

## Chapter 2

# Growth Mechanism of Silicon Nanowires

**Abstract** Among the variety of nanostructural synthesis methods, oxide-assisted growth is unique in terms of not only the quality and quantity of nanostructures synthesized but also its interesting and novel mechanism. It has been revealed by our theoretical calculations that it is the silicon suboxide clusters which possess high reactivity on their surface silicon sites that facilitate the nucleation and growth of silicon nanostructures by allowing them to grow and form  $sp^3$  cores after a critical size. The high possibility and crystallographic dependence of oxygen diffusion allow the so-formed silicon nanostructures grow along certain growth directions ( $\langle 110 \rangle$  and  $\langle 112 \rangle$ ).

**Keywords** Oxide-assisted growth • Silicon oxide clusters • Oxygen diffusion • Nucleation • Reactivity

Large quantity of SiNWs have been synthesized more than 10 years ago by laser ablation using metal containing semiconductor targets [1, 2], following the traditional VLS growth mechanism in which metal or metal compounds are the catalysts for the nanowires growth process [3]. Soon afterward, it was found that the nanowires could be synthesized without any metal [4, 5]. The oxide and crystalline defects were found to play an important role in the nucleation and growth process. The so-synthesized nanowires are not only in large quantity (10 times of the metals catalysis synthesis technique) but also in high quality without any metal impurities. The related research in nucleation of nanomaterials and their growth mechanism has become important topics of the field.

The oxide-assisted growth mechanism has the following unique characteristics over the VLS growth mechanism: (1) reduced metal contamination due to the exclusion of using metal catalyst; (2) rich source materials due to the use of oxide; and (3) capability to produce SiNWs in  $\langle 112 \rangle$  and  $\langle 110 \rangle$  directions in contrast to the VLS growth which is mainly in  $\langle 111 \rangle$  direction.

Obviously, during the synthesis of Si nanowire growth (1) oxygen atoms desorbed from  $SiO_2$  during laser ablation at high temperature may contribute to the growth; (2) different species of Si oxides may have been formed in the presence of oxygen; (3)  $SiO_2$  may change the ability of the target to absorb energy from the

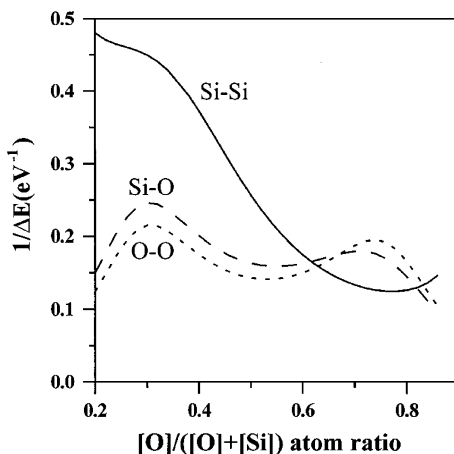
laser beam; and (4) reaction of Si and SiO<sub>2</sub> to form oxides in vapor phase. Thus, the influence of oxide on the formation and growth of Si nanowires is critical here.

Silicon oxide clusters generated and present in the gas phase in Si nanowire synthesis play an important role in the nucleation and growth. There have been rich literatures studying small silicon oxide clusters Si<sub>n</sub>O<sub>m</sub> (*n, m* = 1–8) both experimentally and theoretically [6–13]. In particular, our systematic theoretical research [13] has revealed that silicon monoxide like clusters adopt planar and buckled-ring configurations, while oxygen-rich clusters are rhombuses arranged in a chain with adjacent ones perpendicular to each other.

Based on the calculation results on the gas-phase silicon oxide clusters, we revealed the underneath mechanism at an atomic level. We obtained interesting results such as the gas-phase favorable composition and distinctive features in reactivity of the different silicon oxide clusters. Remarkably, we found that Si suboxide clusters are highly reactive to bond with other clusters and prefer to form Si–Si bonds [14]. Specifically, the analysis of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of silicon oxide clusters uncovered the reactivity for them to form the Si–Si, Si–O, and O–O bonds, according to the well-known frontier orbital theory [15]. The much smaller HOMO-LUMO gap for (SiO)<sub>n</sub> clusters (2.0–4.5 eV) than those for (SiO)<sub>2</sub> species indicates higher chemical reactivity of the (SiO)<sub>n</sub> clusters. The localization of HOMO mainly on the Si atoms at the cluster surface makes these regions highly reactive. The silicon oxide cluster with the O ratio less than about 0.62 presents remarkably larger reactivity to form a Si–Si bond of two silicon oxide clusters than to form a Si–O or O–O bond [14], as shown in Fig. 2.1, facilitating the combination of these clusters through the Si–Si bonding.

Our result revealed that the cluster with a higher ratio of Si atoms has a higher chance to form a Si–Si bond with others. However, in the actual synthesis, the presence of the cluster is also determined by the energetic favorability. Thus, the higher cohesion energy per atom of the silicon-rich clusters indicates a smaller

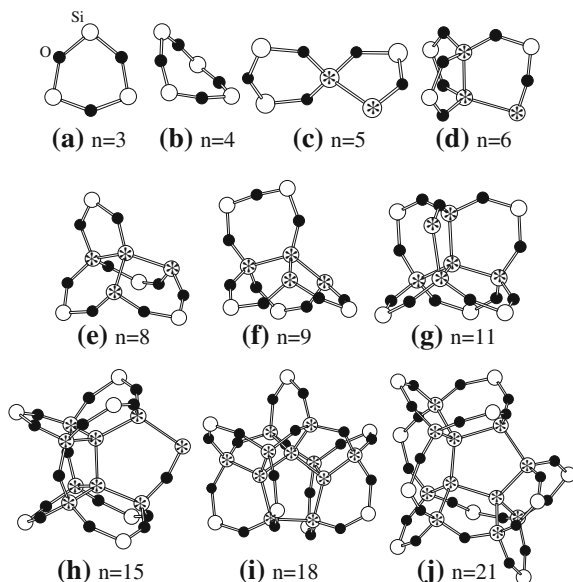
**Fig. 2.1** The inverse of the energy difference  $\Delta E = \text{LUMO (electron acceptor)} - \text{HOMO (electron donor)}$  and thus the reactivity (proportional to the inverse of the energy difference) for the formation of a Si–Si bond, a Si–O bond, or an O–O bond between two silicon oxide clusters as a function of the Si:O ratio. Reprinted with permission from Ref. [14]. Copyright 2001, The American Physical Society



chance of their presence in the gas phase. The most probable cluster to achieve the highest yield and formation of Si nanowire should have an optimum ratio of Si atom to O atom in the silicon suboxide clusters close to 1, as also observed experimentally (about 49 at. % of O) [4, 5]. It is worthwhile noting that there are also experimental reports on the formation of the crystalline phase of Si nanoclusters from the deposition of silicon-rich oxide [16].

According to the above findings, we have elucidated the mechanism of oxide-assisted nucleation of silicon nanostructures according to our calculations. Briefly, it is the silicon suboxide cluster which possesses unsaturated feature and high reactivity on silicon atoms [14] that facilitates the formation of Si–Si bond with the other silicon oxide clusters. In contrast, oxygen-rich silicon oxide cluster prefer to form Si–O bond with the others. Accordingly, we have proposed a clear mechanism of silicon nanowire nucleation [9], in which some highly reactive silicon atoms in the silicon suboxide cluster deposited on the substrate would form bonds with the substrate atoms, sticking to the substrate and protecting the other reactive silicon atoms in the cluster from being deactivated. The latter silicon atoms face outside the substrate and thus can interact with other species in the vapor, acting as the nuclei and facilitating the formation of the silicon nanowires with a certain crystalline orientation.

The nucleation of Si nanocrystals could be expected to take place via the combination of small Si suboxide clusters. It has been further revealed that tetrahedral Si core begins to form at  $n = 5$ , as shown in Fig. 2.2 [17]. It is seen that (1) a Si core (represented by the open circles containing stars) is formed and is surrounded by a silicon oxide sheath; (2) the Si–Si bonds is formed mainly in the center to reduce the strain energy; (3) most of the Si atoms in the Si core have a tetrahedral coordination, similar to that in silicon crystal, quite different from that of pure Si clusters of the same size [18]; (4) the larger the size of the cluster is, the larger the size of the Si core increased and the fraction of Si atoms with three and four coordinates; and (5) beginning at  $n = 18$ , the  $sp^3$  Si cores similar to the configuration in the Si crystal is formed, with all of the Si atoms in Si cores being four-coordinated. Figure 2.3 is the binding energies of  $(SiO)_n$  clusters containing Si cores as a function of  $n$ . Those containing buckled structures are also provided. We found that: (1) the ones containing Si cores become energetically more favorable than the buckled ones for  $n = 5$  and larger; and (2) the cluster becomes increasingly more stable with increasing Si core size. The two kinds of structures from  $n = 5$  to  $n = 8$  in Fig. 2.3 are close in energy and may compete in experiments. We obtained their relative population at 900 °C (the growth temperature of Si nanowires [19]) at equilibrium described by the Boltzmann factor  $\exp(-E/kT)$ , where  $k$  is Boltzmann's constant,  $E$  is the energy difference, and  $T$  is temperature in Kelvin. We confirmed that the structures containing Si cores still dominate at such a high temperature starting at a size as small as  $n = 8$  (see the inset in Fig. 2.3). The formation of  $sp^3$  Si core inside the silicon oxide clusters is important, as it contributes to the nucleation of the Si nanocrystals. Their high chemical reactivity allows these clusters to combine easily and to form a large  $sp^3$  Si core via subsequent reconstruction and O migration from the center to the

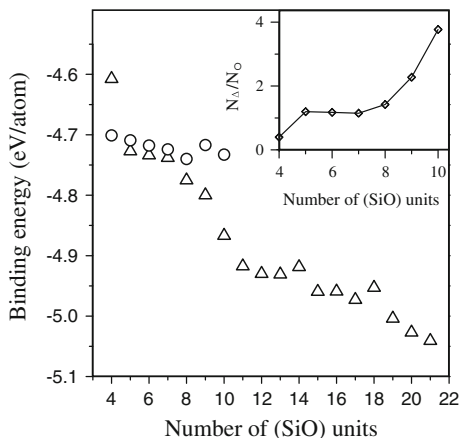


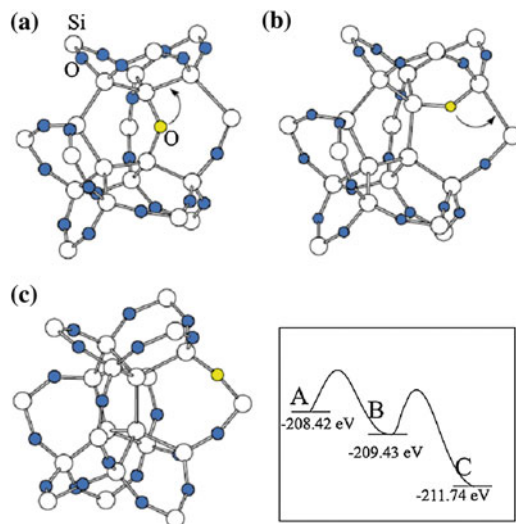
**Fig. 2.2** The most favorable structures of silicon monoxide clusters  $(\text{SiO})_n$  for  $n = 3-21$ . Reprinted with permission from Ref. [17]. Copyright 2004, The American Physical Society

surface of the clusters. The crystalline Si cores thus formed can act as nuclei and precursors for subsequent growth of Si nanostructures.

We further studied three different isomers of the  $(\text{SiO})_{21}$  cluster with an O atom locating at different sites from the center to the surface of the cluster, which are shown in Fig. 2.4. We found that the most stable configuration is the one with O located on its surface, with a total binding energy of 211.74 eV. However, the binding energy decreases as the O atom moves from the surface into the cluster.

**Fig. 2.3** Binding energy (eV/atom) of  $(\text{SiO})_n$  clusters versus  $n$ . The up triangles are  $(\text{SiO})_n$  with the Si-cored structure surrounded by a silicon oxide sheath, and open circles are those with buckled-ring structure. The inset shows the relative population of the former ( $N_\Delta$ ) and the latter ( $N_O$ ) structures at 900 °C. Reprinted with permission from Ref. [17]. Copyright 2004, The American Physical Society





**Fig. 2.4** Possible path of O atom migration from the center of a  $(\text{SiO})_n$  cluster to its surface: **a**  $(\text{SiO})_5$  and **b**  $(\text{SiO})_{21}$ . Reprinted with permission from Ref. [17]. Copyright 2004, The American Physical Society

The result indicates that the O atom could migrate from the center of the silicon monoxide cluster to its surface via bond switching. The estimated migration barrier is about 1.79 eV for the  $(\text{SiO})_5$  cluster. The migration of O atom from the inside to the surface may be caused by the high strain involved in the large  $(\text{SiO})_n$  cluster, giving rise to the formation of a Si core. The Si core in the nuclei would grow larger with the assistance of O diffusion from the core to the surface layer during deposition.

With the above findings, we can describe what could happen in the synthesis of SiNWs using SiO powder or a mixture of Si and  $\text{SiO}_2$  powder as the source. In the experiment, the evaporated  $(\text{SiO})_n$  clusters deposited on a substrate would be anchored due to their high reactivity at Si sites. The deposited clusters would act as the nuclei to absorb  $(\text{SiO})_n$  clusters from the vapor because of their remaining reactive Si atoms facing outward from the substrate. A Si core would start to form at a size of  $n \sim 5$ . The nuclei containing a Si core would grow larger with the assistance of O diffusion from the core to the surface layer during deposition. The O diffusion length depends on the temperature and the crystallographic orientation of the crystalline core formed, leading to the formation of Si nanowires with different crystalline orientations such as  $\langle 110 \rangle$  and  $\langle 112 \rangle$ , as observed in our experiments [19]. The above process may be similarly responsible for the ready formation of Si nanocrystals in the  $\text{sp}^3$  configuration from amorphous SiO [20].

The catalytic effect of the  $\text{Si}_x\text{O}$  ( $x > 1$ ) layers on the nanowire tips is an important driving force for the nanowire growth. Among the number of different forms of Si suboxides, some of them are very reactive. The materials at the Si

nanowire tips (similar to the case of nanoparticles) may be in or near their molten states. This is because that the surface melting temperatures of nanoparticles can be much lower than that of their bulk materials. For example, the difference between the melting temperatures of Au nanoparticles (2 nm) and Au bulk material is over 400 °C [21]. The atomic absorption, diffusion, and reaction are thus largely enhanced at the tips.

After nucleation, the further growth of the silicon domain may be crystallographic-dependent. The oxygen atoms in the silicon suboxide clusters during the growth of silicon nanowires might be expelled by the silicon atoms and diffuse to the edge in some directions of nanowires, forming the silicon oxide sheath. In a certain orientation, e.g., [112], the diffusion might be lower and the high reactive silicon oxide phase can still expose to the outside and facilitate the continuous growth of the wire in such a direction. However, the oxygen-rich sheath resulted in the other directions may possess lower reactivity and thus does not favor further stacking of silicon oxide clusters from the gas phase, leading to the growth suppression in such directions. The reactivity of silicon atoms in oxygen-rich clusters becomes very low at Si:O being 1:2. Instead, the reactivity of oxygen atoms increases a little. However, the overall reactivity is still quite low. It explains the retard of the shell silicon oxide on the sideways or lateral growth of nanowires.

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Zhang, R.-Q.

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