JOURNALOF

Ceramic Processing Research

# Growth kinetics, crystal structures, and properties of silicon nanowires grown by a metal-catalyzed vapor-liquid-solid process

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One-dimensional (1D) silicon nanowires (SiNWs) are currently of great interest as one of the most useful and powerful forms of Si nanostructures that could provide a promising alternative for emerging electronic systems. However, the assembly of SiNWs for nanoelectronics and circuits brings about new challenges such as control of the sizes, structures, and properties of SiNWs during the synthesis step. This paper provides a detailed overview of metal-catalyzed vapor-liquid-solid growth of SiNWs, with particular emphases on the growth kinetics and crystal structures of SiNWs. Furthermore, the synthesizing strategies to systematically control the size, crystallographic orientation, and impurity content of SiNWs are highlighted with the aim of tailoring the properties of SiNWs for future device applications.

Key words: Silicon, Nanowires, Vapor-liquid-solid, Growth kinetics, Crystal structures.

## Introduction

The continuous shrinking of silicon-based devices [1] and observation of bright luminescence in the visible spectral range from nanostructured silicon [2] have triggered tremendous research interest in the synthesis, properties, and applications of silicon on the nanoscale [3]. In particular, one-dimensional (1D) silicon nanowires (SiNWs) have one unconstrained size available for electrical conduction, which, coupled with tremendous improvements in silicon technology, makes SiNW an exciting building block for emerging bottom-up nanotechnology [4].

On the basis of the growth mechanism, the most common synthetic approaches for 1D SiNWs are categorized into several methods, including template-assisted synthesis [5], oxide-assisted growth [6], solution-liquid-solid (SLS) growth [7], and vapor-liquid-solid (VLS) growth [8]. Of the synthetic approaches, the author has focused on VLS as it can be developed for large-scale synthesis of single-crystalline SiNWs with good control of the diameter, location, and electrical properties of the SiNWs [9-11]. The kinetics in the VLS growth of SiNWs have been studied by several groups and the growth rate and crystall -ographic orientation of SiNWs are strongly dependent on their diameter as well as the synthesizing conditions [9, 12-16]. Interestingly, Si whiskers with a micrometrescale diameter exhibited ultrafast growth reaching  $\sim 1 \,\mu m/s$ [17], whereas the growth rate of nanometre-scale diameter Si wires decreased abruptly, presumably due to the surface contribution of the Gibbs-Thomson effect [13, 18]. Until

now, control of the growth rate and structure of SiNWs have not been satisfactorily addressed. Therefore, the rational synthesis and design of SiNWs for electronic applications require a more comprehensive understanding of the kinetics and mechanism of VLS growth.

In this paper, the bottom-up based synthesis, properties and potential of SiNWs are presented to provide researchers with a comprehensive overview of the VLS growth of SiNWs. This paper begins with an introduction to the strategies that can be used to achieve 1D growth of silicon by the VLS process, with a special focus on growth kinetics. Then, the author discusses the dependence of the SiNW growth rate and crystal structure on the diameters of the nanowires as well as the synthesizing conditions, followed by strategies to synthesize SiNWs with control of size and growth direction. Finally, the issue of impurities in SiNWs combined with several approaches to incorporate certain impurities into SiNWs for fine tuning of their electronic properties is discussed.

#### Overview of SiNW VLS growth

Over the past several years, much effort has been devoted to synthesizing various 1D semiconductor nanostructures. Specifically, the VLS process was originally developed by Wanger and Ellis to produce micrometre-sized Si whiskers in the 1,960 s [8], and several modified versions combined with chemical vapor deposition (CVD) [9, 14], laser ablation [11], physical evaporation, and molecular beam epitaxy [10] have been developed to generate a rich variety of inorganic nanowires.

The major steps involved in the VLS process for Aucatalyzed SiNW growth is schematically depicted in Fig. 1(a) As the continuous process of (i) *catalytic adsorption and cracking of the gaseous reactants at the surface of liquid nanoparticles*, (ii) *diffusion of Si through the liquid alloy to* 

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**Fig. 1.** (a) Schematic illustrating the VLS process for Aucatalyzed SiNW growth including (i) catalytic adsorption, (ii) diffusion, and the (iii) precipitation process. (b) Binary Au-Si phase diagram. Arrow indicates the precipitation of solid Si from the supersaturated Au-Si liquid alloy droplet.

a sink, and (iii) precipitation of Si at the initial liquid-solid interfaces, VLS occurs within nanometre-size liquid alloy particles that define the initiation and elongation of nanowires [13, 18-20]. It is predicted from the binary Au-Si phase diagram (Fig. 1(b)) that Au nanoparticles form liquid alloy droplets with Si at a temperature greater than the eutectic temperature (363 °C). The surface of the liquid nanoparticles has a higher sticking coefficient and thus, provides a preferential absorption site for incoming vapor reactants. When the liquid nanoparticle becomes supersaturated with the vapor reactants, nucleation and subsequent crystal growth occur at the Au-Si/Si interface. Once the crystal growth starts, highly anisotropic crystal growth is directed by the continuous precipitation of Si at the initial interface to minimize the interfacial energy. If the temperature and vapor pressure of the Si precursor in the system is kept sufficiently low that there is extremely limited homogeneous deposition of Si on the nanowire sidewalls, the diameter of SiNWs can be kept uniform, comparable to the size of the Au nanoparticles along the micrometre scale length [9, 14].

# Kinetics in VLS growth of SiNWs

In principle, 1D nanowire growth continues only if the liquid nanoparticle remains supersaturated with a continuous supply of the Si precursor, indicating the potential possibility to systematically control the nanowire length by varying the growth time. Meanwhile, the



Fig. 2. SEM images of three types of SiNWs synthesized by Aucatalyzed CVD. (a) Epitaxially-grown Si nanowhiskers (short SiNWs) grown slowly. Reprinted with permission from Ref. [21]. Copyright 2008, American Institute of Physics. (b) Long SiNWs grown fast. (c) Ultra-long SiNWs grown in an ultra-fast growth regime. The SiNW was transferred from the growth substrate (inset) to a clean substrate. Reproduced with permission from Ref. [22]. Copyright 1998 American Chemical Society.

SiNW growth rate can be varied by different growth environments [12, 13]. Thus, a detailed investigation of the key factors affecting the kinetics of VLS growth is essential for rational design and/or synthesis of SiNWs. One important issue is identifying which of the three steps in the VLS growth process is rate-limiting. Based on numerous studies of the crystal growth process, it is generally accepted that Si diffusion within a liquid alloy is fast enough, as crystal growth is not limited by this step, but rather controlled by the supersaturation [18]. However, which of the remaining steps, (i) or (iii), is the rate-limiting step with respect to the supersaturation remains controversial [12-13, 18-19]. Bootsma and Gassen considered step (i), catalytic adsorption, as the ratedetermining step based on the observation that the growth rate of SiNWs was proportional to the vapor pressure of the precursor [19], while Givargizov concluded that step (iii), precipitation, is the rate-determining step due to the growth direction dependence of the growth rate [18]. In contrast, Schmidt et al. proposed a model considering the interplay of both steps (i) and (iii) to account for the different experimental observations [13].

### Growth rate of SiNWs

If the key factors affecting the growth kinetics in the metal-catalyzed VLS process are properly determined, the overall growth rate can be controlled, leading to

Туре	Reactant	Partial pressure	Temperature	Growth rate	Ref.
Nanowhiskers	SiH <sub>4</sub>	80 mTorr (0.1 mbar)	450 °C	~20 nm·minute <sup>-1</sup>	[21]
			490 °C	~50 nm·minute <sup>-1</sup>	
Long NWs	$SiH_4$	3,000 mTorr (4 mbar)	400 °C	~0.2 $\mu m \cdot minute^{-1}$	[22]
			450 °C	$\sim 1.0 \ \mu m \cdot minute^{-1}$	
Ultra-long NWs	$Si_2H_6$	3,000 mTorr (4 mbar)	400 °C	~31 µm·minute <sup>-1</sup>	[22]

 Table 1. Growth rates for three types of SiNWs under different Au-catalyzed CVD conditions

SiNWs with different lengths. Fig. 2 shows representative scanning electron microscopy (SEM) images of three technically important types of SiNWs synthesized with different growth rates: (a) epitaxially-grown Si nanowhiskers (short SiNWs) grown slowly [21], (b) long SiNWs grown fast, and (c) ultra-long SiNWs grown in an ultra-fast growth regime [22]. As summarized in Table 1, the growth rates of SiNWs grown using silane (SiH<sub>4</sub>) as a source gas increased according to the partial pressure of silane ( $pSiH_4$ ); from ~20 nm·minute<sup>-1</sup> at 80 mTorr (0.1 mbar)  $pSiH_4$  to ~1  $\mu$ m·minute<sup>-1</sup> at 3,000 mTorr (4 mbar)  $pSiH_4$ , with a growth temperature of 450 °C. This result indicates that step (i), catalytic adsorption, is critical in this growth regime, where the gas-phase kinetics or interplay between mass-transport and decomposition of the precursor gas to/at the catalyzing liquid surfaces plays an important role in determining the growth kinetics. Both cases (80 mTorr (0.1 mbar) pSiH<sub>4</sub> and 3,000 mTorr (4 mbar) pSiH<sub>4</sub>) show that growth rates are strongly affected by the temperatures, thus it is suggested that decomposition kinetics prevails over gas phase mass-transport [23]. Therefore, the growth rate could be further increased at higher temperatures by accelerating the decomposition step, whereas the side effects, such as uncatalyzed deposition at the NW sidewalls, determine the upper temperature limit.

To explore the new NW growth regime by boosting the decomposition kinetics without increasing the temperature, disilane (Si<sub>2</sub>H<sub>6</sub>) has been introduced as an alternative chemical vapor source [22]. Si<sub>2</sub>H<sub>6</sub> is expected to have a much higher catalytic decomposition rate due to a lower activation energy for the decomposition of the Si-Si bond than for the Si-H bond in SiH<sub>4</sub> [24]. The use of more reactive precursors of Si<sub>2</sub>H<sub>6</sub> as a chemical vapor source provides a lower growth temperature near 390-410 °C, which is roughly 50 °C less than that for SiH<sub>4</sub>, and elongation of the NW length to the millimetre-scale. A series of SEM images of a well isolated, 2.3-mm-long SiNW (Fig. 2(c)) show a uniform diameter along the whole nanowire, with starting and end points of ca. 31 and 33 nm, respectively. Quantitative analysis showed that the average length of 1-hour grown SiNWs is ~1.8 mm and the longest nanowire was 3.5 mm, corresponding to an average growth rate of  $\sim 31 \,\mu m \cdot minute^{-1}$ , which is  $\sim$ 130 times greater than that for SiH<sub>4</sub> at the same temperature (400 °C) and 31 times greater than for SiH<sub>4</sub> at 450 °C (Table 1).



**Fig. 3.** (a-c) TEM images of SiNWs with diameters of (a) 5.7, (b) 13.2, and (c) 25 nm. (d-f) Histograms of the growth direction for SiNWs with diameters in the range of (d) 3-10 nm, (b) 10-20 nm, and (c) 20-30 nm. Reproduced with permission from Ref. [14]. Copyright 2008 American Chemical Society.

## Crystal structures of SiNWs

Properties of nanowires are strongly dependent on the crystal structures, including the growth direction and surface crystal structures. In addition, for epitaxial growth of ordered nanowire arrays, it is critically important to control the growth direction [5, 15]. For SiNWs grown by a metal catalyzed VLS process, three preferential growth directions, <111>, <110>, and <112>, are frequently observed [9, 14-15]. Fig. 3 summarizes the general SiNW growth behavior diameter-dependent preferential growth direction. A histogram of the growth directions for SiNWs with various diameters studied by transmission electron microscopy (TEM) shows that smaller diameter SiNWs tend to grow along the <110> direction (Figs. 3(a) and (d)), whereas a crossover to the <111> direction can be observed for SiNWs with a diameter larger than roughly 20 nm (Figs. 3(c) and (f)). The <112> oriented SiNWs are also observed in the intermediate range (Figs. 3(b) and (e)). To understand the diameter-dependent growth directions in SiNWs, Schmidt et al. proposed a model based on the free energy of SiNWs, which is influenced by the interplay of the liquid-solid interfacial



Fig. 4. TEM images of ultra-long SiNWs with diameters of (a) 18 and (b) 78 nm. The inset in (b) is a lower magnification image of the SiNW. Reproduced with permission from Ref. [22]. Copyright 2008 American Chemical Society.

tension and the Si surface edge tension [15]. Hypothesizing the existence of an intermediate transition layer where Si atoms are not fully settled before they form a crystal, the crossover diameter ( $D_c$ ) from <110> to <111> is given by:

$$D_c = 2\Delta z \frac{\sigma_s - \sigma'_s}{0.39\sigma'_{ls} - 0.43\sigma_{ls}} \tag{1}$$

where  $\Delta z$  is the interfacial layer thickness,  $\sigma_s (1.53 \text{ J} \cdot \text{m}^{-2})$ the surface energy for <111>-oriented NWs,  $\sigma'_s (1.28 \text{ J} \cdot \text{m}^{-2})$ the surface energy for <110>-oriented NWs,  $\sigma_{ls} (0.62 \text{ J} \cdot \text{m}^{-2})$ the interfacial tension for <111>-oriented NWs, and  $\sigma'_{ls} (0.76 \text{ J} \cdot \text{m}^{-2})$  the surface energy for <110>-oriented NWs. By assuming that the transition layer extends to a few atomic layers below the liquid-solid interface ( $\Delta z \approx 1 \text{ nm}$ ), a  $D_c$  of 20 nm was obtained, which is in accordance with previous experimental data.

In contrast, ultra-long SiNWs prefer to grow along the <110> direction without exhibiting a diameter-dependent preference [22]. TEM studies of ultra-long SiNWs showed that the nanowires have a single crystalline structure along a millimetrre scale length, with preferential growth along the <110> direction independent of diameter up to 80 nm (Fig. 4). The anomalous growth habits might be driven by growth kinetics, representing the new criterion that with increasing growth rate, the effect of the solid surface energy on the nanowire growth direction dominates the solid/liquid interfacial energy. As described previously, roughly 1-nm-thick  $\Delta z$ , corresponding to a few atomic layers, was adopted to produce a crossover diameter of approximately 20 nm for slowly grown SiNWs. Meanwhile, it is suggested that would increase with increasing crystallization rate, accompanying the increase of the  $D_c$ . By assuming the  $D_c$  would be larger than 80 nm based on the experimental data, a  $\Delta z$  larger than  $\sim$ 4 nm can be estimated from Equation (1) in an ultrafast growth regime, although detailed kinetic analysis should be supplemented to quantitatively analyze this point.

On the other hand, Lugstein *et al.* have shown that under a low  $pSiH_4$  condition, the growth directions of ~100-nm-thick SiNWs change as a function of total pressure; from the <111> direction at a total pressure of 3 mbar (~2.250 torr) to <112> at a total pressure of 15 mbar (~11.25 torr) [16]. Even though the detailed mechanisms are unclear, the unique growth phenomena -growth rate and total pressure-dependent growth directions suggest that the crystallographic orientation of the nanowires can be controlled by exploiting the VLS growth kinetics.

## **Impurities in SiNWs**

Impurities in semiconductors play an important role in determining the properties of materials and thus, control of the impurities can be exploited as a powerful means to tailor the electrical and optical properties of semiconductors. Diffusion of Au from the catalyst droplets to the nanowire has been a technologically important issue since Au impurities are known to generate unintentional deep trap centers in Si [25]. Some studies have confirmed that a substantial amount of Au diffuses along the SiNWs surfaces [26, 27], whereas studies based on other measurements argued that the amount of Au incorporated into nanowires is negligible [9, 14]. These different results can be attributed to different amount of Au diffusion according to the growth environment, including the reactant partial pressure, temperature, and the presence of oxygen [27-29]. We note that even after the growth of millimetre-long SiNWs, Au clusters remained at their tips, indicating that Au incorporation into SiNWs can be significantly limited during growth under certain growth conditions.

Intentional impurities, *i.e.* dopants, can be introduced into SiNWs with the aim to control the electrical properties of the nanowires. Several doping techniques developed so far can be categorized by the doping sequence: (a) homogeneous electrical doping during synthesis, (b) doping incorporation after synthesis, and (c) delta-doping (Fig. 5).

Homogeneous electrical doping of SiNWs was first demonstrated by introducing boron and phosphorus as *p*-type and *n*-type dopants during their laser catalytic



Fig. 5. Schematics illustrating three types of doping techniques categorized by the doping sequence: (a) doping during synthesis, (b) doping after synthesis by thermal diffusion, and (c) delta-doping. Typical  $I_D V_G$  curves for (d) delta-doped, *p*-type SiNW FETs measured at  $V_D = -1$  V and (e) delta-doped, *n*-type SiNW FETs measured at  $V_D = 1$  V. From Ref. [33].

growth [11]. Following this study, high-performance SiNW FETs were demonstrated based on *p*-type and *n*-type doped SiNWs by incorporating diborane ( $B_2H_6$ ) or phosphine (PH<sub>3</sub>) precursors during metal-catalyzed CVD growth (Fig. 5(a)) [30, 31].

Ho *et al.* demonstrated doping of SiNWs by introducing self-assembled molecular monolayers, where dopant atoms at molecular monolayers formed on the surfaces of as-grown SiNWs are incorporated into SiNW volumes by thermal diffusion (Fig. 5(b)) [32]. Due to the self-limiting surface reaction, this approach can be exploited to dope SiNWs with a well-defined spatial resolution for high-performance FET applications.

Park demonstrated delta-doping in SiNWs by axial growth of undoped core SiNWs, introducing self-limited deltadoped layers and capping of the dopant layers with undoped Si shells (Fig. 5(c)) [33]. In principle, deltadoped semiconductors provide high carrier mobility since the dopants are confined within a few layers and thus, the probability of impurity scattering is reduced. As shown in Figs. 5(d) and (e), drain current versus drain voltage  $(I_D - V_G)$  curves demonstrate that the boronand phosphorus-doped SiNWs exhibit depletion-mode *p*-type and *n*-type behaviors, respectively. The capability to fine tune the electronic properties of SiNWs indicates significant progress towards developing nanoscale comp -lementary logic devices and flexible circuits based on SiNW building blocks.

## **Conclusions and outlook**

In this paper, the growth kinetics, crystal structures, and properties of of SiNWs prepared by metal-catalyzed VLS process were presented. Catalytic adsorption and precipitation steps were discussed as the critical ratelimiting steps in the VLS process. The synthesis of three types of SiNWs, namely Si nanowhiskers, long SiNWs, and ultra-long SiNWs, and the key factors affecting their growth kinetics were discussed. Structural characterization of SiNWs showed that the growth direction of SiNWs generally changes with increasing diameter from <110> or <112> to <111>, while the growth direction is affected by the growth rate and total pressure, suggesting that kinetic effects can be exploited to control the crystal structures of the nanowires. Lastly, several doping strategies introduced to control the electronic properties of SiNWs were discussed; electrical transport measurements have shown that these doped SiNWs behave as *p*-type or *n*-type semiconductors.

## Acknowledgements

This work was supported by the research fund of Hanyang University (HY-2007-N).

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