Modeling Growth Directional Features of Silicon Nanowires Obtained Using SiO

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ABSTRACT

Silicon nanowires (SiNW) grown using Si monoxide source materials are mainly oriented in the \( <112> \) direction, and some in the \( <110> \) direction. These directional features may be understood by postulating that growth of the SiNW is governed by lateral advancement of \{111\} plane layers that are stepped, and the role of particular kinds of dislocations providing perpetuate steps.

INTRODUCTION

Semiconductor nanoclusters and nanowires have interesting electrical and optical properties. Among the various means of growing these materials, the vapor-liquid-solid (VLS) reaction [1-6], and the oxide-assisted (OA) method using unstable semiconductor-oxide source materials either by thermal evaporation or by laser ablation [7-13] produce nanowires in large quantities that are convenient for fundamental studies. A particular growth directional feature of the so-grown long semiconductor nanowires is well documented for the case of Si nanowires (SiNW): for VLS method the SiNW growth direction or its long dimension is \( <111> \) [3,6], while for those obtained by the OA method this direction is primarily \( <112> \), sometimes also \( <110> \) [9,13], see Fig. 1 for an example. In VLS growth, a metal (usually Au) is used as a catalyst, which appears as a small (molten) ball at the tip of the SiNW. This metal ball, super-saturated with Si atoms resulting from decomposition of the source materials \( \text{SiCl}_4 \) or \( \text{SiH}_4 \), renders the SiNW to grow rapidly. On the other hand, the OA SiNW is covered by a layer of oxide. In the OA cases, the supersaturation of Si atoms in the oxide is relatively low or moderate. In this paper we propose a model to explain the above mentioned SiNW growth directional features of the OA cases.

MODELING OF SiNW GROWTH DIRECTIONAL FEATURES

To explain the directional features of the OA cases, we use the postulates that: (i) a Si atom at a surface position is stable if it possesses two or more bonds, i.e., having two or more nearest neighbor atoms; (ii) growth of the SiNW is due to lateral advancement of \{111\} plane layers that are stepped at the growth front, and (iii) some dislocations will provide the growth front with perpetuate \{111\} layer steps. Postulate (i) is intuitively trivial. Postulate (ii) has been previously proposed by Csepregi et al. [14] to explain epitaxial Si growth rate dependence on wafer orientations of ion implantation induced amorphous Si layers. Postulate (iii) is classical in explaining whisker growth of metal and molecular crystals [15,16]. To use these postulates for the SiNW cases, they are further developed for the needed in-depth details.
Under moderate Si atom supersaturation conditions in its surrounding, a Si crystal with an exposed (111) surface cannot grow in the direction normal to this plane, i.e., [111], but it can grow in an arbitrary [hkl] direction that is not this particular [111] direction via lateral growth of the given set of (111) plane layers. Figure 2 shows a [110] projection of the (111) plane in two types of structures: the stable S region with atoms possessing 3 bonds, and the unstable U region with atoms possessing one bond. According to postulate (i), the U region cannot exist. The crystal cannot grow directly in the [111] direction, because (a) due to its instability, the U structure cannot develop from the S structure, and (b) the alternative possibility of forming a minimum sized stable S structure nucleus (X) on an existing S surface needs the simultaneous condensation of 3 Si atoms in a highly ordered manner which is a process involving a very high activation energy barrier. In Fig. 3, an arbitrary (hkl) plane is shown as exposed, and it is seen that this plane is consisting of terminating (111) plane layers forming steps, on top of each other, with double layer structures of the type cA, aB, and bC, which are stable. These steps are of the height $\Sigma=\{111\}/3$ in the [111] direction. The (111) plane layers may grow laterally by the addition of two Si atoms successively occupying the positions marked (1) and (2), starting from the initial step terminating Si atom marked (0). This growth process is energetically favorable because the structure obtained from adding each of the Si atoms is stable, in accordance with postulate (i). To start with, the step is stable, for atom (0) has two bonds. When atoms (1) and (2) are added to the step, each of them is also stable for it forms two bonds. In this way, the collective lateral growth of these (111) layer steps renders the crystal to grow in the [hkl] direction. However, because of the very small lateral dimension of the SiNW, the {111} layer steps will be rapidly exhausted. This occurs when all such stepped layers have swept across the growth front to reach the side-walls of the crystal, e.g., those shown in Fig. 3 have all grown to reach the left edge of the drawing. This will cause the crystal growth process to stop, because (a) now a smooth {111} surface of the S type is obtained which cannot grow in its own normal direction, and (b) surface

Fig. 1. TEM micgraphs of OA grown SiNW. A and B are respectively the general view and the view of a NW showing its growth direction. Taken from reference 12.
steps are not a thermal equilibrium feature (except perhaps very near the melting temperature),
and nucleation of the S-type of structures on top of the smooth S-surface is improbable.

This situation, however, can be remedied by the existence of a proper dislocation which provides the crystal growth front with perpetuate steps, postulate (iii). A dislocation ends on a surface will produces a step running from the point of emergence of the dislocation core, provided its Burgers vector has a component normal to that surface (i.e., a screw component). This is because a screw dislocation is naturally associated with a spiraling lattice plane displacement in the direction of its Burgers vector (and line) and of the magnitude of the Burgers vector. On the surface the dislocation is ending at, this displacement shows up as a step which is permanent if the crystal is stationary and is perpetuating if the crystal surface is growing or shrinking. As the crystal grows, the step usually winds into a spiral, i.e., as illustrated in Fig. 43, and the crystal can grow without the need of nucleating fresh surface steps. The nucleation of such dislocations in the SiNW is assumed to be facilitated by the presence of O atom in the Si crystals.

To provide the OA SiNW with the observed growth directional features, the responsible dislocation must possess two characteristics. First, its line direction must be in the SiNW growth direction. Second, the surface steps produced by the dislocation at the SiNW growth front must correspond to $\Sigma=\langle111\rangle/3$ to allow the $\{111\}$ plane layer lateral growth to proceed.

![Fig. 2. A Si crystal exposing the (111) surface. U is the unstable structure of the plane layer a, S is the stable structure of the plane layer A, and X is a (minimum) nucleated stable structure on S.](image)

![Fig. 3. The exposed stable (hkl) plane structure consisting of stepped (111) plane layers with the initial step at atom (0). Atoms (1) and (2) show the elementary unit of the lateral (step) growth process of the (111) plane layers, which is a stable growth process.](image)

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Fig. 4. The step spiral produced on the crystal growing surface by a dislocation emerging at this surface, which has a screw component in its Burgers vector in the direction perpendicular to the growing surface.

Since Si atoms form covalent bonds that are highly rigid, the dislocation line core energy is a sizable portion of the total energy of the dislocation, making its line directions $\xi$ highly restricted, i.e., it is limited to a few low index crystallographic orientations. By examining possibilities allowing for core atom dangling bonds to reconstruct, which minimizes the dislocation line core energy, Hornstra [17] found three kinds of orientations $\xi$ are likely to adopt in Si: $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 112 \rangle$. Thus, the observed $\langle 112 \rangle$ and $\langle 110 \rangle$ oriented SiNW can be due to the existence of dislocations with $\xi$ lying in the crystal growth direction.

In Si, there are two general kinds of dislocations: total or undissociated dislocations and partial or dissociated dislocations. Here we consider the role of the total dislocations, with the allowed Burgers vectors of the type $b=1/2[110]$, that can produce the needed $\Sigma=<111>/3$ steps to allow the $\{111\}$ plane layer lateral growth to occur. For $\xi=[hkl]$, the step vector on the (hkl) surface, $\sigma(hkl)$, produced by a dislocation is the Burgers vector $b_s$ of its screw component given by $\sigma(hkl) = b_s = (b \cdot \xi) \xi$, where $\xi$ is the unit vector along the direction of $\xi$.

For the case of $\xi=[112]$, there are two $30^\circ$ dislocations, one with the Burgers vector $b=1/2[101]$ and the other with $b=1/2[011]$. For either of these two $30^\circ$ dislocations, we obtain $\sigma(112) = 1/4[112]$. The resolved component of $\sigma(112)$ in the $[111]$ direction is the (111) plane step vector of steps produced by these two dislocations, which is given by $\sigma(111)=[\sigma(112) \cdot \eta] \eta$, where $\eta$ is the unit vector in the $[111]$ direction. Thus, we obtain $\sigma(111) = \Sigma(111) = 1/3[111]$. This means that these $30^\circ$ dislocations will produce steps on the (111) plane which are exactly one of the three double layers cA, aB, and bC in the $\{111\}$ plane stacking sequence. Hence, the two $30^\circ$ dislocations are exactly what is needed to provide the $[112]$ oriented SiNW with perpetuating (111) surface layer steps for continued growth in the $[112]$ direction to occur via the lateral step growth of (111) layers. No other dislocations, including other total dislocations and all partial dislocations, has the same step height property.

We next show that $\langle 110 \rangle$ is also a favored SiNW growth direction. In this case, continued growth of the crystal is made possible in the presence of the screw dislocation with $b=1/2[110]$ and $\xi=[110]$. Now, $\sigma(110) = b_s = b=1/2[110]$ in the $[110]$ direction, and the corresponding step
vector of the (111) plane, as given by \( \sigma(111) = \Sigma(111) = \frac{1}{3}[111] \), just like in the [112] growth direction case. This dislocation produces a perpetuating step in the (111) plane corresponding to a double layer of the {111} plane structure, which facilitates continued SiNW growth along the [110] direction. For this case, no other dislocations, including other total dislocations and all partial dislocations, has the same step height property.

There should be no <111> oriented SiNW of an appreciable length, because a dislocation with \( \xi=<111> \) does not exist to assist the growth of SiNW in a <111> direction. Besides, a smooth \{111\} surface is stable against growth in the <111> direction. We expect to observe faceted tetrahedron- or equivalently-shaped Si nano-bodies bounded by \{111\} surfaces. There should also be no <100> oriented SiNW of an appreciable length, because there is no available dislocation with an appropriate Burgers vector to facilitate a perpetual \{111\} step. Note, however, the \{100\} surface is able to grow directly on its own via our modeling postulate (i), since a Si atom added on top of a Si \{100\} surface is a stable atom having two bonds. This growth process is isotropic, i.e., it is equally probable for all \{100\} surfaces. Thus, it is likely that a bulk Si crystal will be grown, and we expect to observe Si nano-bodies bounded by \{100\} surfaces.

**DISCUSSIONS**

We have presently modeled the OA SiNW growth directional features, with the role of dislocations emphasized. It is obvious that such dislocations can be detected using transmission electron microscopy. Since our model is the first of its kind, in the sense of the depth it gets into, we expect it to form a basis for further works and discussions. The modeling results showed that both <112> and <110> are favored SiNW growth directions. Both <112> and <110> oriented SiNW have been observed, with the <112> SiNW in a much larger proportion. One reason for this quantitative difference to exist is that there is an entropy-like factor which is determined by the possible number of configurations in each case. In the <112> case, there are 12 different <112> directions and hence also 12 choices of \( \xi \), each with one \{111\} plane for which step growth can occur, and for each given \( \xi \) there are two possible \( b \) vectors, resulting in a total of 24 possible configurations. For the <110> case, there are 6 different <110> directions and hence also 6 choices of \( \xi \), and for each given \( \xi \) there is 1 possible \( b \) vector and 2 \{111\} planes for step growth to occur, resulting in a total of 12 possible configurations. Thus, due to this factor, the appearance of <112> SiNW is 2 time more likely than the <110> SiNW. Thus, some hitherto unidentified factors have also contributed to the quantitative difference between the <112> and <110> oriented SiNWs.

The OA SiNWs are not in the <111> orientations, but the VLS SiNWs are oriented in the <111> directions. This discrepancy is most likely related to the driving force difference between the two cases and perhaps also surface energy difference of the various involved planes. For the OA case the Si atom supersaturation is relatively small or mild. Hence, direct nucleation of \{111\} surface steps is unlikely, and the SiNW growth should therefore be dependent upon the dislocation generated \{111\} surface steps. Within the same scope of postulating that SiNW growth via the metal-catalized VLS method is also achieved by \{111\} plane layer lateral advancement, it may be further assumed that, due to the very large Si atom supersaturations, direct
nucleation of \{111\} surface layer steps becomes plausible, hence leading to the observed \(<111>\) growth direction.

**CONCLUSIONS**

A model explaining the growth directional features of SiNW obtained by laser ablation or by thermal evaporation of monoxide source materials has been proposed. The SiNWs are primarily oriented in the \(<112>\) direction, and some in the \(<110>\) direction, but none in the \(<100>\) or \(<111>\) directions.

**REFERENCES**