Chains of crystalline-Si nanospheres: growth and properties

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Chains of crystalline-Si nanospheres (Si nanochains), in which Si nanocrystallites are connected by amorphous Si oxide periodically in nearly equal spacing forming a chain-like one-dimensional structure, have been fabricated via a self-organized formation process. In this paper, we review our recent studies and extend results on structural analysis, formation mechanism and properties of Si nanochains. The structure have been revealed by transmission electron microscopy-based approaches including high-resolution imaging, energy-filtered imaging and energy-dispersive x-ray fluorescence analysis. The one-dimensional growth was attributed to the well-known vapor-liquid-solid mechanism. A formation mechanism of the chain-like structure was proposed: periodical change in diameter in Si nanowire growth and self-limiting surface oxidation during growth. The former was evidenced through numerical simulations of nanowire growth catalyzed by a molten droplet, and the latter through energy-filtered transmission electron microscopy observations. We also developed a method of high-yield chain growth by adding metal impurities such as Pb to the Au catalyst. By adding such metal impurities, a periodic instability in the wetting angle of the catalysts was promoted. Using the dense chain samples, we observed a phonon-confinement effect in the Si nanocrystallites by Raman scattering and also found that the Si nanocrystallites in the nanochains were under compressive stress. We also observed photoluminescence in visible-light region, and the luminescence was tentatively attributed to the exciton recombination in the Si oxide. Electronic transport property of the Si nanochains characterized well the chain-like feature: staircases were observed in I–V curves. The result opens possibility that Si nanochains can be used as components of single-electron devices. Finally, it was demonstrated that more complex nanostructures can be fabricated using Si nanochains as templates. [DOI: 10.1380/ejssnt.2005.131]

Keywords: Electron microscopy; Growth; Silicon; Nano-wires

I. INTRODUCTION

Much effort has been focused on fabricating semiconductor nanowires/nanowhiskers via non-lithographic self-organized processes [1]. Stimulated by early works of growing semiconductor whiskers in the 1960’s [2], much effort has been made to reduce diameter from micrometers to nanometers in the late 1990’s meeting with success [2–5]. Needless to say, their formation mechanisms, optical and electronic transport properties are extremely fascinating and have been studied by many research groups so far, and they have reported various fascinating properties such as anomalous luminescence due to quantum confinement and/or surface-related phenomena, lasing [6], ballistic transport of electrons, quantized conductance, sensitive response of conductance to biological and chemical species [7], enhanced photothermal effect [8], and so on. In spite of the difficulty in controlling position and arrangement of self-organized nanostructures against lithographic approaches, some proto-devices using semiconductor nanowires as building blocks have successfully been fabricated [9, 10]. After these progress, very recent interest is also in fabrication of functional composite nanowires based on self-organization approaches [11–17].

The chains of crystalline-Si nanospheres (Si nanochains), which are hetero-structured nanowires grown via a fully self-organized process, were first reported by Kohno and Takeda [18]. Because the Si nanochains have an alternate semiconductor/insulator structure, the formation mechanism, properties and possibility of applying Si nanochains to device fabrications have been of great interest. In this article, we review our studies on Si nanochains. First, we will describe the structure and growth mechanism of Si nanochains [19–21]. Next, their properties such as plasmon excitation [21], phonon structure [22], photoluminescence and electron transport [23] will be examined. Finally, we will show that Si nanochains can be used as templates for fabricating more complex nanostructures [24].

II. GROWTH PROCEDURE AND STRUCTURE

The procedure for fabricating Si nanochains is simple and only basic equipment is needed. First, a Au thin film several nanometers thick was deposited on a Si substrate. Next, the sample was sealed in an evacuated (10−5 Torr) silica container with a small piece of additional metal such as Pb, then heated to several hundreds degree centigrade for 30 minutes to make catalytic alloy droplets. After the first heat treatment, only the Si substrate was taken out of the container and sealed in a new silica container in a vacuum of 10−5 Torr. Then the sample was heated in a furnace for two or three hours. After the second heat treatment the sample was taken out of the furnace and cooled to room temperature slowly for the growth.

Figure 1 is a low-magnified transmission electron microscopy (TEM) image of nanochains. The nanochains basically have a wire-like structure. Their diameters range from several to tens nanometers. Interestingly, their diameters change periodically. In fact there is a Si nanocrystallite in each knot and the Si nanocrystallites are connected by and covered with amorphous Si oxide as shown in Fig. 2. The surface oxide is typically a few nanometers thick. It should also be noted that some Si nanocrystallites in nanochains are twinned [25], where the twinning plane is {111} (see Fig. 3). In Fig. 4, we show a field-emission scanning electron microscopy (FESEM) image of

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Si nanochains on a Si substrate. Dense nanochains were grown uniformly on the substrate.

When nanochains were grown without the first thermal treatment, chains were sparse and many Si nanowires were also grown as byproducts as shown in Fig. 5. Meanwhile by adding very small amount of metal such as Pb through the first heat treatment, the high yield of the nanochain growth was achieved (see Fig. 6) [21]. The nanochains were examined by energy-dispersive x-ray fluorescence spectroscopy (EDX); however, Pb was not detected. Accordingly, the amount of Pb added to Au catalysts and nanochains was very small and was presumably bellow a few percent. We also examined other metals and found that Sn, Sb and In promoted the chain growth while Cu suppressed the chain growth and promoted Si nanowire growth [21].

III. GROWTH MECHANISM

In this section, we describe the formation mechanism of Si nanochains. First, the one-dimensional growth will be attributed to the well-known vapor-liquid-solid (VLS) mechanism. Then, the periodic instability in the wetting property of catalytic droplets and the surface oxidation will account for the formation of the chain-like structures. We propose the following mechanism: the diameter changes periodically due to the periodic instability and necks are oxidized to the core while only surface is oxidized at knots.
A. Vapor-liquid-solid growth

Basically, we attribute the nanochain growth to the VLS growth [2–5] which is well-known to account for nanowire growth from vapor-phase catalyzed by metal particles. A Au-Si droplet can be found at the tip of a nanochain as shown in Fig. 7. The droplet is molten during the growth and has a large accommodation coefficient for Si vapor, and therefore acts as catalyst for the one-dimensional growth. Another piece of evidence for the VLS growth is given in Fig. 8, which shows a wire-chain transition. This TEM image strongly suggests that nanochains and nanowires share the same growth mechanism, namely the VLS mechanism, as concerns the one-dimensional growth. Si source gas is considered to be produced during the heating at around 1200 °C by the sublimation from the Si substrate. Meanwhile, Si nanochains were considered to be grown during the cooling process, not during the heating at around 1200 °C. At the high temperature of around 1200 °C, no products can be formed because of sublimation of themselves. During the cooling, supersaturated Si vapor is captured by the catalytic droplets and nanowire growth is enabled. As shown in Fig. 9, the chain growth was sensitive to the cooling rate. When a sample container was left in the furnace and power was off to be cooled which resulted in very slow cooling (−10^{-2} \sim -10^{-1} K/s), products were only crystalline-Si nanowires. When a container was taken out of the furnace and cooled in air to room temperature for moderate cooling (−10^{0} \sim -10^{1} K/s), dense nanochains were grown. On the other hand, when a container was taken out of the furnace and dropped in ethylene glycol for rapid cooling (−10^{3} K/s), no products were obtained. It is likely that during the rapid cooling the Si vapor was adsorbed on the inner wall of the container, not on the droplets or the Si substrate, because the container must have been cooled much faster than the droplets or the Si substrate. The results also show that whether the products are nanochains or nanowires depends on supersaturation: nanochains can be grown with relatively high supersaturation.

It is known that single-crystalline Si wires/whiskers grow preferentially along (111) or (112) for relatively thick [2] and thin [4] wires, respectively. If a wire is thick and the growth direction is (111), the liquid-solid interface is \{111\} which has the lowest surface energy. On the other hand if a wire is thin and the growth direction is (112), the side of the wire can be bounded by surfaces of low energy such as \{111\}, \{113\} and \{011\} [4]. Accordingly it is likely that if a nanowire is thin enough, the surface energy of the liquid-solid interface is negligible because the area of the interface is very small, and the growth direction is determined to minimize mainly the surface energy of the side of the nanowire. In order to survey crystal orientation of Si nanocrystallites in a nanochain, a series of electron diffractions was recorded (Fig. 10); however, it seemed that there was no preferable crystal orientation of Si crystallites nor correlation between adjacent crystallites. We attribute this result to the frequent twinning.
and polycrystallization during growth (see Fig. 3): the nanowires which were converted to nanochains by oxidation were polycrystalline. Tentatively, we speculate that the polycrystallization was related to the degree of supersaturation. Westwater et al. [3] fabricated Si nanowires via Au/SiH\textsubscript{4} VLS reaction and they studied the dependence of the morphology of the nanowires on the growth temperature and silane partial pressure. They found that kinking occurred frequently at high SiH\textsubscript{4} partial pressure, namely at high supersaturation, although the nanowires were single crystalline, and there was no grain boundary at the kinks. Although their observations do not support directly our hypothesis, it could be at least said that high supersaturation prevents stable wire growth. We speculate that the polycrystallization was induced by high supersaturation for a similar reason.

B. Periodic instability

Givargizov [26] reported a periodic instability in Si whisker growth: the diameter of whiskers were modulated periodically. The whiskers were straight and grew along the same direction against the substrate, implying that the whiskers were single crystalline and epitaxial to the substrate. Additionally, they were as thick as sub-micrometer in diameter. In these senses, Givargizov’s whiskers differ from the nanochains because the nanochains are neither single crystalline, epitaxial to a substrate, nor thick to such an extent. In addition, the growth procedures are quite different: Givargizov used SiH\textsubscript{4} as a source gas. Meanwhile, both nanochains and Givargizov’s whiskers were grown via the VLS process and that the similarity in their morphology is clear. Accordingly, we believe that both Givargizov’s whiskers and our nanochains share the same mechanism of the periodic change in diameter, namely the periodic instability. A basic idea on the mechanism of the periodic instability was given by Givargizov [26], and then modified by us [19].

We performed numerical simulations of the periodic instability based on the proposed model. Some phenomena which occur at the two interfaces, namely the vapor-liquid and the liquid-solid interfaces, are related to each other resulting in a complex feedback mechanism. A schematic illustration of our model is given in Fig. 11. In our simulations, the droplet was always attached to a flat plane for a simplification. Off course, the droplet is actually on a cylinder and the direction of the vapor-solid interface tension must be very sensitive to the nanoscopic structure of the edge of the cylinder. We are aware that our simulation model is very simplified. Nevertheless, we believe that an essential aspect of the periodic instability can be revealed through our simulations.

Given that the diameter of a wire decreases, the curvature of the droplet at the tip of the wire decreases, which works to suppress the intake of Si vapor at the vapor-liquid interface due to the Gibbs-Thomson effect. Quantitatively, when a Si atom is adsorbed on the surface of a molten droplet with radius \( d \) and Si mole fraction \( c \), the gain in the chemical potential, \( \Delta \mu_{d,c} \), is given by

\[
\Delta \mu_{d,c} = \Delta \mu_{\infty,c} - \frac{2 \gamma_v}{d}, \tag{1}
\]

where \( \gamma_v \) is the vapor-liquid interface energy and \( v \) is the volume of a Si atom. The gain of chemical potential in the case of a flat surface, \( \Delta \mu_{\infty,c} \), is expressed using Raoult law as

\[
\Delta \mu_{\infty,c} = kT \ln \left( \frac{p}{p_{\infty,c}} \right) = kT \ln \left( \frac{p}{p_{\infty,1}} \right), \tag{2}
\]

where \( p \), \( p_{\infty,c} \) and \( p_{\infty,1} \) are the pressure of Si vapor, the equilibrium pressure when the interface is flat and the Si mole fraction is \( c \), and the equilibrium pressure when the interface is flat and the Si mole fraction is 1, respectively.
The supersaturation of Si in the droplet at the vapor-liquid interface is given by
\[
\frac{\Delta \mu_{\text{v}, \text{l}}}{kT} = \ln \left( \frac{p}{p_{\infty, \text{l}}} \right) - \ln(c) - \frac{2\gamma v}{kTd}.
\]
When the contact angle is \( \theta \), the area of the vapor-liquid interface is \( 2\pi d^2 (1 - \cos \theta) \). Thus, the amount of Si which is taken in the droplet is
\[
\propto \left( \frac{\Delta \mu_{\text{v}, \text{l}}}{kT} \right) 2\pi d^2 (1 - \cos \theta).
\]

Clearly, the decrease in the area of the liquid-solid interface works to suppress the consumption of Si in the droplet at the interface. The Si mole fraction in the molten droplet is determined by the balance of intake and consumption at the vapor-liquid interface and the liquid-solid interface, respectively.

Next, we consider the liquid-solid interface where supersaturated Si crystallizes to form a nanowire. The difference in the chemical potential between the liquid and solid phases is assumed to be given by
\[
\Delta \mu' = kT \ln(c) + \Delta \mu'_{\text{l}},
\]
where \( \Delta \mu'_{\text{l}} \) is the gain in chemical potential of a Si atom in liquid (\( c = 1 \)) and solid Si and assumed to be proportional to temperature. As a result, the amount of Si which is consumed to form crystalline phase at the liquid-solid interface is given using the radius of the liquid-solid interface \( x \) by
\[
\frac{\Delta \mu'}{kT} \pi x^2 r,
\]
where \( r \) is an increment factor of the liquid-solid interface due to the roughening of the interface. In our model, the roughness of the liquid-solid interface is related to the concentration of Si in the droplet. When the concentration of Si in the droplet is high, Si atoms in the droplet are adsorbed frequently on the liquid-solid interface. As a result, a kinetic roughening is considered to occur at the interface. On the other hand, the interface can smooth thermally when the Si concentration is low. In our simulations, we assumed that the roughness \( g \) is related to the Si concentration in the droplet by the following simple equation using the critical mole fraction \( c_c \),
\[
g = \frac{1}{2} \left\{ \tanh \left( \frac{c - c_c}{a} \right) \right\},
\]
The parameter \( a \) determines the steepness of the kinetic roughening transition. In order to include the thermal effect, we also assumed that the critical concentration \( c_c \) depends on temperature \( T \) by the following simple form,
\[
c_c = \frac{1}{2} \left\{ 1 - \tanh \left( \frac{T - T_c}{h} \right) \right\},
\]
The increment factor \( r \) is assumed to have a linear correlation with the factor \( g \) as
\[
r = (\beta - 1)g + 1.
\]
The increment factor \( r \) is 1 on a smooth surface and can be increased up to its maximum value \( \beta (> 1) \) as the roughness increases. After calculating the interface roughness, we calculate the liquid-solid interface tension, because the liquid-solid interface tension depends on the interface roughness as well as the consumption rate on the interface, and as a result, the diameter changes. In our simple model, we calculate the change in the diameter \( x \), \( \Delta x \), using the following expression
\[
\Delta x \propto \alpha_{\text{vs}} - \rho \alpha_{\text{ls}} - \alpha_{\text{vl}} \cos \theta,
\]
where \( \alpha_{\text{vs}}, \alpha_{\text{ls}} \) and \( \alpha_{\text{vl}} \) are the vapor-solid, liquid-solid and vapor-liquid interface tensions, respectively, and \( \theta \) denotes the contact angle of the droplet on the substrate. We also assume that the vapor-liquid interface tension follows the Katayama-Guggenheim equation,
\[
\alpha_{\text{vl}} = \gamma_0 \left( 1 - \frac{T}{T_{\text{KG}}} \right).
\]
Then, the Si mole fraction, the roughness of the liquid-solid interface and the liquid-solid interface tension are re-calculated, and the diameter is altered again.

One of the results of numerical simulations of the periodic instability based on the model described above is shown in Fig. 12. The periodic instability was sensitive to the parameters such as temperature, interface tensions, and so on: the periodic instability appeared under adequate conditions. The result of simulations appears to be related to the experimental result that products were sensitive to the growth conditions in the actual growth. For instance chain growth was promoted by adding Pb to Au catalyst while adding Cu resulted in nanowire growth restraining the periodic instability. We speculate that such metal impurities changed interface tensions resulting in promotion/restraint of the periodic instability.

C. Oxidation

Our model of the nanochain formation says that diameter-modulated Si nanowires are oxidized from surface and as a result one-dimensional crystalline Si core is fragmented resulting in chain-like structures. A piece of experimental evidence for the oxidation was obtained by energy-filtered TEM [20]. As shown in Fig. 13, Si
nanocrystallites in nanochains were not spherical but have tails which elongate along the axial direction of wires. Furthermore, Si nanowires which had periodic modulation in diameter but were not fragmented were found. These observations strongly support our formation mechanism.

The oxidation is considered to be self-limited [27–30] in the nanochain formation. When Si is oxidized, its volume increases by 2.25. As a result, compressive stress works on the inner Si core and suppresses oxidation as is known. It is also known that the self-limiting oxidation is shape dependent and the stress perpendicular to the interface is important because extra work has to be done against the stress to create room for the newly formed oxide [30]. At necks, the surface has a saddle-like shape, therefore the compressive stress can be readily relaxed. Accordingly oxidation can reach the core. On the other hand, the compressive stress can work effectively at knots because the shape is roughly spherical, and as a result oxidation is suppressed. As shown later, the compressive stress was determined experimentally to be $10^8 - 10^9$ Pa by Raman scattering spectroscopy [22]. The value is consistent with the reported critical stress of $\sim 10^9$ Pa which causes the oxidation reaction to stop [30].

![Energy-filtered TEM image of Si nanochains.](http://www.sssj.org/ejssnt) The arrows indicate the tails of Si, and the arrowhead indicates a connection of Si.

**FIG. 13:** Energy-filtered TEM image of Si nanochains. Electrons each of which excited a Si volume plasmon were used. The arrows indicate the tails of Si, and the arrowhead indicates a connection of Si.

**FIG. 14:** Electron energy-loss spectrum of Si nanochains. Energy resolution: 1.5 eV, accelerating voltage: 300 kV.

where $E_p$ is the volume plasmon energy, $l$ is an integer and $\epsilon$ denotes the relative permittivity around the particle. For a very small particle, the lowest frequency mode, $l = 1$, dominates others. When the surface is flat, $l = \infty$ is predominant. Assuming $\epsilon = 1$ (vacuum), the surface plasmon energy is calculated to be 9.8 eV and 12.0 eV for $l = 1$ and $\infty$, respectively. Even for $l = 1$, the calculated value is much larger than that observed. This means that the effective relative permittivity of surroundings is larger than 1. This results from the fact that the Si nanoparticles are covered with thin surface oxide. By using $\epsilon = 2.2$ for silica [31], we obtain 7.3 eV and 9.5 eV for $l = 1$ and $\infty$, respectively. We attribute the difference between the observed value of 8 eV and that calculated for $\epsilon = 2.2$ and $l = 1$ to the fact that the surface oxide is thin. In addition to the plasmon excitation on the Si surface, the surface plasmon on the oxide surface must have been excited and contributed to the energy-loss spectrum. We estimated the surface plasmon energy on the oxide to be about 13 eV and 16 eV for $l = 1$ and $\infty$, respectively. However, we did not find any other distinct structures on the energy-loss spectrum at these values of energy loss. We suppose this was because the peak due to the surface plasmons on the oxide surface was too broad to give a distinctive feature on the energy-loss spectrum. This is supported by the fact that the volume plasmon in bulk Si dioxide has a linewidth of a resonant peak in energy-loss spectrum as broad as about 10 eV. It is likely that the surface plasmon on oxide was broadened as well as the bulk plasmon.
B. Raman scattering

Raman scattering is very sensitive to bonding, size of materials, order/disorder and stress which materials suffer. When a material is under compressive stress, a Raman peak blue-shifts. In addition, if a material is small enough, we can detect phonon confinement by analyzing spectral shape. Si nanochains are in nanometer scale and Si nanocrystallites are covered with surface oxide which gives compressive stress on the Si nanocrystallites and self-limits the oxidation. Accordingly, Raman scattering spectroscopy is a strong tool for inspecting Si nanochains.

In Fig. 15, we show a Raman scattering spectrum of nanochains with that of bulk crystalline-Si for comparison. The Raman scattering spectrum of nanochains was broader than that of bulk crystalline-Si and asymmetric. These significant features on spectral shape are due to phonon confinement in Si nanocrystallites. According to a phonon confinement model [32, 33], a phonon wave function is no longer a plane wave in nanometer-scaled materials. As a result, the selection rule of wave vectors relaxes. In the case of nanochains, phonon confinement is in three dimension and nearly spherical. Thus, the weighting factor of a phonon wave function is chosen to be Gaussian,

\[ W(r, L) = \exp \left( -\frac{8\pi^2 r^2}{L^2} \right) , \]

where \( r \) and \( L \) denote the position from the center of a spherical nanocrystallite and the size of phonon confinement, respectively. Thus, the square of the Fourier transform of this function is given by

\[ |C(q)|^2 = \exp \left( -\frac{q^2 L^2}{16\pi^2} \right) . \]

By integrating Lorentzian, an one-phonon Raman scattering spectrum is calculated to be

\[ I(\omega) = \int_{-\infty}^{\infty} \frac{|C(q)|^2}{\omega - \omega(q)^2 + (\Gamma_0/2)^2} dq , \]

where \( L \) and \( q \) are measured in units of the lattice constant \( a \) and \( 2\pi/a \), respectively. The linewidth of the Lorentzian \( \Gamma_0 \) includes instrumental broadening in addition to the intrinsic linewidth of the Raman spectrum of bulk crystalline Si. The phonon dispersion \( \omega(q) \) of

\[ \omega(q) = A - Bq^2 \]

was employed in our calculations, where \( A = 520 \text{ cm}^{-1} \) and \( B = 120 \text{ cm}^{-1} \). As shown in Fig. 15, the spectrum calculated using the phonon confinement model agrees well with the observed spectrum in its shape. In the calculation, the size of confinement of 5.4 nm was used and was also in good agreement with the average diameter of Si nanocrystallites (5 ± 1 nm for this sample) in nanochains. As shown, the phonon confinement itself gives red-shift, while the observed spectrum showed much smaller red-shift. The difference is considered to be due to the compressive stress by the surface oxide (2.7 ± 0.3 nm thick for this sample). By using the reported frequency shift on pressure \( P \) (in kbar) for bulk Si [34],

\[ \Delta\omega = 0.55P - 8.66 \times 10^{-4}P^2, \]

we determined the compressive stress to be 5.3 kbar for this sample.

C. Photoluminescence

Photoluminescence (PL) measurements were performed using the opto-TEM system [35, 36], where a PL apparatus was equipped in a TEM, JEM2000EX. The 514.5-nm emission from an Ar ion laser was used for excitation. The excitation light was focused on a sample into a spot of about 0.1 mm in diameter. The laser power was 200 mW at the laser exit, and the incident power on a sample was roughly estimated to be one tenth of the initial output. The PL measurements were performed at room temperature after stable laser power had been reached. We speculate that samples were actually at higher temperature during measurements due to laser heating. At this moment, we are not able to estimate the sample temperature, and the effect of the laser heating on PL is not discussed in this paper. A single monochromator with a grating of 150 lines/mm was used for dispersion and a liquid nitrogen-cooled CCD was used for detection. The total accumulation time for one measurement was typically 10 s. PL intensities were strongly dependent to the position of the excitation light probe on a sample, thus we do not argue absolute PL intensities.

A TEM image of the as-grown nanochains is shown in Fig. 16(a). The as-grown Si nanochains contained Si nanocrystallites of 14 ± 2 nm in diameter which were covered with Si oxide of about 2 nm thick. After oxidation, no lattice fringe was observed by high-resolution TEM, and only a halo pattern was observed by transmission electron diffraction as shown in Fig. 16(b). Thus, it is considered that the chains were oxidized completely. In Fig. 16(c), we show PL spectra of the as-grown and oxidized chains. A
FIG. 16: TEM images and selected area electron diffraction patterns of (a) as-grown and (b) oxidized nanochains. (c) Photoluminescence spectra of as-grown and oxidized Si nanochains.

A broad peak was observed at around 570 nm (2.2 eV) from nanochains. For the oxidized sample, a similar broad luminescence was also observed at around 570 - 580 nm. We speculate that the PL of 2.2 eV from the as-grown sample and that from the oxidized sample was due to same origin and from oxide. Tentatively, we attribute the PL to the recombinations of self-trapped excitons in oxide, where two holes and two electrons are trapped by an O \(_2\) linkage and oxygen vacancy, respectively \([37, 38]\).

PL properties of related nanostructures, amorphous Si-dioxide nanowires, have been reported so far \([39]\). They observed luminescence of 2.65 eV and 3.0 eV, not 2.2 eV. The luminescence of 2.65 eV and 3.0 eV were attributed to the recombinations of electron-hole pairs at neutral oxygen vacancies (≡Si-Si≡) and twofold coordinated Si lone pair centers (O-Si-O), respectively. Both two types of defects arise from oxygen deficiency, while the defect related to the PL of 2.2 eV does not. Accordingly, it is likely that their oxide nanowires were deficient in oxygen, while our nanochains were not. The difference is very likely due to the difference in growth procedures of the oxide nanowires and nanochains: the oxide nanowires were fabricated by a laser ablation method.

So far we have not observed luminescence from Si nanocrystallites in nanochains. It must be necessary to make Si nanocrystallites smaller and control the chemical conditions at oxide/Si crystal interface as studied on porous Si.

D. Electronic transport property

Since a Si nanochain is an alternate serial junctions of semiconductor and insulator in nanometer-scale, one would expect that Si nanochains will exhibit Coulomb staircase. Although electronic transport property of a single Si nanochain have not been revealed so far due to experimental difficulties, a bunch of nanochains/nanowires has been measured \([23]\). For measuring electronic transport property, nanochains/nanowires were deposited between a pair of Cr electrodes fabricated on a glass substrate by electron lithography. The electrodes were 840 nm apart and 0.5 mm wide. Numerous wire-like materials were deposited as shown in the scanning electron microscopy (SEM) image (Fig. 17a). Due to the limited resolution of SEM, it was very hard to distinguish nanochains from nanowires. Thus, the possibility that nanowires also contributed to the electronic transport property could not be excluded. The \(I-V\) curves were measured using a semiconductor parameter analyzer (Hewlett Packard: 4156A) at room temperature in the atmospheric and dark condition.

Observed transport property was very unstable presumably because chains/wires were mobile during measurements due to Coulomb repulsion. Nevertheless, we observed some stair-case like electronic transport behaviors as shown in Fig. 17b. The width of the plateaus \(\Delta V\) was \(10^{-1}\) V. Given that the behaviors were Coulomb staircases, the capacitance \(C\) of tunneling junctions was estimated to be \(10^{-18}\) F from the width of the plateaus using

\[
\Delta V = \frac{e}{2C}. \tag{18}
\]

This value is in good agreement with that estimated from the average size of nanoparticles and the spacing of the junctions. In addition, the number of junctions was roughly estimated to be 5 ∼ 10 since the threshold voltage \(V_t \approx 1\) V is related to the number of serial junctions \(N\) as \([40, 41]\)

\[
V_t \approx \frac{e}{2C}(N - 1). \tag{19}
\]

Accordingly, total length of the junction was estimated to be 150 ∼ 300 nm using average period of junctions for this sample, 30nm. This length is much shorter than the width of the gap, 840 nm. Therefore it seems reasonable to suppose that the conducting path was a serial junction of a nanochain and a nanowire, or it would be also possible that many parallel junctions of nanochains resulted in the observed behaviour. If stable nonlinear response is realized, nanochains can be utilized as building blocks of single electron devices via a bottom-up approach.

V. DERIVATIVE NANOSTRUCTURE:
SILICON/SILICIDE/OXIDE NANOCHAINS

When Si nanochains were heated with a small piece of Cu to 700 °C for 10 min in a vacuum, Cu infused into nanochains and partial silicidation of Si nanocrystallites occurred resulting in the formation of Si/silicide composite nanoparticles in nanochains as shown in Fig. 18 \([24]\).
FIG. 17: (a) SEM image of nanochains/nanowires between a pair of electrodes. (b) Current-voltage curves showing staircase-like behaviors.

FIG. 18: TEM image of Si/silicide/oxide nanochains. Inset, HRTEM image.

In many particles, Cu silicide crystal which appears in dark contrast was semi-spherical and the rest half was crystalline-Si (see the HRTEM image in Fig. 18 and the result of EDX analysis in Fig. 19). From the EDX analysis and electron diffraction, the Cu silicide was determined to be of $\eta$ phase [42].

This is a simple method of fabricating more complicated nanostructures from Si nanochains. Si nanochains can be used as templates for fabricating new nanostructures. Using this method, various hetero-junctions will be formed, and we expect such hetero-nanostructures will show anomalous electronic transport properties.

VI. CONCLUSIONS

The growth and properties of Si nanochains have been described in this article. We showed that the self-organized composite nanostructure could be fabricated through the simple procedure. The one-dimensional growth of the nanochains was attributed basically to the well-known VLS process. It was concluded that the chain-like structure was formed through (i) the periodic oscillation of diameter of silicon nanowires due to the periodic instability of the wetting property of catalytic droplets and (ii) self-limiting surface oxidation of the nanowires resulting in fragmentation of crystalline Si core. In addition, properties of Si nanochains have also been studied. The EELS measurements revealed the microscopic feature of the nanochains, namely the strong excitation of surface plasmons. By the Raman scattering spectroscopy, we also revealed that Si nanocrystallites in the nanochains were under compressive stress, in addition to the phonon confinement in Si nanocrystallites. PL was observed in visible-light region, and was attributed to the recombination of excitons in oxide which covered and connected Si nanocrystallites. We suppose that in order to make Si nanocrystallites luminescent it is necessary to control chemical conditions of the oxide/Si interface, for instance by infusing H in nanochains as well as reducing diameter of Si nanocrystallites. Electronic transport properties were also investigated. The staircase-like behaviors were observed and were tentatively attributed to Coulomb staircase. Finally, the fabrication of related nanostructures were reported. The formation of Si/silicide/oxide nanochains exhibited the availability of Si nanochains as templates for fabricating more complex nanostructures.

So far, fundamental aspects of the Si nanochains have
been studied as described in this article; however, no technological application of Si nanochains has been reported. It is still difficult to integrate Si nanochains into conventional Si-based devices because Si nanochains are small and winding. In addition, to control growth position is also still a challenging task. After overcoming these difficulties, the Si nanochains will find their applications in single electron and opto-electronic devices.

Nanochains have been grown in oxidative atmosphere resulting in the oxide necks. We expect that nitride nanochains may be formed in nitride-rich atmosphere. We also expect that nanowires with various types of morphology will be grown by controlling composition of catalytic alloy particles. Very recently, nanowires with various chain-like morphologies or diameter fluctuation have also been reported not only in Si/SiO$_2$ [43] but also in Ga$_2$O$_3$ [44] and In$_2$O$_3$ [45]. We believe this class of materials will contribute to developments of devices with fascinating functions.

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