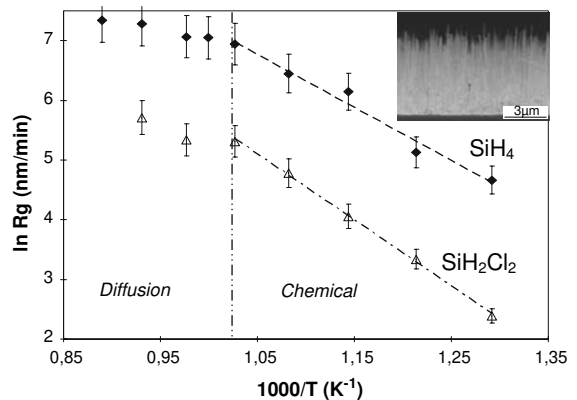


Fig. 1 Si nanowires growth rate as a function of reverse absolute temperature (Arrhenius plot) for two gas precursors: SiH_4 (full diamonds) and SiH_2Cl_2 (empty triangles). Inset: SEM micrograph of Si nanowires grown with SiH_4 at 600 °C

not depend strongly on the temperature which is certainly indicative that mass transport limitation becomes significant beyond 700 °C. The slight increase of the growth rate observed above 700 °C might be attributed to enhanced diffusivity of the reactant species in the gas phase. The second regime, at lower temperature, from 500 °C to 700 °C, was limited by the chemical reaction kinetics, the growth rate decreasing exponentially with increasing reverse absolute temperature (Fig. 3 inset shows Si NWs for a synthesis at 600 °C using SiH_4 as gas precursor). In the latter case, the activation energy E_a was calculated to be 74 kJ mol^{-1} using SiH_4 as the gaseous precursor. This value is much lower than the reported activation energy for Si epitaxy with SiH_4 of 196 kJ mol^{-1} (Hartmann et al. 2002), thus suggesting a catalyzed reaction process. The activation energy calculated when using SiH_2Cl_2 as gaseous precursor was significantly higher than that with silane, a value of 92 kJ mol^{-1} being extracted from experimental data. Although it was difficult to determine exactly the limiting stage of growth, it seems reasonable to assume that the observed difference between SiH_4 and SiH_2Cl_2 was due to the Si precursor decomposition. Indeed, the Si–Cl bond (456 kJ mol^{-1}) has a much higher energy than the Si–H bond (298 kJ mol^{-1}) and therefore requires more energy to be broken during the catalytic process.

It must also be noted that SiH_2Cl_2 decomposition generates HCl as a by-product, which may lead to a specific Si NWs shape at high temperatures (*vide infra*).

Effect of pressure

Effect of pressure was studied at 600 °C using silane. It was observed that the rate of growth was strongly dependent on the reactor pressure (Fig. 2). At low pressure, i.e., below 1000 Pa, the growth rate was below $0.1 \mu\text{m min}^{-1}$. It increased following a linear increase of $2.5 \times 10^{-4} \mu\text{m min}^{-1} \text{Pa}^{-1}$ up to $1.5 \mu\text{m min}^{-1}$ at 6000 Pa. The growth rate was then stabilized whatever at the higher pressure. Even though a high growth rate was desirable, it lead in these conditions to randomized structured nanowires with many kinks. To obtain reproducible nanowires for making nanoelectronics devices, nanowires were grown at 10 Torr (1333 Pa).

Effect of incubation time for nanowires grown with silane

Growth rate was not observed to vary with experiment duration. Nevertheless, it has been noticed that a few seconds to a few minutes, were needed before the commencement of Si NW growth was observed. This delay corresponded to an actual physical phenomenon necessary for the beginning of growth and not to the reactor filling time which was very fast. If one carefully observed the morphologies of the nanowires following the beginning of growth (Fig. 3a), it appeared that the nanowires with small diameters were longer than corresponding nanowires with bigger diameters. As a consequence, it appears logical that

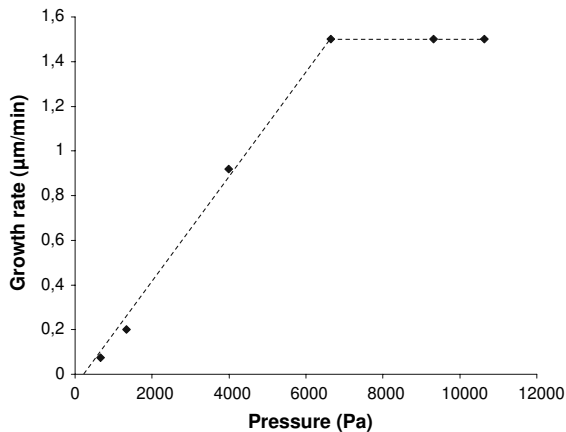


Fig. 2 Growth rate as a function of pressure at 600 °C with silane

this nucleation step may be directly linked to the volume of the droplet. The observed incubation time cannot be attributed to the diffusion of silicon inside the liquid Au-Si droplet which was a fast process. These incubation times have already been discussed and attributed to the time of diffusion of silicon through the solid catalyst (Kalache et al. 2006). It seems reasonable to assume that the upper limit of silicon solubility in liquid droplets of catalyst was first obtained for small droplets since they present the highest surface/volume ratios. In our work, although thinner nanowires begin their growth earlier than thicker nanowires, no significant difference is observed between thin and thick Si NWs averaged lengths when the Si NWs are at least $2 \mu\text{m}$ long (Fig. 3b). It indicated that incubation delay is short with respect to the overall synthesis duration.

Effect of the chemical nature of the gaseous precursor

To the best of our knowledge, only one synthesis of Si NWs with SiH_2Cl_2 as reactant has been reported (Kamins et al. 2001). In this work, the Si NWs were grown with Ti as catalyst and without VLS mechanism.

The first difference between SiH_2Cl_2 and SiH_4 nanowire growth is the activation energy of the catalyzed reaction (*vide supra*). Another difference is the growth mechanism at high temperature. When SiH_2Cl_2 was used, the decomposition of one molecule of the precursor led to the formation of one Si atom and two HCl molecules. Whereas the latter did not have visible effect on Si NWs below 700 °C, the acidic molecules began to attack the Si NWs walls above this temperature. It induced a morphology change from straight nanowires to nanowires thinner at the basis than at the tip (Fig. 4a). The nanowire diameter decrease, at 800 °C, from the apex to the basis was measured to be $250 \text{ nm } \mu\text{m}^{-1}$.

In contrast, when using SiH_4 as precursor, at growth temperature exceeding 700 °C, the nanowires were clearly larger at the basis than at the tip (Fig. 4b). A similar trend was already observed in CVD process for which tapered Si NWs were obtained (Cao et al. 2006). This phenomenon was explained by catalyst mass loss through the V-L interface due to electrostatic charge-induced dissociation of the droplet. The nanowire diameter increase from the tip to the basis was

Fig. 3 (a) SEM image showing droplet size related incubation time at the very beginning of the synthesis (SiH_4 precursor). (b) SEM image of 2 μm long Si nanowires. No significant different average length was observed for thin and thick nanowires

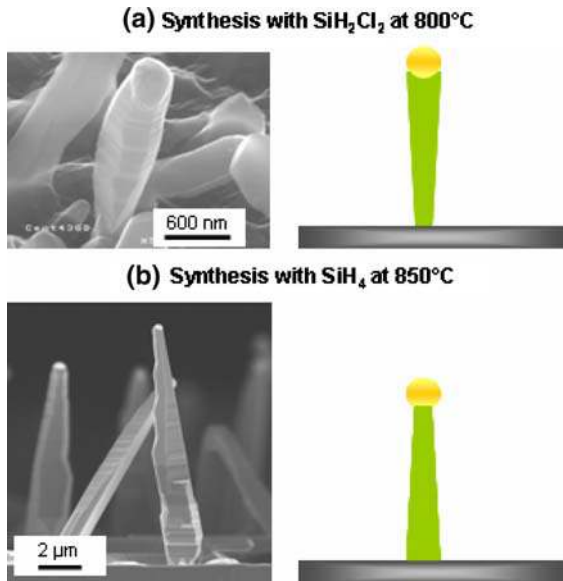
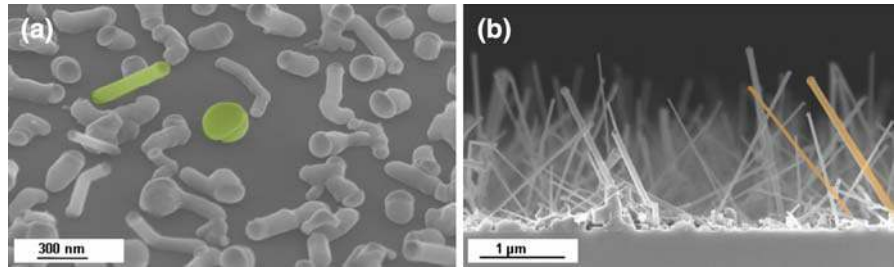


Fig. 4 (a) SEM image of a Si nanowire obtained from SiH_2Cl_2 at 800 °C. (b) SEM image of Si nanowires grown at high temperature (850 °C) with SiH_4

about 140 nm μm^{-1} at 850 °C. These nanowires also show longer facets at the base than at the tip.

These two examples demonstrated that Si NWs with different shapes may be obtained. Whereas both gas precursors allow the synthesis of very straight nanowires below 700 °C, conical shapes nanowires varying from the base to the apex or vice versa may be achieved at high temperature by an appropriate choice of the gas precursor.

Structural characterization

Most Si NWs exhibited $\langle 111 \rangle$ growth directions, with some nanowires exhibiting $\langle 112 \rangle$ and very few $\langle 110 \rangle$ growth directions. The Si NWs were either single crystal or polycrystalline with structural defects such

as twins, micro-twins and stacking faults. It should be noted that the same defects were observed using both chemical gaseous precursors. A full study on their structural analysis will be published elsewhere.

Conclusion

The effects of temperature and pressure on Si NW growth by the VLS method have been investigated. It has been shown that at high temperature (>700 °C), the limiting growth step was the diffusion of the gaseous species whereas at low temperature (500–700 °C), the limiting step was the decomposition of the gaseous precursor. By an adequate choice of the chemical nature of the precursor and appropriate temperature, it was possible to obtain various shapes of Si NWs i.e. either straight, larger at the basis or larger at the tip.

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