

Rapid thermal oxidation of silicon nanowires

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Oxidation kinetics of silicon nanowires (SiNWs) subjected to rapid thermal oxidation (RTO) at 900 °C and 1000 °C in dry oxygen for exposure times ranging from 1 to 7.5 min is reported. For 1 min, SiNWs exhibit an enhanced oxidation rate compared to planar silicon, but for longer exposures the oxidation rates of SiNWs and planar Si are similar. Compared to furnace oxidation of SiNWs, RTO provides faster average oxidation rates and a weaker dependence of oxide shell thickness on the NW diameter. Our results demonstrate that RTO is an efficient approach for controlled oxidation of SiNWs. © 2009 American Institute of Physics. [DOI: 10.1063/1.3079395]

Silicon nanowires (SiNWs), especially those grown using the vapor-liquid-solid (VLS) mechanism,¹ attracted substantial attention as prospective building blocks for nano-scale electronic devices. Thermal oxidation of SiNWs has been demonstrated as a promising approach to modify their properties and produce advanced SiNW-based devices, such as wrap-gated² and top-gated³ field-effect transistors. Seo *et al.*⁴ reported that surface-charge density in SiNWs could be decreased by replacing the native oxide with a higher-quality thermal oxide. Oxidation has been used to reduce the SiNWs diameter below the Bohr exciton radius to obtain visible photoluminescence due to quantum confinement effects.⁵ For these and other applications, accurate control over the oxidation rate is critical. Additionally, nondestructive methods to determine oxide thickness on device-integrated individual SiNWs are needed. Thermal oxidation of VLS-grown SiNWs has been the subject of several investigations that often yielded controversial results. For example, recent investigations of dry furnace oxidation revealed reduced oxidation rate of SiNWs compared to planar Si and showed the dependence of oxidation rate on the NW diameter.^{3,6,7} This behavior is in a qualitative agreement with a model by Kao *et al.*⁸ for the oxidation of cylindrical Si microstructures. However, in some cases, enhanced oxidation of SiNWs compared to Si wafers has been observed.^{3,7,9}

In the present study, we analyzed the oxidation kinetics of SiNWs using rapid thermal oxidation (RTO). RTO offers several advantages over conventional furnace oxidation for planar silicon, including superior-quality gate oxide layers with low fixed-charge density, high breakdown dielectric field, and smooth Si/SiO₂ interface.¹⁰ Therefore, it is interesting to explore the RTO to fabricate oxide shells on SiNWs. To the best of our knowledge, no RTO studies for SiNWs have been reported (the only report, where RTO was used in Raman studies for the SiNWs doping, contained no data on the oxidation kinetics¹¹).

SiNWs were grown by the VLS method on Si {111} substrates. Prior to the growth, the Au-coated Si substrates were *in situ* annealed at 500 °C for 15 min in a H₂/N₂ atmosphere to form Au-based islands, required for the catalytic VLS

growth. The growth was carried out at 500 °C for 15 min in a horizontal hot-wall chemical vapor deposition reactor using 500 SCCM (standard cubic centimeters per minute) flow of 1% SiH₄ in N₂ mixture, which was further diluted with 500 SCCM N₂ and 50 SCCM H₂. The total reactor pressure was 300 Torr. As-grown SiNWs were oxidized in ultrahigh purity oxygen at 800, 900, and 1000 °C for times ranging from 1 to 7.5 min using a commercial rapid thermal processing (RTP) furnace. Prior to RTO, the SiNW samples and the reference lightly doped *n*-Si {111} wafers were treated using a diluted (1:5) hydrofluoric acid to strip off the native oxide, rinsed in isopropyl alcohol (IPA), and dried in N₂. Both the NW samples and reference wafers were immediately loaded into the RTP system and processed simultaneously. During heating and cooling, the samples were kept under a 5000 SCCM flow of ultrahigh purity (UHP) argon to avoid uncontrolled oxidation. Oxidation was performed in a 1000 SCCM flow of UHP oxygen. The oxidized SiNWs were analyzed using a field emission scanning electron microscope equipped with an electron backscatter diffraction (EBSD) detector and a transmission electron microscope (TEM). TEM samples were prepared by releasing NWs from the substrate using ultrasonic agitation in IPA and dispersing the NW suspension on lacey-carbon coated grids. The oxide thickness on SiNWs and on planar reference samples was measured by TEM and spectroscopic ellipsometry, respectively. Spectroscopic ellipsometry has been shown to provide accurate thickness values for oxides as thin as 2 nm.¹² For both methods, uncertainty of measurements was estimated at less than 10%.

Both electron diffraction in TEM and EBSD confirmed the NWs to be single crystals with their growth axes parallel to <112> directions; additionally, TEM imaging revealed occasional {111} stacking faults parallel to the NW axis. The radius r_0 of as-grown NWs ranged from 10 to 30 nm. Regardless of conditions, a uniform oxide shell along the entire NW length was attained. A representative TEM image of a SiNW oxidized at 1000 °C for 1 min is shown in Fig. 1.

The average oxide thickness after 5 min RTO at 800 °C was about 6 nm, which is close to the oxide thickness of 5.8 nm measured on the planar Si sample. This thickness is sufficient for device applications; however, the inferior quality of low-temperature oxides is known to compromise device performance. Therefore, our work focused on oxides produced at higher temperatures of 900 and 1000 °C.

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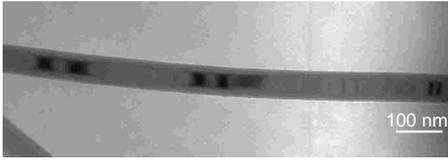


FIG. 1. TEM image of a SiNW oxidized at 1000 °C for 1 min. The bandlike contrast is associated with the NW bending.

Figure 2 displays a correlation between the SiO₂ thickness t_{ox} and the radius of the remaining Si core r_c for the SiNWs oxidized at 900 and 1000 °C. Solid lines are linear fits to the experimental data and horizontal dashed lines refer to the oxide thickness measured on reference Si {111} samples. (The fits are only used to guide the eye as the actual dependence can be nonlinear.) For both temperatures, after 1 min, the average oxide thickness $\langle t_{\text{ox}} \rangle$ on SiNWs is $\approx 50\%$ larger than that on planar Si, which reflects enhanced oxidation of NWs during initial stages of the reaction. At 900 °C, $\langle t_{\text{ox}} \rangle$ for NWs approaches the planar value after 3 min, and the difference vanishes completely after a 5 min exposure [Fig. 2(a)]. Similar trends are observed for 1000 °C [Fig. 2(b)]. The time dependence of $\langle t_{\text{ox}} \rangle$ is shown in the inset of Fig. 3. For a given value of r_c , the oxide thickness varied by $\approx 20\%$. This relatively large spread can be attributed in part to a thickness variation along the SiNW circumference due to the different oxidation rates of distinct SiNW side facets.³

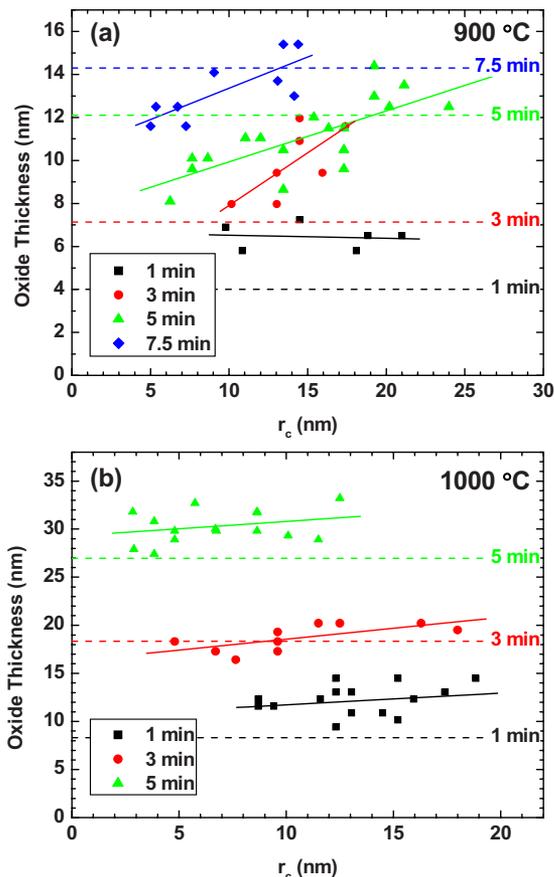


FIG. 2. (Color online) Dependence of the oxide shell thickness on the remaining Si core radius after RTO at (a) 900 °C and (b) 1000 °C for different exposure times. Solid lines are the linear fits to experimental data and are shown to guide the eye only. Horizontal dashed lines represent oxide thicknesses on Si {111} reference samples.

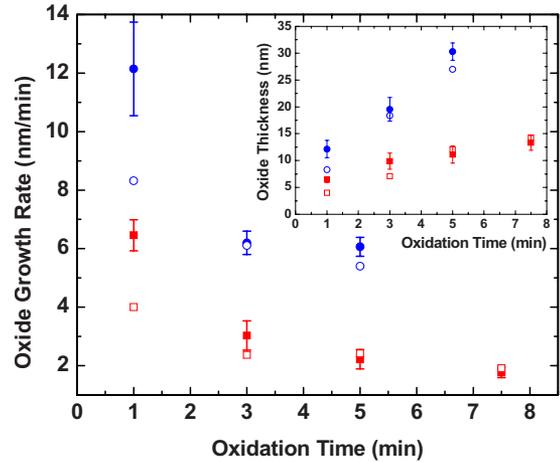


FIG. 3. (Color online) Average oxide growth rate vs oxidation time for 900 °C (squares) and 1000 °C (circles). The inset shows the average oxide thickness vs oxidation time. In both figures, solid and open symbols correspond to SiNWs and planar Si(111) reference samples, respectively. The error bars represent the standard deviation of data shown in Fig. 2.

The oxide shell thickness is largely independent of r_c for the RTO at 900 °C for 1 min, but after 3 min, a discernable r_c -dependence is evident [Fig. 2(a)]. Longer exposures for 5 and 7.5 min both yield weaker dependence of t_{ox} on r_c compared to the 3 min RTO; the origin of such nonmonotonic dependence of $t_{\text{ox}}(r_c)$ on oxidation time requires further investigation. For RTO at 1000 °C, the dependence of the oxide thickness on the NW radius is weaker than at 900 °C for all oxidation times, except 1 min oxidation [Fig. 2(b)].

Figure 3 compares the average oxide growth rates on SiNWs and planar Si(111). After a fast initial oxidation (1 min), the oxidation rates of SiNWs are similar to the respective values for the planar samples and decrease slowly with time. For example, for the 900 °C RTO, the NW oxidation rates are 2.2 nm/min and 1.8 nm/min for 5 and 7.5 min, respectively. The oxidation rates at 1000 °C are about three times higher (i.e., 6.2 nm/min and 6.1 nm/min for 3 and 5 min, respectively).

We identified the following differences between the RTO and the furnace oxidation^{3,6} of SiNWs: (i) the difference in thickness for the RTO oxides grown on planar Si and SiNWs appears to be much smaller than that for the furnace oxides; (ii) no evident retardation of NW oxidation is observed for the present RTO conditions; (iii) the dependence of oxide thickness on the SiNW radius is less pronounced for the RTO, and it can further be minimized by tuning the oxidation temperature and time. These features are beneficial for well-controlled oxidation of SiNWs. For example, the oxide shell thickness on SiNWs can be simply estimated from the oxide thickness on planar samples processed under identical conditions. Moreover, due to photoenhanced oxidation, RTO yields much higher oxidation rates compared to conventional furnaces.¹³ Therefore, in RTO, the targeted oxide thickness can be attained after a much shorter annealing time thereby minimizing adverse side effects such as dopants segregation and/or interdiffusion.

A model by Kao *et al.*⁸ describes oxidation of cylindrical Si surfaces and accounts for viscous stresses associated with a two-dimensional deformation of oxide; the stresses are inversely proportional to the cylinder radius. According to this model, compressive stresses normal to the Si-SiO₂ interface

reduce the interfacial reaction rate compared to planar Si surfaces, whereas tensile stresses generated within the oxide shell reduce effective oxide viscosity and enhance oxygen diffusivity and solubility. Despite existing reservations regarding the applicability of the “viscous model” to the thin oxide/small radii geometries,⁸ we observed a qualitative agreement between the model of Kao *et al.* and our RTO results. In particular, faster initial (1 min) oxidation of SiNWs in Fig. 3 can be readily explained by the emerging tensile stress in the oxide, which enhance oxygen supply to the Si-SiO₂ interface. As the oxide continues to grow, the increasing normal stress diminishes the oxidation rate, which eventually approaches a bulk Si value. We expect that longer RTO treatments would result in further decrease in the growth rate as observed for conventional furnace oxidation.^{3,6,7,9} A weaker dependence of oxide thickness on r_c for 1000 °C oxidation as compared to 900 °C (Fig. 2) is also consistent with the model of Kao *et al.* because 1000 °C is higher than the viscous flow point for SiO₂ (≈ 960 °C) (Ref. 14) thus facilitating stress relaxation at this temperature. However, a fully quantitative description of SiNWs oxidation kinetics likely requires use of viscoelastic models^{15,16} that reproduce the temperature-dependent behavior of SiO₂ in a wide temperature range.

In summary, we report the kinetics of RTO on VLS-grown SiNWs at 900 and 1000 °C. Our results demonstrate that RTO can be employed for rapid fabrication of a uniform oxide shell over SiNWs with thicknesses sufficient for device applications. Compared to furnace oxidation, RTO eliminates oxide growth retardation with respect to planar Si and exhibits much weaker dependence of oxide thickness on the initial radius of SiNWs. These features are beneficial for

well-controlled oxidation of SiNWs for the device structures. RTO can be easily combined with other high-temperature treatments, such as rapid thermal annealing or nitridation, to grow oxide structures with improved properties. Studies are underway to assess the structural and dielectric properties of RTO SiNW oxides.

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