Epitaxial growth of vertically free-standing ultra-thin silicon nanowires

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Abstract

We report epitaxial growth of ultra-thin vertically free-standing silicon nanowires (Si NWs) on Si(111) and Si(110) substrate, by an ultra-high vacuum chemical vapor deposition method. The epitaxial growth direction of Si NWs with sub-10 nm diameters was found to be dependent upon the orientation type of the Si substrate. The \{112\} and \{110\} epitaxial growth directions are crystallographically preferred on Si(111) and Si(110) substrates, respectively. Especially, for the epitaxy on Si(110), most of the Si NWs are grown vertically in the [110] direction with sub-5 nm diameters. Based on transmission electron microscope investigations, a growth model for ultra-thin Si NWs was deduced from the morphology of interface between catalyst and nanowire, and the growth direction at a very early stage of epitaxy was determined.

Keywords: Si nanowires, ultrathin, epitaxial growth, nucleation

(Some figures may appear in colour only in the online journal)

1. Introduction

Recent developments in Si-based electronic devices have led to many important nano-fabrication methods for shrinking the dimensions of the integrated components. As promising building blocks, silicon nanowires (Si NWs) are of special interest because of their high compatibility with standard complementary metal-oxide semiconductor (CMOS) technology and their potential application in many fields [1–4]. In feasibility studies, researchers have focused much attention on the potential of nanowire-based vertical wrap-gated field-effect transistors (FETs), on account of their superior electrostatic control of the conductivity in the FET channel [5, 6]. The generic process for fabrication of wrap-gated FETs could be based on epitaxially grown vertical Si NWs [2]. Furthermore, the crystal orientation of the ultra-thin (sub-10 nm in diameter) Si NWs vertically grown on Si substrate is important in realizing the high-speed and high-density vertical-Si nanowire-based FETs [7, 8]. Moreover, for future post-CMOS technology which requires further transistor scaling, a lower limit is hard to define—wires of 5 nm in diameter are realistic options for this technology [9]. For these reasons, alternative means of down-scaling to vertically aligned ultra-thin Si NWs are exploited. Controllable size and growth direction of ultra-thin Si NWs with high reproducibility is, therefore, one of the key issues for potential post-CMOS applications.

Typically, the diameter of the nanowire grown by the vapor–liquid–solid (VLS) mechanism is dependent on the diameter of the catalytic seeds [10]. Cui \textit{et al} reported non-epitaxial growth of Si NWs catalyzed by Au nanoclusters (NCs) with diameters as small as 3 nm, and their growth direction was [110] [11]. However, for the epitaxial growth on a Si substrate, a high density of sub-10 nm diameter Si NWs with a uniform size distribution and a vertical orientation to the surface is difficult to achieve. One specific reason is the conventional process for the Au/Si eutectic droplets formation by annealing the Au film on H-terminated Si substrate, during which the bigger Au/Si droplets always grow at the expense of smaller ones in their neighborhood (Ostwald
It is also difficult to achieve a uniform dispersion of Au seeds directly on a H-terminated Si substrate without using substances which contaminate the substrate, such as lysine. For example, Au-apoferritins, together with other Au colloids as catalysts, can realize the Si NWs growth with several nanometers in diameter without epitaxy [11, 12]. However, in order to achieve a high density of ultra-thin Si NWs grown epitaxially on Si substrate with a uniform size distribution, small catalytic seeds on H-terminated Si with a uniform size distribution should be maintained at the growth temperature above its eutectic liquid temperature in a VLS growth mechanism.

The control of epitaxial growth directions for sub-10 nm diameters is also absent. Crystal orientation of the substrate, nanowire diameter and gas pressure all have a strong influence on the epitaxial growth direction of free-standing Si NWs (grown on substrate without any template assistance) in an interdependent manner. Si NWs using gold as the catalyst prefer the (111) direction with larger diameters; otherwise, the (112) and (110) directions are dominant with smaller diameters in free space [13]. In addition to the diameter effect, Hyun et al showed that Au-catalyzed Si NWs synthesized on Si(111) substrates at a total pressure of 3 mbar grew along (111) directions, while the ones grown at 15 mbar favored (112) directions with a diameter of 80 nm [14]. In general, Si NWs of diameters below 20 nm are mostly in the (110) and (112) directions. In this paper, we focus on the epitaxial growth control of ultra-thin Si NWs and provide crystallographic explanations for different epitaxial growth models on Si(111) and Si(110) substrates.

3. Results and discussions

3.1. Small catalytic seeds on Si substrate

In order to realize epitaxial growth of ultra-thin Si NWs with a uniform size distribution and growth orientation vertical to the Si substrate, the role of the commonly used metal catalyst particles and Si substrate must be better understood. Figures 1(a) and (b) are 25°-tilt top view SEM images of the Au NCs formed on Si(111) and Si(110) substrates, respectively, using an MBE method. The condition of the Si surface has a strong influence on the formation of NCs [15]. Steps and other surface defects on Si substrates can be responsible for the formation of small Au NCs after a deposition of a few atomic layers. Before the deposition of Au, the H-terminated Si wafers were heated to form a reconstructed surface, working as a surface template for the formation of metal NC arrays [16, 17]. The small Au NCs formed directly on the Si surface with a high density and a small size distribution. It was shown by Gaussian fitting of the diameter distribution (see figure 1(a)) that the Au NCs had a mean diameter of 4.5 ± 1.1 nm with a nominal deposition thickness of 0.15 nm. With the same growth conditions, Au NCs formed on a Si (110) substrate had similar sizes. The atomic force microscopy (AFM) measurement in figure 1(c) shows that the Au NC had a width of about 5 nm and a height less than 2 nm. The measured mean diameters of Au NCs on Si substrate increased with the nominal thickness of Au deposition at 350 °C; the curve is plotted in figure 1(d).

3.2. Epitaxial growth of ultra-thin Si NWs

Using an MBE method, small Au NCs were formed directly on the H-terminated Si surface and used as catalytic seeds for the epitaxy of ultra-thin Si NWs. The SEM images in figure 2 illustrate the influence of the substrate crystal orientation on the epitaxial growth direction of Si NWs, showing the side-view and the top-view on both Si(111) and Si(110) substrates, respectively. With the same Au deposition condition on both Si substrates, the CVD growth time of Si was 10 min. In the side-view image (figure 2(a)), the viewing direction is perpendicular to the cracking plane along Si [110] direction, and most of the straight Si NWs show tilts of 80° and 71° relative to the Si(111) substrate. In 3D space, these wires are tilted by 19° with respect to the normal of the substrate, which is predicted for (112)-oriented Si NWs, as shown in the schematic insert. The orthographic projection on the Si (111) substrate in the top-view image (figure 2(b)) shows a triangular network. There are three (112) directions almost perpendicular to the substrate, and six other (112) directions with proper minus signs on some indexes are almost parallel to the surface. We are looking only for standing wires, not for those grown along the surface. However, there are a few bright spots which correspond to the Au-catalyst tips of some Si NWs grown perpendicular to the substrate, or the Au NCs remained on the surface without catalyzing Si NWs growth. The insert diagram of figure 2(a) shows a Gaussian
fitting of the narrow diameter distribution. The $\langle 112 \rangle$-oriented Si NWs have a mean diameter of $8.4 \pm 0.9$ nm.

According to our observations, the Au-catalyzed sub-10 nm diameter Si NWs preferred $\langle 112 \rangle$ orientations grown epitaxially on Si(111) substrate. However, the $\langle 110 \rangle$ growth directions of Si NWs were prevalent for diameters below 10 nm grown epitaxially on Si(100) substrate and non-epitaxially in the free space case [16, 18]. In the side-view image (figure 2(c)), we observed that most of the Si NWs were grown vertically to the Si(110) substrate, which was confirmed by the bright spots in the corresponding plan-view orthographic projection (figure 2(d)). Furthermore, if the viewing direction is perpendicular to the cracking plane along Si $[\bar{1}11]$ direction, most of the straight Si NWs show tilts of $30^\circ$ and $60^\circ$ relative to the Si(110) surface. These wires with the two tilts are predicted for $\langle 110 \rangle$-oriented NWs, as shown in the schematic insert of figure 2(c), which have a $30^\circ$ angle with respect to the normal of the substrate in 3D space. The plan-view orthographic projection on the Si(110) shows two types of growth directions: the $\langle 110 \rangle$ family with a percentage of more than 98%, and the possible $\langle 111 \rangle$ directions (white lines inset of figure 2(d)) with only a small percentage.

Measured from the $\langle 110 \rangle$-oriented Si NWs, the Gaussian fitting of the diameter distribution shows a smaller mean diameter of $5.6 \pm 1.2$ nm in figure 2(c), which was smaller than the one characterized in figure 2(a). Obviously, on the Si (110) substrate, the $\langle 112 \rangle$ growth directions seem to be completely missing, replaced by the $\langle 110 \rangle$ growth directions.

Because the Au NCs formed on Si(110) were similar to the ones on Si(111) with the same Au deposition condition, the mean diameters of Si NWs on both substrates should be similar. However, according to SEM characterizations, the mean diameter of $\langle 110 \rangle$-oriented Si NWs was smaller than that of $\langle 112 \rangle$-oriented Si NWs. Meanwhile, the $\langle 110 \rangle$-oriented Si NWs have a wide distribution of growth length from 10 ~ 150 nm, which was similar to the $\langle 112 \rangle$-oriented ones.

According to the growth model presented by Lew and Redwing [19], the growth rate at 370 °C and 0.65 Torr SiH₄ partial pressure was about 20 nm min⁻¹ for a 200 nm diameter Au-catalyzed Si NW. If the nucleation process at the nanowire base caused a short delay, the reported growth rate exceeds our observed maximum growth rate by about...
5 nm min\(^{-1}\) in sub-10 nm diameter Si NWs. A diameter-dependent reduction in growth rate has been reported by Schmidt \textit{et al}, which was attributed to the Gibbs–Thomson effect \cite{20}. Considering the diameters and growth rates on both substrates, during the initial stage of nucleation, the competition of different surface conditions affects the epitaxial growth direction in the sub-10 nm scale, which needs further support from the crystallographic analysis.

3.3. Growth model of ultra-thin Si NWs

3.3.1. Si NW epitaxy on Si(111) substrate. Figure 3 shows HRTEM images taken from the cross-sectional specimens on Si(111) substrate; a growth time of 5 min was used. The Au catalyst can be distinguished from Si by a much higher atomic number, \(z\), which results in a dark contrast. A shorter wire with a diameter of about 6.5 nm is shown in figure 3(a). The Au catalyst is not shaped in the typical equilibrium hemisphere for free-standing Si NWs. The interface is probably affected by the oxidization of Si surrounding the small Au tip during storage in air at room temperature \cite{18}. Distinguished from the crossed \{111\} lattice planes, side surfaces of the wire base are curved as a result of typical VLS homoepitaxial growth. Estimating the difference of curvatures on both side surfaces, the left one tends to be parallel to the \{111\} lattice planes with a [112] growth direction, and the diameter decreases from 10 nm to 6.5 nm. To confirm this, a longer wire with a height of 40 nm is shown in figure 3(b). Obviously, this was grown along the [112] growth direction with a tilt of 70.5° to the Si (111) surface. By counting the lattice planes, the wire is seen to have a diameter of 10 nm. A step-like 1 nm shrinkage occurred on the left sidewall at a growth length of 11 nm. The diameter increase at the base could be a result of the lateral growth of Si beside the expansion of the wire base occurring during the initial VLS growth. Together with the initial stage of Si NWs epitaxy shown in figure 3(a), notably, the Si [112] epitaxy originates from the interface between the original Si(111) with a defect-free interface. The base expansion corresponds to the liquid phase of the Au–Si catalyst at the growth temperature of 370 °C. Other growth directions such as \{110\} directions were not found during the TEM observations. With different nominal thicknesses of Au deposition, but thinner than 0.3 nm, [112]-oriented Si NW epitaxy with sub-10 nm diameter was dominant on Si(111) substrate.

Next, we will consider the nucleation and growth mechanism of sub-10 nm Si NWs on Si(111) substrate. In a typical VLS growth, the liquid diffusion pathways in the droplet dominate the transportation. Surface diffusion along the nanowire and on the Si substrate should be considered as
well, since nanowire growth was experimentally found to be in an unsteady state [21]. For example, faceting and tapering of Au-catalyzed Si NWs were observed at elevated growth temperatures due to surface migration of Si and Au [22, 23]. In our experiments, a growth temperature approaching the 363 °C of the Au–Si eutectic was adopted to minimize these phenomena. The growth of Si NWs is believed to be a dynamic process [24]. The theory of crystal growth from a liquid predicts a close relationship between surface roughness and nucleation behavior [25]. The competition between these two Si transportation processes, surface diffusion and bulk diffusion in the liquid, leads to a characteristic profile of the supersaturation as a function of the radius. The supersaturation at the rim has the highest value and thus the nucleation probability is highest at the three-phase line. If high supersaturations are used, nucleation will also occur with high probability at other positions at the interface of liquid and solid. This can result in a rough interface by polycentric nucleation. The interface between solid catalyst and Si was usually flat and a Si(111) plane terminated the nanowire. The Si(111) plane has a low interface energy to the catalyst droplet, and some models of the growth discuss a layer-by-

Figure 3. Cross-sectional HRTEM images of Si NWs grown epitaxially on Si(111) substrate with different growth heights: (a) 4 nm and (b) 40 nm growth height, with a diameter of 6.5 nm and 9 nm, respectively. (c) Cross-sectional HRTEM image of top side of a Si nanowire grown epitaxially on the Si (111) substrate; the growth direction is illustrated as [112]. The zone axis is along the Si [110] direction for the samples. Scale bars are 5 nm. (d) Illustration of the growth model with a ledge-flow propagation direction indicated by the white arrow shown in (c); the Si atoms with white outlines are the growth front of the ledge consisting of three Si(111) planes, which results in the [112] growth direction. (e) Modified growth model with consideration of the steps of the right sidewall indicated by the black arrow shown in (c).
layer growth at (111) planes [26]. This model requires the nucleation of a new plane as soon as one plane was completed. Experiments with solid silicide as the catalyst for nanowire growth, or with the growth of a silicide on a Si surface, showed a ledge-flow mechanism. Hesse et al demonstrated HRTEM images of a Ni-silicide/Si interface with ledges [27]. The height was three Si(111) planes. Later, Hofmann et al used Pd-silicide in an in situ TEM to grow Si NWs, and again observed ledges with a height of three or more Si(111) planes [28]. A low-resolution, in situ TEM investigation of the growth of Si NWs using a liquid catalyst showed a moving contrast at the interface [29]. The low resolution of the images did not allow for quantifying the height of the moving step. The precipitation of Si from the catalyst during cooling will usually result in a completed Si (111) plane at the interface to the catalyst. Only for small-diameter NWs it might happen that a new layer nucleates just before cooling down, and the amount of Si stored in the catalyst is so small that the layer is not completed during cooling.

For the Au-catalyzed Si NW epitaxy on the Si(111) substrate, we observed that the solid–liquid interface with a diameter above 40 nm was always perpendicular to the growth direction. However, for Si NWs grown epitaxially on Si(111) with sub-10 nm diameters, the interface of the [112]-oriented wires was observed to be a Si(111) plane as well (shown in figure 3(c)). This wire grew epitaxially on Si(111) with a diameter of 8 nm. The growth direction is illustrated as [112]. Au catalyst remained on the tip with a dark contrast, outlined by the dashed curves. The Si–Au interface is atomically flat with a Si(111) interface plane. It contained a ledge consisting of three Si(111) planes. The ledge-flow direction was indicated by a white arrow. The nucleus started from the left sidewall and stopped at the right one, which resembles the lateral propagation process from one sidewall to the other as reported for in situ solid-catalyst growth [28]. However, it contradicts the interfacial morphology on a liquid-catalyst interface proposed with two symmetric ledges from both sidewalls [30]. Thus, we postulate a ledge-flow growth mechanism for the [112]-oriented Si NW epitaxy on Si(111) in the sub-10 nm diameter scale, even with a liquid catalyst. A simplified 2D cross-sectional growth model is depicted in figure 3(d), according to the HRTEM image. Initially, a Si nucleus formed at the left sidewall, on the three-phase boundary, as the birth of the ledge-flow. Accompanying the propagation of that ledge-flow to the other sidewall, three Si(111) planes formed on the solid–liquid interface with the tilted sidewalls along the [112] direction. The sidewall of the nanowire is terminated at the left side by a Si{111} plane. This gives some hint as to how to develop a model of nucleation. The nucleus of a three-layer-thick ledge could be formed by extending the {111} plane at the left side. As soon as a nucleus height of three layers (one unit cell) is reached, the ledge-flow can start, and the new ledge propagates from left to right. This nanowire was somewhat special, with a small thickness of the Au catalyst on top. Perhaps the wire lost Au by surface diffusion during growth. This would also explain the steps at the right sidewall, which decreased the diameter during growth. This model (figure 3(e)) is supported by the observation of a step at the right sidewall with a height of three (111) planes, marked in figure 3(c) by a black arrow. The nanowire seems to grow preferentially by extending existing [111] planes.

3.3.2. Si NW epitaxy on Si(110) substrate. Cross-sectional HRTEM images taken from Si NWs grown epitaxially on Si (110) substrate and growth models are shown in figure 4. In a [112] viewing direction, only the vertically aligned [110]-oriented Si NWs could be observed. Si NWs shown in figures 4(a)–(d) all have sub-5 nm diameters in a [110] growth direction, and have continuously grown Si(111) planes parallel to the normal of Si(110) surface with a [112]
viewing direction. Obviously, the base expansion observed implies VLS epitaxial growth since the start of nucleation. We can distinguish the wire trunk from the connected Au catalyst. The sidewalls of the wires and the interface between Au and Si are highlighted by the white dotted lines in figures 4(a)–(c). By counting the numbers of Si[111] lattice planes, the diameters of Si NWs shown in figures 4(a)–(c), are found to be 4.1 nm, 3.8 nm and 4.4 nm, respectively. The minimum diameter observed was confirmed to be 2.8 nm, as shown in figure 4(d) by white dotted lines, which was considered to approach the thermodynamically allowed minimum diameter in the VLS growth model [31]. It consisted of 9 Si[111] lattice planes, which continuously stretched from the Si(110) substrate to the Au catalyst with a length of 10 nm.

The interface between [110]-oriented Si NWs and the Au catalyst particles was not flat as observed for [112] wires, but showed a considerable roughness. Three interfacial shapes of inclined, concave and zigzag were found as illustrated in figures 4(e)–(g), corresponding to the Si NWs shown in figures 4(a)–(c), respectively. Crystallographic analysis shows that such an interface consists of two [111] planes: (111) and (111) [32]. Wu et al also suggested that the nucleation of Si occurred at [111] planes, which are the lowest-energy liquid–solid interfaces in (110) growth directions [26]. The growth model for [112] wires assumed a stacking of (111) planes to build a wire, as discussed earlier. If for [110] wires the [111] planes were also planes of rapid growth, two different growth scenarios could be expected. First, the (111) planes with 35° tilt relative to the (110) plane could be the growth planes. Figure 4(a) shows an inclined interface which might be the result of the first growth model, which is shown schematically in figure 4(e). A second possibility would be growth using both (111) and (111) planes. Figures 4(b) and (c) show concave and zigzag interfaces, which consist of (111) and (111) planes as schematically shown in figures 4(f) and (g), respectively. According to the configuration of the (110) family epitaxial growth directions, inclined (110)-oriented Si NWs are grown beside the vertically aligned [110] ones on Si (110) substrate. Other growth directions such as (112) and (111) directions were not found in the extensive TEM observations. In general, in the sub-10 nm diameter, vertically aligned [110] growth direction is dominant for Si NWs grown epitaxially on Si(110) substrate.

4. Conclusion

In summary, on both Si(111) and Si(110) substrates, Si NWs were grown epitaxially with uniform size distributions in the sub-10 nm diameter range, and the epitaxial growth direction was strongly affected by the orientation type of the Si substrate. The dominant (112) growth directions on Si(111) substrate were confirmed, whereas on Si(110) most of the Si NWs grew vertically in a [110] direction. Based on crystallographic analysis, two growth models were presented: a three-layer (111) ledge-flow model for [112]-oriented Si NWs, and a {111} planes growth model for [110]-oriented Si NWs. The ability to realize epitaxial growth of vertically free-standing ultra-thin Si NWs on Si should open up new opportunities for fundamental research in post-CMOS applications.

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