# Interfacial reaction-dominated full oxidation of 5 nm diameter silicon nanowires

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(Received 4 July 2012; accepted 3 October 2012; published online 5 November 2012)

While almost all Si nanostructures, including Si nanowires (SiNWs), Si nanocrystals, and Si nanotrench-like structures on a supra- or sub-10 nm scale exhibit self-limiting oxidative behavior, herein we report full oxidation of SiNWs 5 nm in diameter. We investigated the oxidative behavior of SiNWs with diameters of 5 nm and compared our findings with those for SiNWs with diameters of 30 nm. Single-crystalline SiNWs 5 and 30 nm in diameter were grown by a chemical vapor deposition (CVD) process using Ti as a catalyst. The SiNWs were then oxidized at 600–1000 °C for 30 min to 240 min in $O_2$. The thicknesses of the resulting oxide layers were determined by transmission electron microscopy (TEM). As expected, the SiNWs 30 nm in underwent self-limiting oxidation that was parabolic in nature. However, under the same conditions, the SiNWs 5 nm in diameter underwent full oxidation that was linear in nature. Atomic-scale molecular dynamic simulations revealed that the compressive stress in the oxide layer, which is generated owing to the increase in the volume of the oxide formed, decreased in the case of the SiNWs 5 nm in diameter. It is likely that this decrease in the compressive stress results in a lowering of the energy barrier for the diffusion of oxygen into the oxide layer, leading to the full oxidation of the SiNWs 5 nm in diameter. It is also responsible for the oxidation in the case of SiNWs 5 nm in diameter being interfacial reaction-dominated as opposed to the diffusion dominated-oxidation typical for SiNWs. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4764004]

## I. INTRODUCTION

Semiconductor nanowires (NWs) have attracted significant interest owing to their unique physical properties and their potential for use as building blocks for nanodevices on the sub-10 nm scale.[1–4] Among the various semiconductor NWs being explored, silicon NWs (SiNWs) are the most promising because of their compatibility with complementary metal-oxide-semiconductor (CMOS) technology.[5–9]

The use of SiNWs in nanodevices requires that the surfaces of the NWs be modulated. For example, the passivation of the surfaces of the NWs or the use of a sacrificial SiNW spacer is crucial for assembling a NW array.[10,11] It is also essential that sheath layers of materials exhibiting high relative permittivity be used in SiNWs-based metal-oxide-semiconductor (MOS) and bipolar devices. In this regard, the oxidation of SiNWs is interesting as it can lead to the formation of a silica ($SiO_2$) shell around the NWs with ease, and this shell can be used for surface passivation or as a dielectric layer, leading to the fabrication of a wider range of devices.

Investigations of the oxidation of SiNWs have revealed that the process depends on the diameter of the NWs to differing degrees.[10,12–15] It has also been shown that SiNWs exhibit self-limiting oxidative behavior, in that the oxidation rate decreases to the point that the oxidation nearly ceases over time. In fact, almost all Si nanostructures on a supra- or sub-10 nm scale, including SiNWs, Si nanocrystals, and Si nanotrench-like structures, exhibit this self-limiting oxidative behavior.[12–18] This self-limiting oxidative behavior is important as it can provide a way of controlling the diameter of the Si core and the thickness of the $SiO_2$ layer as well as the modulation of the surfaces in the case of SiNWs. Moreover, it can be used to fabricate Si quantum wires, which can be used to develop nanodevices to explore novel physical phenomena in Si quantum structures.[11,13,18]

Studies thus far have suggested that the self–limiting nature of the oxidation is due to the compressive stress that arises at the Si core/$SiO_2$ sheath interface.[15–17] The oxidation of Si is accompanied by a increase in the volume of the $SiO_2$ layer, which results in the generation of compressive stress in the Si structures. This stress is due to the formation of a dense layer of $SiO_2$ at the Si core/$SiO_2$ sheath interface. In the case of bulk or thin films, this stress remains constant and thus constantly affect the oxidation process.[19–21] However, in the case of NWs, the stress at the Si/$SiO_2$ interface of NWs varies with oxidation because of the curved geometries of the NWs.[14–16,20,22] The magnitude of the stress is inversely proportionally to the diameter (or curvature) of the NWs and becomes high enough to retard the diffusion of oxygen, eventually terminating the oxidation process as the diameter is reduced to the nanometer level.[3,12] An important point to explore is whether this self-limiting oxidative behavior of SiNWs is noticed even in the case of NWs that have diameters on sub-10 nm scale.[11,13] Knowing this is important

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since NWs with diameters in the sub-10 nm range can be used in novel nanodevices and having this information will widen our knowledge of the oxidative behavior of sub-10 nm Si nanostructures.

In this study, we systematically investigated the oxidative behavior of SiNWs having diameters of 5 nm and compared the findings with those for SiNWs with diameters of 30 nm. Contrary to our expectations, we found that the SiNWs with diameters of 5 nm underwent full oxidation that was linear in nature, whereas the NWs with diameters of 30 nm underwent self-limiting oxidation that was parabolic in nature. Molecular dynamic (MD) simulations of the oxidation of the SiNWs using a reactive force field for the Si-O system[23] revealed that the compressive stress at the Si/$SiO_2$ interface, which is generated owing to the increase in the volume of the $SiO_2$ formed, decreases as the diameter of the NWs decreases. This decrease in the stress generated in the case of NWs with a diameter of 5 nm is believed to be due to a lowering of the energy barrier limiting the diffusion of oxygen into the NWs and results in the interfacial reaction-dominated full oxidation of the SiNWs 5 nm in diameter.

## II. EXPERIMENTAL

The SiNWs having a diameter of 5 nm were synthesized by a chemical vapor deposition (CVD) process. 5 nm-thick Ti films, which acted as a catalyst, were deposited onto a Si wafer prior to the growth of the SiNWs. Silicon chloride ($SiCl_4$) (Aldrich, 99.999%) was introduced into the reactor using $H_2$ as the carrier gas. $H_2$ was also used as the diluting gas. Typically, the system was heated to 1000 °C and its temperature maintained at this level for 10 min with $SiCl_4$ flowing into the reactor. The system was then subsequently cooled to room temperature. For comparison, SiNWs having a diameter of 30 nm were also synthesized using the same process. The fabricated SiNWs were then oxidized in a vacuum chamber that had $O_2$ flowing into it. The oxygen pressure was maintained at 6 torr for temperatures of 600–1000 °C. The oxidized SiNWs were then observed using transmission electron microscopy (TEM) to determine the thicknesses of the oxide layers formed. We calculated the thickness distributions for the SiNWs using the arithmetic means of 10 NWs each of the NWs with diameters of 5 nm and 30 nm. The errors in the diameter distributions of both the SiNWs 5 nm in diameter and those 30 nm in diameter were within 5% (supplementary information, Figure S1).[32]

Classical-molecular-dynamics-based simulations of the SiNW oxidation process were performed using a reactive force field for the Si-O system proposed by van Duin *et al.*[23] In the simulations, SiNWs oriented along the [311] direction were prepared by removing Si atoms from a Si bulk single crystal. SiNWs having diameters of 5 and 10 nm were used for the simulations of the oxidation process, and the temperature used was 800 °C. During the simulations, the NWs were initially relaxed for 100 ps at 800 °C, and the oxidation process itself was simulated by having oxygen molecules flood the simulation box. A periodic boundary condition was applied in all directions, implying that SiNWs of 18 nm length were used in the simulations. The molecular dynamics (MD) time step was set to 0.1 fs, considering the stability of the simulation. Additional details of the simulation conditions used are available in literature.[24]

## III. RESULTS AND DISCUSSION

SiNWs were grown successfully by using Ti as a catalyst and managing the flow rate of the processing gas, $H_2$. Our investigation revealed that the diameter of the fabricated SiNWs could be reduced by increasing the flow rate of $H_2$. For example, the SiNWs having diameters of 5 nm and 30 nm were grown using $H_2$ flow rates of 3000 sccm and 100 sccm, respectively. It was also found that using Ti instead of other catalysts such as Au, Pt, or Fe helped control the diameter of the NWs under the experimental conditions used in our study.

Figure 1(a) shows TEM images of the SiNWs grown using a $H_2$ flow rate of 3000 sccm. The diameters of the NWs ranged from 4 to 7 nm with the average being 5 nm. The length of the NWs was several hundred nanometers. The high-resolution transmission electron microscopy (HRTEM) image in Figure 1(b) shows the single-crystalline nature of the NWs. It also shows that a thin layer of the native oxide having a thickness of $< 0.8$ nm was formed on the NWs. A selected-area electron diffraction (SAED) pattern recorded along the [001] zone axis, shown in the inset of Figure 1(b), indicated that the NWs grew along the [311] direction. A compositional analysis performed using energy dispersive spectroscopy (EDS) showed the presence of only Si and oxygen from the native oxide and no other elements.

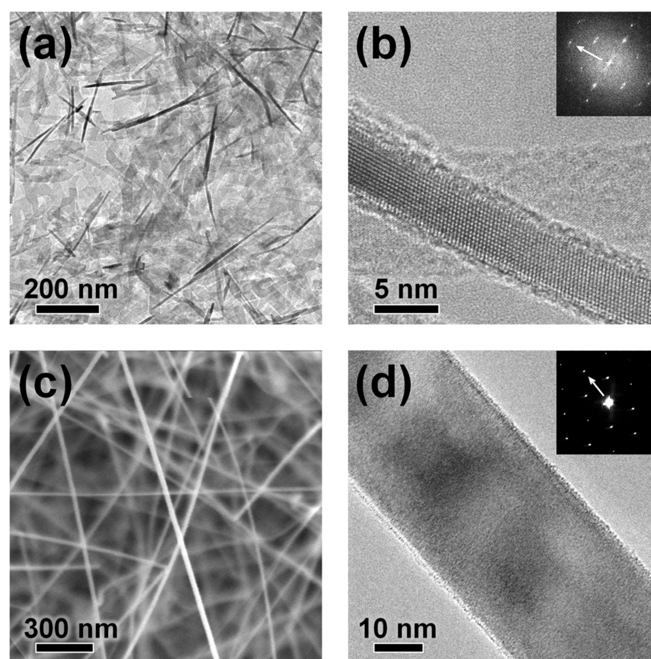


FIG. 1. TEM and SEM images of the synthesized SiNWs. (a) A typical low-magnitude TEM image and (b) HRTEM image of a SiNW 5 nm in diameter. The inset SAED pattern in (b) shows that the direction of growth of the NWs 5 nm in diameter was [311]. (c) Typical SEM image and (d) HRTEM image of a SiNW 30 nm in diameter. The inset SAED pattern in (d) shows that the direction of growth in the case of the NWs 30 nm in diameter was [110].

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Figure 1(c) shows a scanning electron microscope (SEM) image of the SiNWs grown using a $H_2$ flow rate of 100 sccm. The length of the NWs is several tens of micrometers. Figure 1(d) shows a TEM image of these SiNWs. As can be seen in this figure, the diameter of the SiNWs was about 30 nm, and they had a layer of the native oxide of a thickness of <2 nm. The SAED pattern shown in the inset indicated that the NWs were single crystalline in nature and that they grew in the [110] direction.

We first oxidized the fabricated SiNWs at 600 °C (supplementary information, Figure S2). The oxidation of Si films or of SiNWs is typically performed at temperatures in excess of 700 °C.[10,12,13,19–21] However, the NWs fabricated in this study were unprecedentedly thin and were thus initially oxidized at a relatively low temperature to investigate how the oxidation process would proceed. Figures 2(a) and 2(b) show TEM images of typical NWs that were oxidized at 600 °C for 240 min. As can be seen in these figures, the oxide layer formed is extremely thin and the core of the Si NWs has not been completely converted into the native oxide, indicating full oxidation of the SiNWs did not take place at 600 °C. This was true for the nanowires having a diameter of 5 nm as well as those 30 nm in diameter.

Figure 2(c) shows the rate of oxidation, i.e., the increase in the thickness of the oxide layer formed on the SiNWs at 600 °C with the oxidation time. The initial diameter of the SiNWs was determined on the basis of the increase in the volume of $SiO_2$ over that of Si (the molecular volume of $SiO_2$ is 2.25 times the atomic volume of Si) and can be expressed by the following equation:

$$a_0^2 = \frac{b^2}{2.25} + \frac{1.25}{2.25}a^2. \tag{1}$$

where $a_0$ is the initial diameter of the SiNWs, $b$ is the total diameter of the SiNWs after oxidation, and $a$ is the diameter of the Si core after oxidation.[25] Oxidation-related data were collected for 10 NWs under each condition and averaged. As can be seen in Figures 2(a) and 2(b), all the NWs were partially oxidized after being oxidized for 240 min, with the oxidation rates being 0.21 and 0.27 nm/h for the NWs 5 nm and 30 nm in diameter, respectively.

We then oxidized the NWs at 800 °C, and at this temperature, most of the SiNWs underwent self-limiting oxidation (supplementary information, Figure S3).[12–16] TEM images of the NWs 30 nm in diameter showed that the thickness of the formed oxide layer reached a maximum value of 9.4 nm after a period of 4 h, with the average oxidation rate being 1.9 nm/h (Figure 2(e)). In addition, as seen in Figure 2(f), the growth of the layer of the oxide was parabolic in nature and the NWs were not completely oxidized, i.e., they exhibited typical self-limiting oxidative behavior. In contrast, the SiNWs that were 5 nm in diameter underwent linear oxidation at 800 °C (Figure 2(f)), i.e., the thickness of the oxide layer increased linearly with time, as can be seen in Figure 2(d). More importantly, these NWs were completely oxidized, with the SiNWs turning completely into NWs of $SiO_2$ after 4 h of oxidation. As can also be seen in Figure 2(d), after oxidation, the SiNWs with a diameter of 5 nm comprised only $SiO_2$, with the core/shell structure being absent. The results of the EDS-based characterization of these NWs showed that the atomic percentage of oxygen and silicon in

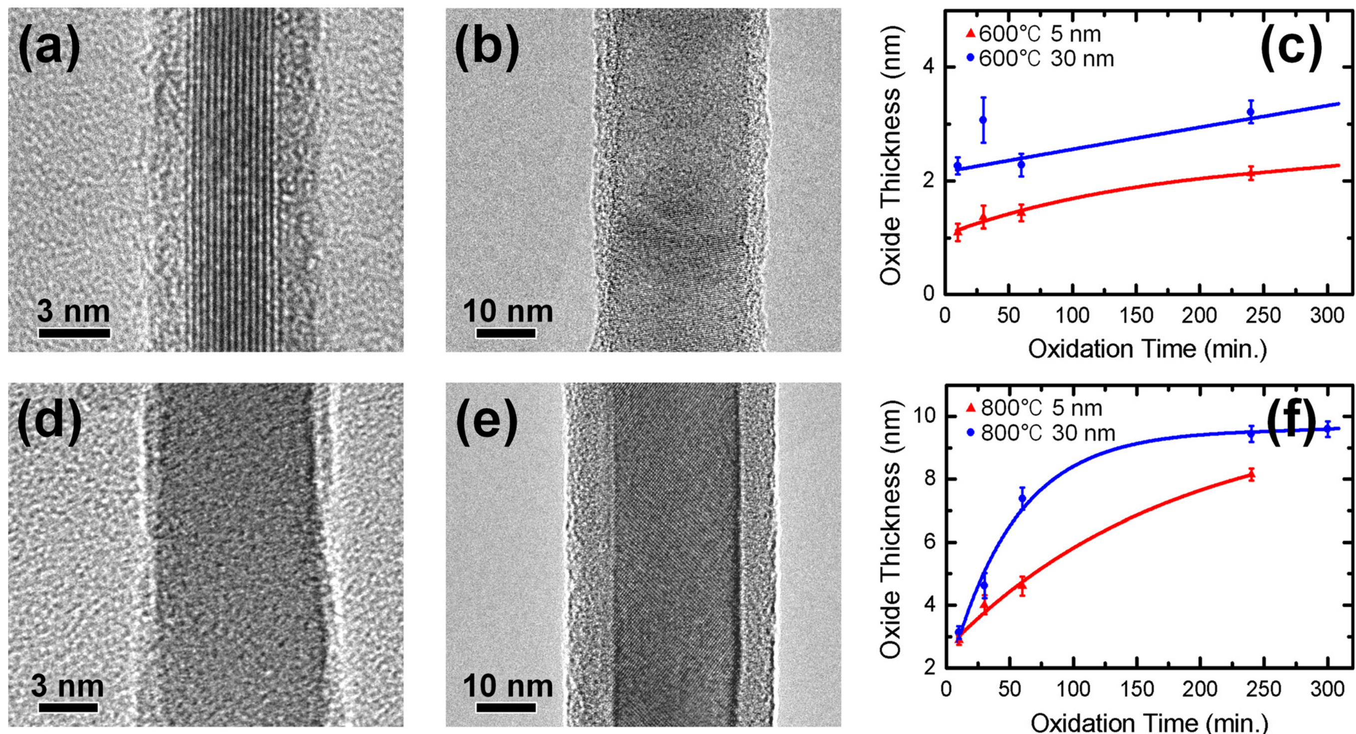


FIG. 2. Microstructures and oxidation rates of SiNWs 5 and 30 nm in diameter. (a and b) HRTEM images of the SiNWs 5 and 30 nm in diameter after oxidation at 600 °C for 240 min, respectively. (c) Oxidation rates of the SiNWs 5 and 30 nm in diameter heated until 600 °C. (d and e) HRTEM images the SiNWs 5 and 30 nm in diameter after oxidation at 800 °C for 240 min, respectively. (f) Oxidation rates of the SiNWs 5 and 30 nm in diameter heated until 800 °C.

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them was 69.06 and 30.94, respectively, which corresponded to a mole ratio of 2:1 as in the case of $SiO_2$. It should be noted that the SiNWs 5 nm in diameter were completely oxidized to $SiO_2$, whereas the SiNWs 30 nm in diameter were not under the same conditions. To the best of our knowledge, this is the first instance of full oxidation of a Si nanostructure. Other Si nanostructures, including SiNWs, Si nanocrystals, and Si nanotrench-likes structures, that are on the supra- or sub-10 nm scale have all exhibited self-limiting oxidative behavior.[12,13,16,18,26]

Figure 3(a) shows the oxidation of SiNWs as a function of the temperature as determined over a period of 300 min (supplementary information, Figure S4). The thickness of the oxide layer formed on the SiNWs 30 nm in diameter increased slowly between temperatures of 600–900 °C and then increased rapidly till up to 1000 °C. However, even after being oxidized at 1000 °C, the NWs were not completely oxidized. In contrast, the thickness of the oxide layer in the case of the NWs 5 nm in diameter increased linearly, and these SiNWs were again seen to have been completely oxidized after being heated to 1000 °C. It was also noticed that the SiNWs 30 nm in diameter showed one of two oxidation regimes, depending on the temperature, whereas the SiNWs 5 nm in diameter showed a single oxidation regime.

Kao *et al.*[10,20] have reported that, in general, SiNWs and other Si nanostructures with concave surfaces (e.g., quantum dots) show self-limiting oxidative behavior. This self-limiting oxidative behavior is due to the presence of compressive stress normal to the $Si/SiO_2$ interface, as shown in Figure 3(b), which shows oxidized SiNWs 5 nm and 30 nm in diameter. As the oxide continues to form at the interface, the layer of the previously formed oxide expands owing to the increase in the volume of $SiO_2$ compared to that of Si. This result in the generation of compressive stress normal to the $Si/SiO_2$ interface, and this stress heightens the energy barrier for the diffusion of oxygen through the $SiO_2$ layer. The magnitude of the compressive stress is inversely proportional to the radius of curvature of the surface, and this dependence of the stress of the curvature explains why SiNWs with diameters of several tens of nanometers undergo self-limiting oxidation. However, as noted previously, we were able to achieve full oxidation in SiNWs 5 nm in diameter. Since the oxidation of SiNWs is controlled by the stress generated in them, it can be assumed that the compressive stress in SiNWs 5 nm in diameter was lower than that in the SiNWs 30 nm in diameter. This was contrary to the previous explanation and is schematically illustrated in the oxidized SiNW 5 nm in diameter shown in Figure 3(b).

To confirm whether this assumption was true, classical-molecular-dynamics-based simulations of the oxidation of the SiNWs were performed. These simulations showed that the residual stress in the oxide layer is proportional to the radius of curvature of the SiNWs in the sub-10 nm diameter regime. The SiNW models used in the molecular dynamics simulations had diameters of 5 nm and 10 nm and a length of 18 nm, with the direction of growth of the SiNWs being [311] (Figure 4(a)). Figure 4(b) shows the cross-sections of

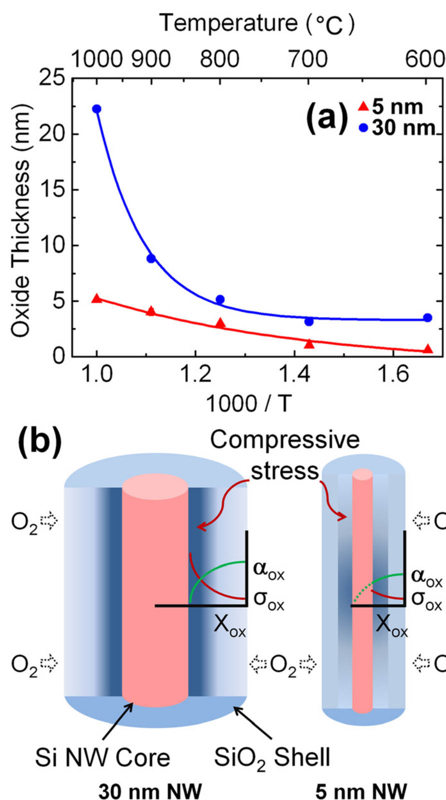


FIG. 3. (a) Oxidative behaviors of the SiNWs as a function of temperature. The SiNWs 30 nm in thickness showed one of two oxidation regimes, depending on the temperature, whereas the SiNWs 5 nm in diameter showed a single oxidation regime. (b) Schematic illustration of the oxidation of the SiNWs 5 and 30 nm in diameter and the effect that the stress had on the oxidation processes ($\alpha_{ox}$ is the activation energy for the diffusion of oxygen and $\sigma_{ox}$ is the compressive stress energy).

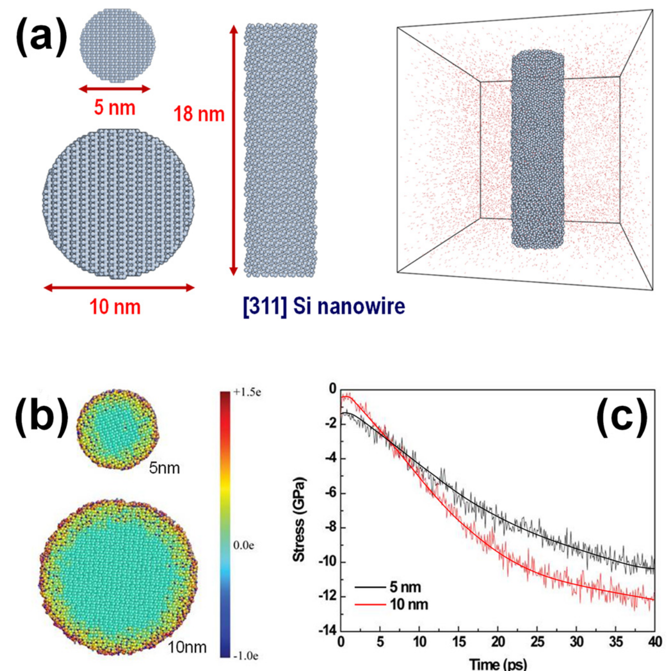


FIG. 4. (a) The model SiNWs used for the classical-molecular-dynamics-based simulations of the oxidation process. (b) Cross-sectional images of oxidized SiNWs, as calculated by the MD simulations. The atoms are colored on the basis of their Mulliken charges, shown in the color bar. (c) Evolution of the compressive stress in the radial direction of the oxide layer with time.

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the SiNWs along with the distribution of charges on the SiNWs that had been subjected to simulated oxidation for 40 ps at 800 °C. All the atoms are colored on the basis of their Mulliken charges. On the oxidized surfaces, the Si atoms have a charge of approximately +1.4 e while that of the oxygen atoms is about −0.8 e. These values are consistent with the results of an earlier calculation performed using quartz[23] and prove that the oxidized surface layers stoichiometrically comprised $SiO_2$. It was also observed that the interfaces between the layer of Si oxide and the unoxidized Si core were not sharply defined and that the interface exhibited a gradient layer with a thickness of about 1 nm. This has been observed in a number of previous studies as well.[27–29]

Figure 4(c) shows the evolution of the residual stress in the oxide layer over time. A negative sign for the stress denotes compressive stress and vice versa. The residual stress was calculated in the cylindrical layer for values of r ranging from 1.75 to 2.0 nm in the case of the SiNWs 5 nm in diameter and from 4.0 to 4.5 nm for the SiNWs 10 nm in diameter, with r being the distance from the center of the wire. The cylindrical layer was chosen from the radial distribution of the stress in the SiNWs in order to exclude the effects of surface relaxation. The stress in the circumferential direction exhibited behavior similar to that of the stress in the radial direction. The initial stress in the layer (at 0 ps) was lower in the SiNWs 10 nm in diameter because the stress before oxidation, given by Young's and Laplace's equations, is proportional to the curvature of the surface of the NWs. As the oxidation proceeds, the SiNWs 10 nm in diameter experience greater compressive stress in the oxide layer compared to that in the case of the SiNWs 5 nm in diameter. The difference in the stress generated in the SiNWs 5 and 10 nm in diameters increases as the oxidation process proceeds further. One should note that this result is in contrast to the dependence of the stress in the oxidized layer on the curvature of the surface in the case of thick NWs with diameters larger than 10 nm.[12–15]

This phenomenon can be understood in terms of the mechanical constraint placed on the oxide layer by the Si substrate. In case of Si oxidation, the equilibrium dimension of the Si oxide is larger than that of the Si substrate. When the oxide layer is very thin compared to the substrate, the difference in the dimensions of the oxide layer and the Si substrate causes the oxide layer to deform, resulting in a high level of compressive stress in the oxide layer. The thick Si substrate acts as a rigid mechanical constraint preventing the relaxation of the oxide layer formed on its surface. However, when the thickness of the substrate is comparable to (or less than) that of the surface oxide layer, the substrate itself would also be deformed by the oxide layer. In this case, the residual stress in the oxide layer becomes smaller than that in the case of a thick substrate.

During the oxidation of the SiNWs, the Si core serves as a mechanical constraint for the evolution of stress in the oxide layer. When the diameter of the core is large, the unoxidized Si core would act as a rigid mechanical constraint. However, in the case of very thin SiNWs, it would be energetically more favorable for the Si core to deform when the thickness of the surface oxide layer increases. We did indeed find greater deformation of the core Si region by surface oxidation in the case of the SiNWs 5 nm in diameter. Thus, a smaller compressive stress was generated in the SiNWs 5 nm in diameter, which may have resulted in the lowering of the energy barrier for the diffusion of oxygen into the Si core and therefore the full oxidation of the SiNWs.

Based on our simulation, the full oxidative behavior of SiNWs below 10 nm in diameter was explained by the compressive stresses. In the MD simulation, we tried to mimic the experimental thermodynamic condition by setting the same dimension of the SiNWs and the oxidation temperature. However, because of the limit in time scale of the MD simulation, we adopted an accelerated oxidation simulation condition by using a very high level of oxygen partial pressure during reaction. Therefore, the kinetic information from this simulation might have the least physical meaning. However, the energetic during oxidation caused by the residual stress, which is the main concern of the present work, would be still meaningful.

It may interest to predict the critical diameter for full oxidation of SiNWs. Further work is in progress regarding this. Even if we obtained the strain energy evolution by the MD simulation, this behavior is only for the initial stage of the oxidation due to the time scale limit of the simulation. Therefore, multiscale modeling by employing finite element method (FEM) analysis is in progress.

It was noticed that the time-dependent oxidative behaviors of the SiNWs 5 and 30 nm in diameter differed, i.e., the former showed a linear oxidation curve and the latter a parabolic curve on being oxidized at 800 °C (Figure 2(f)). The lower compressive stress generated in the SiNWs 5 nm in diameter can also explain this difference. The oxidation of Si takes place in two steps: the dissolution of oxygen into the oxide layer at the gas/solid interface and the diffusion of oxygen through the oxide layer. In the steady state, the oxidation rate is determined by three physical parameters: the diffusivity of the oxidant in the oxide D, the solid solubility of the oxidant in the oxide C*, and the surface reaction coefficient k.[19,30] In SiNWs having diameters greater than 5 nm, high compressive stresses are generated during oxidation, raising the diffusion energy barrier and resulting in diffusion-dominated oxidation such that the oxidation rate follows a parabolic curve, as shown in Figure 2(f). However, in the case of SiNWs 5 nm in diameter, the stress does not appear to act as a barrier. Thus, the diffusion of oxygen through the $SiO_2$ layer occurs readily. In this case, interfacial reactions dominate the overall oxidation process, which thus follows a linear curve with time, as also shown in Figure 2(f).

The compressive stress also influences the effect that temperature has on the oxidative behavior of the SiNWs, shown in Figure 3(a). The oxidation rate of the SiNWs increases steeply at temperature higher than 900 °C. This is because the compressive stress, which retards the diffusion of oxygen, eases around that temperature due to the transformation of the rigid $SiO_2$ shells into viscoelastic shells.[20,31] However, the SiNWs 5 nm in diameter showed no such steep increase in the oxidation rate while showing linear oxidation with respect to the temperature. As described above, this was so because the level of the compressive stress level was low

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and had less of an effect on the diffusion of oxygen and in turn the overall oxidation of the SiNWs.

Lastly, the crystallographic direction can be considered when considering the unprecedented oxidative behavior of the SiNWs 5 nm in diameter. In contrast to most SiNWs that grow in the [110] or [111] direction, the SiNWs 5 nm in diameter grew along the [311] direction. It has been reported previously that the oxidation rate of Si depends on the orientation of its crystals.[30] Hence, the difference in orientation may have had an effect on the oxidation of SiNWs. However, this possibility can be excluded as previously reported research results indicate that the rate of oxidation along the [311] direction is lower than that noted in the case of the [110] or [111] direction.[30]

## IV. CONCLUSIONS

In summary, SiNWs with an average diameter of 5 nm underwent full oxidation that was linear in nature while those with a diameter of 30 nm underwent self-limiting oxidation that was parabolic in nature. The results of MD simulations indicated that the directional development of a lower compressive stress at the oxide/Si interface was responsible for the full oxidation of the SiNWs 5 nm in diameter. The complete oxidation could have been the result of the mechanism of oxidation of the SiNWs in the case of the NWs 5 nm in diameter being different, i.e., interfacial reaction-dominated, from that for the NWs with a diameter of 30 nm, which was diffusion dominated. This was because the oxidation process is dependent on the diameter of the NWs. These results will help widen our knowledge of the oxidative behavior of sub-10 nm structures and enable us to exploit them for use in more complex nanodevices.

## ACKNOWLEDGMENTS

This work was supported by a grant (No. 2012R1A2A1A03010558) from the National Research Foundation of Korea (NRF), funded by the Ministry of Education, Science, and Technology (MEST), Korea and the Pioneer Research Program for Converging Technology (2009-008-1529) of the Korea Science and Engineering Foundation, funded by the Ministry of Education, Science, and Technology, Korea. Research performed at the Korea Institute of Science and Technology (KIST) was financially supported by the Converging Research Center Program (2010K000992) of the Ministry of Education, Science, and Technology, Korea.

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