

Early Stages of Oxide Growth in H-terminated Silicon Nanowires: Determination of Kinetic Behavior and Activation Energy

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Supplementary Information

Experimental Procedure

SiNWs were grown by the vapor-liquid-solid (VLS) technique as can be found in our previous work.¹⁶ SiNWs size and length distributions are illustrated in Fig SI-1. Hydrogen termination is conducted through HF and NH₄F etching as explained in the references.^{4,5} H-SiNWs were annealed in ambient conditions in seven distinct temperatures of 50 °C, 75 °C, 150 °C, 200 °C, 300 °C, 400 °C and 500 °C, each for five different time-spans: 5 min, 10 min, 20 min, 30 min and 60 min. Notice that surface contamination by organic species was constant 20±5% during annealing. This has been monitored in C1s spectra of the samples heated for 60min at each temperature. Annealing and hydrogen termination were gentle in the sense that they did not impose noticeable changes on size and orientation of SiNWs. X-ray photoelectron spectroscopy (XPS) was employed to examine impacts of each annealing stage on the thermally grown oxide amount and composition. Core level and valance band photoelectron spectra were excited by monochromatic Al K α radiation (1487 eV) and collected by a hemispherical analyzer with adjustable overall resolutions of 0.8 to 1.2 eV. In an overall binding energy survey, samples were first scanned from 0 to 1000 eV detecting the signals for Si, C, and O. The Si2p at 98.0-105.0 eV, C1s at 282.0-287.0 eV and O1s at 520-550eV were monitored more accurately in discrete number of scans.

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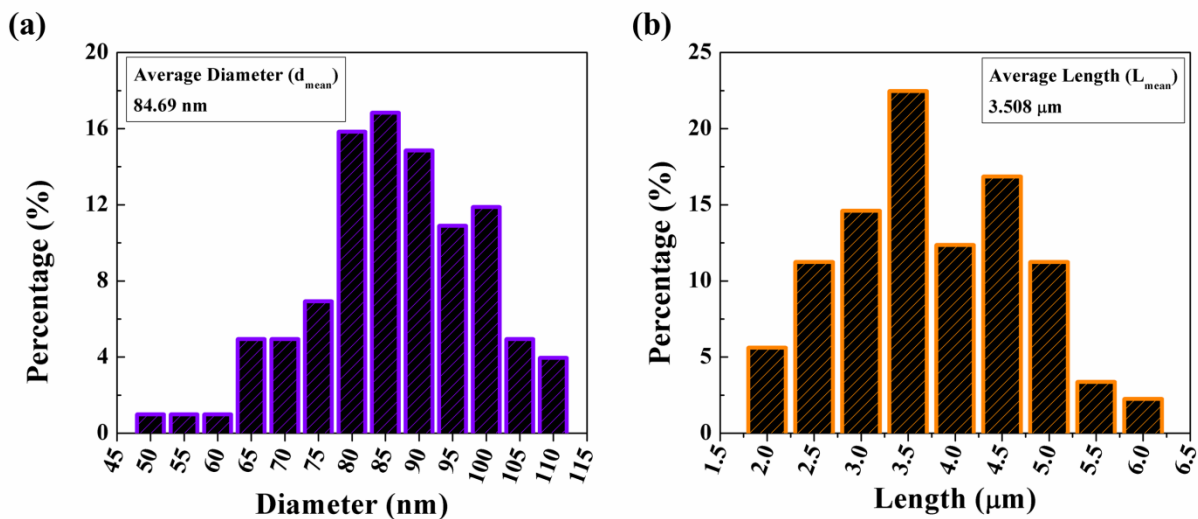


Figure SI-1. Distribution of VLS-grown SiNWs' (a) diameter and (b) length measured by analysis of their SEM micrographs.

Humidity Level Variation over Temperature

Figure SI-2 depicts variations of relative humidity over annealing temperature for the atmosphere above the hotplate. Measurements were done by a commercially available hygrometer (Oregon Scientific – BAR122HGN). At lower temperatures ($T < 200$ °C), humidity shows relative stability oscillating decreasing up to 1%. Contrarily, above 200 °C, it starts to decrease dramatically down to 7% at 500 °C.

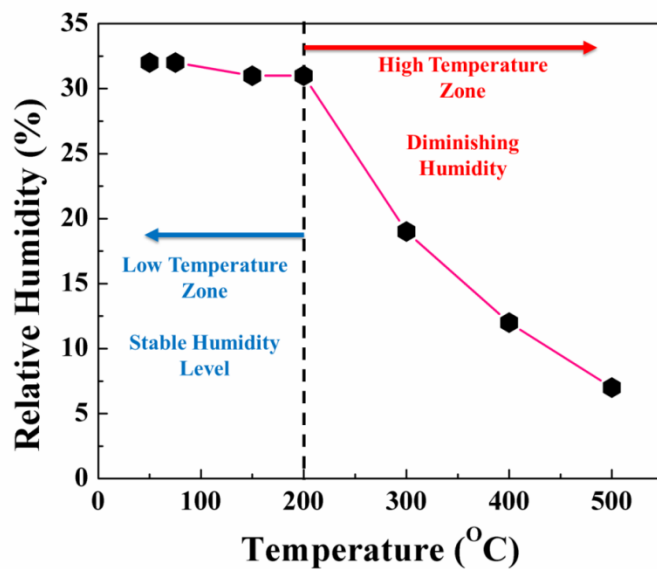


Figure SI-2. Relative humidity above the hotplate as a function of plate's surface temperature.

Variations in RH level can change the role of water molecule as the second oxidant. Oxidation under the simultaneous act of H₂O and O₂ can be well described by the oxidation/hydroxylation mechanism wherein oxide growth depends on the thermally activated electron tunneling through the initially formed oxide layer.¹⁻³ At lower temperatures (T < 200°C) SiO₂ formation limits the tunneling and increase of relative humidity from 33% to 50% and 75% makes this limitation more significant as water-assisted oxidation becomes more relevant (Table SI-1).

Table SI-1. Si₂O peak intensity in different oxidation environments and temperatures

Oxidation Environment	Temperature (°C)	I _{SiO₂}
Air -RH 33%	150	0.165386946
Air - RH 50%	150	0.049075689
Air - RH 75%	150	0.032787252
Air -RH 33%	25 (RT*)	0.015730107
Distilled H ₂ O	25 (RT)	0.023298278
Distilled H ₂ O	100 (BT*)	0.120510612

* RT ≡ Room Temperature, BT ≡ Boiling Temperature

Nevertheless, due to extremely low amounts of oxygen in pure distilled water, the competition between O₂ and H₂O is absent and H₂ evolution takes over other possible mechanisms.⁴ H₂ evolution is slower in comparison with hydroxylation/oxidation at room temperature despite both are thermally activated. Its thermal activation can be proven by the considerable increase in SiO₂ amount (Table SI-1) for room temperature to boiling temperature oxidation.

References

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