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We have measured the growth rate of silicon nanowires (SiNWs), which were grown at temperatures between 365 and 495 °C via the vapor-liquid-solid (VLS) mechanism. We grew SiNWs using gold as catalysts and monosilane (SiH_4) as a vapor phase reactant. Observing SiNWs by means of transmission electron microscopy, we have found that SiNWs with smaller diameters grow slower than those with larger ones, and the critical diameter at which growth stops completely exists. We have estimated the critical diameter of SiNWs to be about 2 nm. We have also measured the temperature dependence of the growth rate of SiNWs and estimated the activation energy of the growth of SiNWs to be 230 kJ/mol. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1888034]

Nanowires, or nanorods are one of the most important nanomaterials for future nanotechnology. Among various processes of growing nanowires, chemical vapor deposition (CVD) via the vapor-liquid-solid (VLS) mechanism has been most extensively studied. In fact, the precursors of electronic and MEMS devices have been fabricated from Si nanowires (SiNWs).[1,2] Nevertheless, a fundamental question remains on nanowires, that is the minimum diameter of them which is attainable by the growth method. In order to address the question, the growth of nanowires is needed to study quantitatively. Previous studies dealt with only much thicker wires,[3–5] and the growth of actual nanowires, the diameters of which are smaller than 50 nm, has never been studied systematically. In this letter, we have quantitatively examined the growth of SiNWs, and have found that the growth rate of SiNWs depends on both their diameter and growth temperatures. We have estimated the critical diameter of SiNWs grown via the VLS mechanism to be about 2 nm.

We grew SiNWs by CVD, using gold as catalysts and monosilane (SiH_4) as a vapor phase reactant, as in the previous study.[6] First, we prepared several small pieces of Si{111} substrates, the surfaces of which were terminated by hydrogen (H).[6,7] Gold was deposited on these H-terminated surfaces in a vacuum of 10^{-4} Pa. The average thickness of gold was estimated to be 0.5 nm. After deposition, the substrates were set up on the appropriate positions on a quartz board, and then the board was loaded into the certain position in a quartz reaction tube set in a furnace. The substrates were preannealed in the reaction tube at the growth temperatures for 1 h, forming nanocatalysts of various sizes. Accordingly, nanowires of different diameters were grown from the substrates. Finally, SiH_4 gas, which was diluted to 1% in argon, was introduced into the reaction tube at a flow rate of 1500 sccm and the total pressure in the reactor was held constant at 98 kPa. Utilizing the temperature distribution in the reaction tube, we could grow SiNWs at different growth temperatures simultaneously, as mentioned below.

Before the growth of SiNWs, we measured the temperature distribution in the reaction tube, changing both the heater current and the flow rate of SiH_4 gases up to 2000 sccm. According to the systematic measurement, we have found that, in the certain zone in the reaction tube, the distribution of temperatures were much less changed when the gas was introduced up to 2000 sccm. Since the growth rate of SiNWs is extremely fast, it is important to avoid the change of temperature when a source gas is introduced. We found a zone of stable temperature distribution from 365 to 440 °C at the certain heater current and the other zone from 415 to 495 °C at the other heater current. Utilizing this stable temperature distribution, we have grown SiNWs at the different growth temperatures simultaneously, in which the flow rate was set constant at 1500 sccm. It is known that the concentration gradient of a SiH_4 gas along the flow direction is small at low temperature from 400 to 500 °C and at a large flow rate[8] as in this work.

SiNWs were observed after growth by transmission electron microscopy (TEM). The growth processes of SiNWs can virtually be pursued, for instance, at 400 °C [Figs. 1(b)–1(d)]. Precursors of SiNWs were already formed just after the growth of 15 s [Fig. 1(b)]. After the growth for
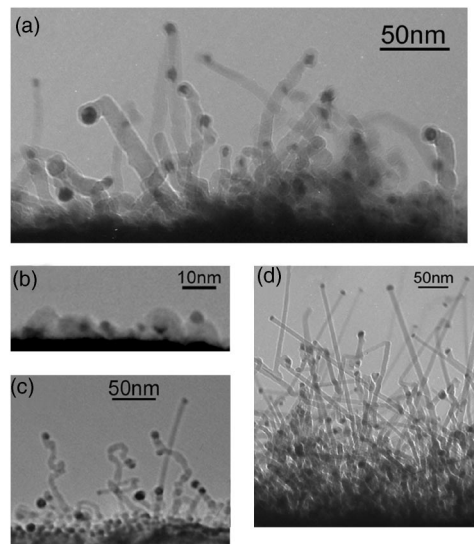

FIG. 1. Post-growth TEM observation of SiNWs. Growth time and growth temperature are (a) 900 s at 365 °C; (b) 15 s, (b) 180 s, and (c) 900 s at 400 °C, respectively.

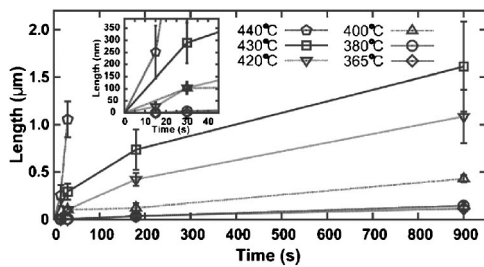a)Electronic mail: takeda@phys.sci.osaka-u.ac.jp

FIG. 2. Length of SiNWs as a function of growth time at temperatures from 356 to 440 °C. Error bars indicate standard deviations. Data at the very early stage are enlarged in the inset.

FIG. 4. Correlation between the length and the diameter of SiNWs grown at 430 °C for 30 s.

180 s, we find SiNWs [Fig. 1(c)] at the top of which nano-catalysts locate, assuring us that they are grown via the VLS mechanism. After prolonged growth for 900 s, SiNWs grow fully as shown in Fig. 1(d). Comparing SiNWs grown at 400 °C [Fig. 1(d)] with those at 365 °C [Fig. 1(a)] for the same growth time of 900 s, we find that growth rate depends on growth temperature. SiNWs grew straight in the temperatures higher than 400 °C [Fig. 1(d)], while those grown at lower temperatures below 400 °C were kinked [Figs. 1(a) and 1(c)], as observed.[9]

Figure 2 summarizes the length of SiNWs versus growth time in the temperature range from 365 to 440 °C. Lengths of SiNWs are slightly dispersed, so we plot the averaged ones with the corresponding standard deviations. For SiNWs with kinks, we summed up the lengths of all the segments. As seen in Fig. 2, the growth rate is gradually saturated as SiNWs grow. It is very likely that the temperature of a nano-catalyst decreases as a SiNW grows, since the nanocatalyst becomes away from a substrate. At the very early stage, however, the dependence seems linear, as seen in the inset in Fig. 2. Therefore, we estimate the growth rates, v_g at these early stages. Estimating the growth rate at different growth temperatures, T, we summarize v_g vs T as shown in Fig. 3. Clearly, the growth of SiNWs is a thermal activation process. The growth rates range from 2.0×10^{-1} nm/s at 365 °C to 1.8×10^2 nm/s at 495 °C. Assuming the Arrhenius equation, the preexponential factor[5] α and the apparent activation energy E_g were roughly estimated to be 7.7×10^{17} nm/s and 230 kJ/mol, respectively. E_g well corresponds to the activation energy of the decomposition of a SiH_4 gas, E_a, which ranges between 213 and 234 kJ/mol in the temperature range of 375–1200 °C.[8,10,11] E_g has been estimated of much thick silicon wires (SiWs),[4,5] which were grown by the similar CVD process as our growth process, using gold as cata-
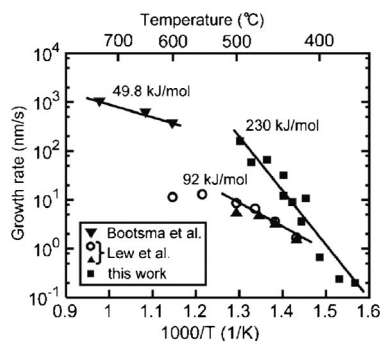
lysts and SiH_4 as a source gas. As seen in Fig. 3, the activation energy of SiWs with the diameters of 100–340 nm was estimated to be 92 kJ/mol,[5] while that for SiWs with diameters of 0.5–1.6 μm was estimated to be 49.8 kJ/mol.[4] These estimated energies are much smaller than E_a and this decrease of energy was attributed to catalytic decomposition[12,13] of SiH_4 at the surface of liquid droplets.[4,5] Generally speaking, the growth rate of SiWs and SiNWs may be governed by the decomposition of SiH_4 and/or the crystallization at the liquid–solid interface.[3–5] In our preliminary experiment, the growth rate was varied according to the partial pressure of SiH_4. Therefore, we suggest that the decomposition of SiH_4 is rate determining in our growth processes as well as the previous studies.[4,5]

As mentioned earlier, the length of SiNWs is dispersed at any growth stages. This dispersion arises partly from the dispersion of the diameter of SiNWs. We plot the length versus the diameter of SiNWs at an early stage of growth (T=430 °C and t=30 s), as shown in Fig. 4. The diameter of most SiNWs ranges from 3 to 12 nm, while SiNWs with the diameter larger than 40 nm are occasionally found. We have found that SiNWs of smaller diameters are likely to grow slower than those of larger diameters. Looking into Fig. 4, one can estimate the critical diameter of SiNWs to be about 2–3 nm, at which the growth of SiNWs is completely suppressed. Givarigozov[3] determined the critical diameter of much thicker SiWs three decades ago, examining SiWs of 0.05–5 μm in diameter. He found experimentally that the growth rate is proportional to the square of supersaturation and becomes zero at the critical diameter, $d_c \lesssim 50$ nm. This classical limit was accounted for by the Gibbs–Thomson effect: the supersaturation of silicon becomes smaller in smaller catalysts of Au–Si liquid. Since then, no experimental evidence has come up on the growth rate of either SiWs or SiNWs of much smaller diameter. Recently, SiNWs were grown by molecular-beam epitaxy (MBE) at 525 °C, in which silicon was supplied by not a source gas but an ordinary solid source in MBE and catalysts were gold. The growth rate of MBE-grown SiNWs from 70 to 200 nm of diameter was extremely low, i.e., about 600 nm/240 min, and it increases with the decrease of diameter in contrary to both Givarigozov's and our results. This peculiar behavior is attributed to surface diffusion of Si adatom on a substrate as well as sidewalls of SiNWs, which only becomes evident in slow growth in MBE.[14]

Returning to the ordinary VLS growth, the critical diameter that we determined seems far beyond the Givarigozov limit. According to Givarigozov, the growth rate, v_g is represented by the square of supersaturation $\gamma = \Delta \mu / k_B T$, multiplied by b, which may depend on growth temperature, T the

FIG. 3. Change of growth rate with temperature for SiNWs of d=3–40 nm (this work), for SiNWs of d=100–340 nm [Lew *et al.* (Ref. 5)] and SiWs of d=0.5–1.6 μm [Bootsma *et al.* (Ref. 3)].
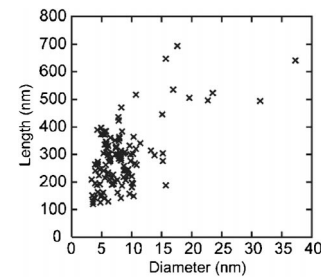
partial pressure of source gas, and other parameters such as the diameters of SiNWs, d. Here, $\Delta\mu$ represents the difference of chemical potential between gas and solid phases, and k_B does the Boltzmann constant. Setting the partial pressure to be constant at this moment, we obtain

$$v_g(T,d) = \gamma^2(T,d)b(T,d). \qquad (1)$$

The supersaturation, γ can be rewritten as follows:[3,15]

$$\gamma = 2\Omega\sigma k_B^{-1}T^{-1}[d_c^{-1}(T) - d^{-1}], \qquad (2)$$

where Ω is the atomic volume of Si, σ is the surface energy density of SiNWs. The critical diameter of SiNWs, d_c may depend on T and other parameters. The length of a SiNW, L is proportional to growth time, t at the early stage of growth:

$$L(T,d) = v_g t. \qquad (3)$$

Changing several parameters, we have attempted to fit Eqs. (1), (2), and (3) into our experimental data (Fig. 2, 3, and 4) without success. We have not yet made a definite conclusion whether the theory can be adopted to the growth of thin SiNWs systematically, and we deduce the two parameters which well correlates with experiments. Assuming that γ is independent on T, and that b does not depend on d, then we obtain the following equations:

$$v_g(T,d) = \gamma^2(d)b(T), \qquad (4)$$

Given the Arrhenius plot (Fig. 3) and Eq. (4), v_g may be expressed as follows:

$$v_g(T) = \gamma_0^2\alpha' \exp(-E_g/k_BT), \qquad (5)$$

in which γ_0 means the supersaturation of SiNWs with the average diameter. We assume here that E_g may not depend on d or the curvature of nanocatalysts greatly at $d \leqslant 40$ nm. E_g that we determined above is based on this assumption. Suppose we again impose d dependence on Eq. (5) rudely, we obtain

$$v_g(T,d) = \gamma^2(d)\alpha' \exp(-E_g/k_BT), \qquad (6)$$

Fitting our experimental data shown in Figs. 2 and Fig. 4 ($T=430\,°C, t=30$ s) with Eqs. (2), (3), and (6), we can estimate d_c to be 1.7 nm at $T=430\,°C$. This seems to correspond to the minimum diameter experimentally determined above.

SiWs were grown by Givarigozov at 1000 °C with a $SiCl_4$ gas, while, in our condition, SiNWs were grown at 430 °C with a SiH_4 gas, the partial pressure of which was estimated to be 0.98 kPa. For comparing the growth processes, we consider the growth at an extreme condition. Setting d to infinity in Eq. (2), we simply obtain the equation with the supersaturation at flat surface, $\gamma(\infty)$. Putting the growth conditions in Eq. (2), we obtain,

$$\gamma_2(\infty)/\gamma_1(\infty) = (T_1/T_2) \cdot [d_c^{(1)}/d_c^{(2)}] \approx 53, \qquad (7)$$

in which the subscripts 1 and 2 means the previous and the present growth processes, respectively. Supersaturation is greatly different in the two processes. This is presumably accounted for by the difference of Si vapor pressure, even though there is no clear description on the pressure of gases in the previous study.[3] Recently, Tan, Li, and Gösele[15] have shown that d_c depends on the concentration of Si in liquid droplets, C_l as well as the minimum size of liquid droplets, d_c^l. For decreasing d_c at a given temperature, we need to decrease d_c^l and to increase C_l. In order to accomplish this

requirement, we should increase the vapor pressure of silicon, P and the vapor pressure of metal, P_M simultaneously, keeping the ratio of P/P_M a maximum value. In this way, we can keep droplets as "liquids." As a result, d_c has thermodynamically no limit on the attainable minimum size until reaching some growth kinetic limit that is presently unknown.[15] Recently, Wu et al.[16] reported that the minimum diameter of SiNWs is 3 nm, which are grown at 435 °C using gold as catalyst with a SiH_4 gas, the partial pressure of which is 6.7 kPa. Even though the partial pressure of SiH_4 is 6.8 times as high as that in our study, the minimum size of SiNWs is the similar to our study. In another viewpoint, it is somewhat unlikely that an extremely thin SiNWs, or atomic chains of Si grows even from metal clusters smaller than, for instance 1 nm. In fact, small metal clusters which consist of only a few to several hundreds of gold atoms are very likely formed on a H-terminated template surfaces in our condition. We have nevertheless observed no thinner SiNWs with the diameter smaller than 1 nm. Clearly, we need an atomistic theory on the minimum diameter of SiNWs. Classically, the critical diameter may be described by the potential barrier in a complex system of solid and liquid phases. Also, it is noteworthy that there is the minimum size of stable Si crystallite with diamond-type structure around 1.8 nm.[17] The minimum size of stable nucleolus may be one of important factor which determines the diameter of SiNWs.

Finally, we have measured the growth rate of SiNWs quantitatively. We have analyzed a part of experimental data based in the classical theory; the activation energy is estimated to be 230 kJ/mol and the minimum diameter of SiNWs is estimated to be 1.7 nm in our growth condition. All the experimental data have not yet fully accounted for by the thermodynamical theory, and we suggest that an atomistic theory on the growth of SiNWs are probably needed to describe the phenomena more precisely in addition to the thermodynamical theory.

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