Stress evolution during the oxidation of silicon nanowires in the sub-10 nm diameter regime

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Using a reactive molecular dynamics simulation, the oxidation of Si nanowires (Si-NWs) with diameters of 5, 10, and 20 nm was investigated. The compressive stress at the interface between the oxide and the Si core decreased with increasing curvature in the sub-10 nm regime of the diameter, in contrast to the theory of self-limiting oxidation where rigid mechanical constraint of the Si core was assumed. The Si core of the thinner Si-NW was deformed more with surface oxidation, resulting in a lower compressive stress at the interface. These results explain the experimental observation of full oxidation of very thin Si-NWs. © *2011 American Institute of Physics*. [doi:10.1063/1.3643038]

In the last several decades, both experimental and theoretical investigations have revealed that the oxidation behavior of Si nanowires (Si-NWs) or nanoclusters strongly depends on the surface curvature.[1–13] Because of the large difference in molar volume between SiO_2 and Si (the molar volume of SiO_2 is 2.25 times larger than that of Si), surface oxidation induces a compressive stress near the Si/SiO_2 interface. The residual stress results in "self-limiting oxidation" when the strain energy at the interface is larger than the energy gain for the ambient oxygen to diffuse and oxidize the inner Si.[1–4] Because the old oxide should expand more to accommodate the volume expansion in thinner Si-NWs, the self-limiting oxidation is more significant in the Si-NWs with smaller diameters.[2–13]

However, recent experimental work with Si-NWs with diameters of approximately 10 nm reported full oxidation of the NWs.[10–14] These experimental observations are puzzling from the viewpoint of the previous theoretical model that the self-limiting oxidation is caused by the interfacial compressive stress which is proportional to the curvature of NWs.[7–9] The theoretical analysis would imply that the oxidation is extremely limited or totally suppressed in very thin Si-NWs. In this letter, we report the reactive molecular dynamics (MD) simulation results to address the full oxidation of Si-NWs in the sub-10 nm regime. The present work showed that in this regime, the residual stress decreased with increasing curvature because the unoxidized Si core was deformed by the volume expansion in the surface oxide layer.

Semiclassical MD simulation of Si-NW oxidation was performed using the reactive force field (ReaxFF) for the Si-O system proposed by van Duin *et al.*[15] The present authors validated the ReaxFF by simulating the reaction behaviors of oxygen on the Si(100) surface that are consistent with previous *ab initio* calculations and experimental observations.[16] Si-NWs of the [311] direction with different diameters, 5, 10 and 20 nm, were prepared to mimic the recent experiment.[14] After relaxing the NWs for 100 ps at 1073 K, the simulation box was filled with O_2 molecules for the oxidation reaction, as shown in the supplementary information.[17] The oxidation temperature was set to 1073 K, which is lower than the critical temperature for viscoelastic flow of SiO_2 (approximately 1223 K).[11,18] The periodic boundary condition was applied in all directions, and the simulation time step was set to 0.1 fs for the stability of the simulation. "Large-scale atomic/molecular massively parallelized simulator" (LAMMPS) code was used for all of the simulations.[19] The O_2 partial pressure in the present simulation was set very high (approximately 275 atm) to investigate the rare events in the MD time scale. To prevent overheating the system during simulation, the temperature of the system was rescaled to the oxidation temperature at every time step. It must also be noted that the present simulation did not consider the oxygen diffusion over a long time scale. Our simulation would thus be limited to the early stage of oxidation.

Figure 1 shows the calculated charge distributions of the Si-NW cross section and the corresponding distributions of the stress in the radial direction (σ_r) before and after oxidation for 40 ps. All atoms are colored by the Mulliken charge according to the color scale bar in the figure. At 40 ps of oxidation, Si atoms in the oxidized surface region have approximately $+1.4e$ and O atoms approximately $-0.8e$; these values are similar to those of the previous calculation with α-quartz.[15] The surface oxidation slightly increased the surface roughness on the atomic scale. A gradient interface with a thickness of approximately 1 nm was observed between the surface oxide and the Si core, which agrees well with the experimental observations.[20–22] The present simulation showed that the O atom can notably diffuse into the bulk Si during the short period of 40 ps. This rapid diffusion could be ballistic, as suggested in the previous experimental works on the early stage of Si oxidation.[23]

The residual stress in Fig. 1 was obtained by averaging the atomic stress in the concentric shell between r and $r + \delta r$, where r is the radial distance from the center of the

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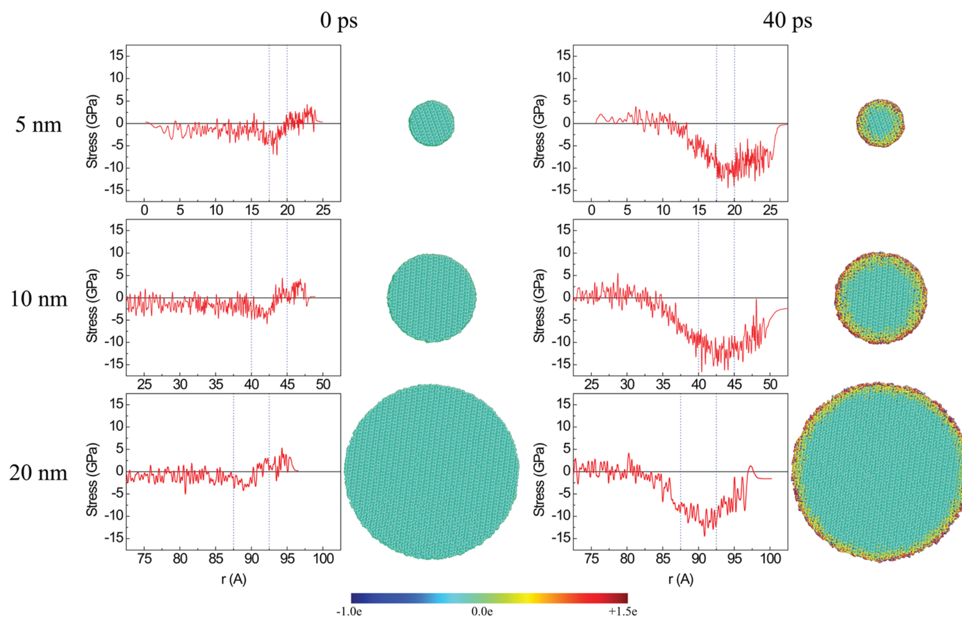

FIG. 1. (Color online) Calculated charge distributions in the cross section of the Si-NW and the corresponding residual stress distribution in the radial direction before and after oxidation for 40 ps. All atoms are colored by the Mulliken charge as in the scale bar.

NW. The stresses in the circumferential (σ_θ) and axial (σ_z) direction exhibited behavior that was qualitatively the same as that of σ_r. The compressive (tensile) stress was presented as a negative (positive) value. Before oxidation (at 0 ps), the inner part of the relaxed Si-NW yielded a small compressive stress because of the curved surface with a negative curvature. The stress on the surface was relaxed by the atomic rearrangement. As the surface was oxidized, the compressive stress in the Si core was relieved, while the oxidized outer shell yielded a compressive stress because of the volume expansion. The calculated stress value in the shallow region of the oxidized surface (approximately 0.5 nm in thickness) had a large uncertainty because of the surface roughness. Therefore, the stress evolution during oxidation was characterized in the range of r from 1.75 to 2.0 nm for 5 nm Si-NWs, from 4.0 to 4.5 nm for 10 nm Si-NWs and from 8.75 to 9.25 nm for 20 nm Si-NWs (indicated by two vertical broken lines in the figure).

Figure 2 shows the time evolution of σ_r of the selected shell. Before oxidation (at 0 ps), a small compressive stress, inversely proportional to the diameter of the NW, was observed. As the oxidation proceeded, the compressive stress evolved further in all NWs in the selected shell region. As the diameter decreased from 20 to 10 nm, the higher value of the residual stress was evolved, in consistent with the previous theoretical work of the Si-NW oxidation.[7–9] However, it must be noted that the 5 nm Si-NWs exhibited a smaller compressive stress than the 10 nm Si-NWs. This result is in contrast to the previous theoretical works that have shown that the interfacial compressive stress increases with the curvature.[7–9]

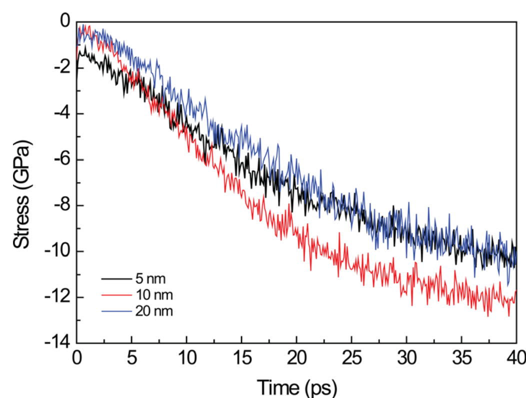

FIG. 2. (Color online) The time evolution of the residual compressive stress in the surface oxide layer for 5, 10, and 20 nm Si-NWs.

This phenomenon can be understood in terms of the mechanical constraint applied to the oxidized surface layer by the Si core. When the surface layer is very thin compared with the Si core, deformation in the surface layer compensates for the difference in dimensions, resulting in a stressed surface layer. This is the case when the unoxidized Si core is large enough to serve as a rigid mechanical constraint as in the 20 nm Si-NW of the present work. In contrast, if the size of the Si core is comparable with (or smaller than) that of the surface layer, it would be energetically more favorable for the Si core to deform to partly compensate for the difference in dimensions. In this case, the residual stress of the surface layer will be smaller than that for a large Si core as in 5 nm Si NW of the present work.

To investigate the deformation in the core, we monitored the potential energy of the core region ($r < 1.0$ nm for 5 nm Si-NWs, $r < 2.0$ nm for 10 nm Si-NWs, and $r < 4.0$ nm for 20 nm Si-NWs) during the simulation. Because of the small number of atoms in the core region, the potential energy showed more consistent behavior than the calculated stress. In the very initial stage of oxidation for a few ps, the potential energy of the core slightly decreased as the initial compressive stress originating from the surface curvature was relieved by the oxygen incorporation into the surface. In the sub-10 nm Si-NWs, the potential energy increased beyond the minimum points (indicated by arrows in Fig. 3) as the oxidation proceeded. In contrast, no significant change in the potential energy was observed in the 20 nm Si-NW. The change in the potential energy evidently shows the deformation of the Si core occurring with the surface oxidation. The deformation of the core was tensile as investigated in the radial distribution function of the core. The tensile

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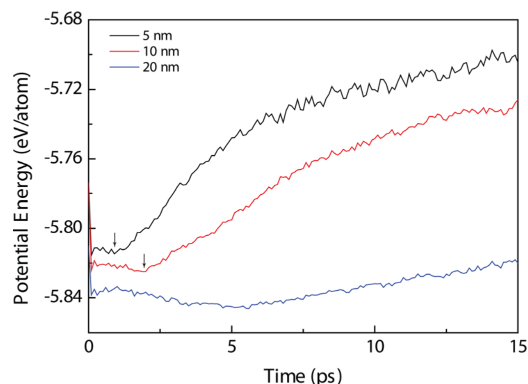

FIG. 3. (Color online) The time evolution of the potential energy in the unoxidized Si core for 5, 10, and 20 nm Si-NWs.

deformation of the unoxidized core was also observed during the Si nanoparticle oxidation.[4,5] This result shows that the Si core cannot be considered a rigid mechanical constraint against the volume expansion of the surface oxide layer. It must also be noted that the increase in the potential energy was more significant as the diameter of the Si-NWs decreased especially in sub-10 nm Si-NWs. Deformation of the unoxidized Si core resulted in a smaller residual stress at the interface of the thinner Si-NWs. Consequently, the thinner Si-NWs will be readily oxidized under the same driving force of oxidation, leading to full oxidation, as observed in the sub-10 nm Si-NWs.[10–12,14]

In summary, the present MD simulation showed that the residual stress decreased with increasing curvature in the sub-10 nm regime of the diameter. In this regime, the unoxidized Si core of the thinner Si-NWs deformed more to compensate for the volume expansion of the surface oxide layer, resulting in the smaller compressive stress. The present simulation explains the experimental observation that thin Si-NWs with a diameter in the sub-10 nm regime were fully oxidized without retardation.

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