Silicon nanowires (Si NWs) represent an attractive class of building blocks for nanoelectronics and sensors. However, for many applications, the presence of oxide on the Si NW surface is undesirable, because a defective oxide layer (e.g., native SiO2) induces uncontrolled interface states in the band gap of the Si.

Freshly prepared H-terminated Si NWs have low surface recombination velocities but are not stable in air for more than a few hours, because disordered oxide layers form. Recently, we have reported on Si NWs that were chemically modified by CH3 functionalities through a covalent Si–C bond. The resulting CH3–Si NWs allowed formation of air-stable Si NW Field Effect Transistors (FETs) having on–off ratios in excess of 105 over a relatively small gate voltage swing (~2 V). Though CH3 termination gives full coverage of the Si atop sites, subsequent functionalization is not possible. The ability to attach a controlled functionality to a stable, fully passivated Si NW is highly desirable for a wide range of applications, especially for biosensors and systematic control over the electrical properties of Si NWs.

Here, we report on Si NWs modified by covalent CH3–CH=CH– scaffolds, via Si–C bonds, that give nearly full coverage of the Si atop sites and, at the same time, provide a route for subsequent functionalization. The obtained CH3–CH=CH–Si NWs exhibit superior oxidation resistance over Si NWs that are modified with CH3– or CH3–C=C– functionalities, which give nearly full coverage of the Si atop sites too.

The Si NWs investigated here were composed of 50 ± 10 nm diameter Si cores coated with 3–4 nm native SiO2 skins (see Supporting Information, Figure 1S) and contained pronounced low index facets, such as (111), (100), and (112). These Si NWs were terminated with methyl (CH3–), propenyl (CH3–CH=CH–), and propynyl (CH3–C≡C–) functionalities using a chlorination/alkylation route, as described in section 2 of the Supporting Information. The obtained samples were characterized by high resolution X-ray photo electron spectroscopy (XPS); see Supporting Information, section 3.1. The measurements were done three times for each sample, and averages have been taken.

Figure 2S of the Supporting Information shows an XPS scan of Si2p and C1s regions of propynyl-terminated Si NWs. The Si2p spectrum shows Si2p1/2 and Si2p3/2 in the expected 2:1 area ratio. No oxidized Si between 101.0 and 103.5 eV was observed (see Supporting Information, Figure 2SA). Three peaks were observed in the C1s region (see Supporting Information, Figure 2SB): (i) a peak at 284.0 eV for carbon atoms covalently bonded to silicon (C–Si); (ii) a peak at 285.0 eV for carbons bonded to either hydrogen or another carbon atoms; and (iii) a peak at 286.6 eV for adventitious carbons bonded to oxygen from the wet chemical processing with THF and/or methanol rinse after functionalization. All the C1s and Si2p peaks mentioned were also observed for methyl- and propynyl-terminated Si NWs. The peak area ratio of C–Si to the Si2p signal (C–Si/Si2p) of each alkyl group was measured relative to the C–Si/Si2p ratio for the CH3 termination, which was found to provide nearly full coverage of the Si atop sites of 2D Si(111). CH3–CH=CH–Si NW surfaces showed a C–Si/Si2p ratio of 103 ± 5% relative to that of CH3–Si NW surfaces indicating that CH3–CH=CH–Si NW can be packed at very high density. Similarly, the C–Si/Si2p ratio for CH3–C≡C–Si NWs produced 97 ± 5% relative to that of CH3–Si NW surfaces. Fourier transform infrared (FTIR) spectroscopy on CH3–CH=CH–Si samples showed that the double bond character of the surface ligand is preserved in the functionalization reaction (see Supporting Information, Figure 5S).

Figure 1 shows the ratio of the SiO2 to Si2p peak areas for the functionalized Si NWs upon exposure to ambient air. As shown in the figure, the oxidation of CH3–CH=CH–Si and CH3–Si NWs started only after ~100 h of exposure. Following this exposure period, the Si2p/SiO2 ratio of CH3–CH=CH–Si NWs increased by 0.027 ± 0.005 (~0.12 monolayer of oxide) within ~50 h of exposure, after which time it stabilized at a level that was comparable (0.036 ± 0.012 SiO2/Si2p; ~0.15 monolayer of oxide) to the value at ~150 h. In contrast, the oxidation of CH3–Si NWs increased continuously after ~100 h of exposure, reaching 0.115 ± 0.017 SiO2/Si2p (~0.50 monolayer of oxide) after ~720 h, without showing any indication for stabilization. The oxidation of CH3–C≡C–Si NWs increased continuously at higher rates than the other two samples, reaching 0.154 ± 0.022 SiO2/Si2p (~0.67 monolayer of oxide) after ~720 h of exposure. The high stability of the CH3–CH=CH–Si NW can be attributed to the π–π interactions between the adjacent molecules. In the case of CH3–C≡C–Si NW, π–π interactions occur between the adjacent molecules but leave one pair of electrons free. This pair of free electrons might easily transfer to the top Si site (beneath the molecule) and interact with oxidizing agents (water, O2, etc.). It is noteworthy to point out that modification of Si NWs with (simple) C2–C6 alkyl chains showed C–Si/Si2p peak ratios of (49–68) ± 5% relative to that of CH3–Si NW surfaces and a 3–5-fold higher oxidation rate than that of CH3–Si NWs.

Figure 2 below and section 2.3 of the Supporting Information give an overview of a representative example for subsequent covalent functionalization of CH3–CH=CH–Si NWs. In this
approach, a photoactive aryldiazirine cross-linker, 4’-[(3-trifluoromethyl-3H-diazirin-3-yl)]-benzoic acid N-hydroxy-succinimide ester (TDBA-OSu), was used as the key compound. This functionality enters into the C—H bonds of the terminal methyl groups through a highly reactive singlet-state carbene intermediate at one end and reactive functionality for further chemical modifications. In contrast, CH$_3$—C=C— and CH$_3$— functionalities, which give nearly full coverage of the Si atom sites too, could not achieve (simultaneously) the combination of stability and subsequent functionalization. The reported approach has the advantage of controlling the density of reactive cross-linkers without affecting the stability of the Si NWs. Formation of monolayers with a variety of termination groups is expected to open up a wide range of opportunities for producing stable molecule-based electronic devices. Immobilization of biomolecules or selective receptors on the Si NWs offers opportunities for the development of novel (bio)-chemical sensors. Attachment of redox active molecules or “molecular switches” to Si NWs could enable fabrication of molecular scale memory or logic elements integrated with conventional Si-based nanoelectronic devices.

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 Supporting Information Available: TEM images of the Si NWs, functionalization procedure of Si NWs and 2D Si(111), and surface analysis by XPS and FTIR. This material is available free of charge via the Internet at http://pubs.acs.org.

References