

## Stable Scaffolds for Reacting Si Nanowires with Further Organic Functionalities while Preserving Si–C Passivation of Surface Sites

Ossama Assad,<sup>†</sup> Sreenivasa Reddy Puniredd,<sup>†</sup> Thomas Stelzner,<sup>‡</sup> Silke Christiansen,<sup>‡,§</sup> and Hossam Haick<sup>\*†</sup>

The Department of Chemical Engineering and Russell Berrie Nanotechnology Institute, Technion - Israel Institute of Technology, Haifa 32000, Israel, Institute of Photonic Technology e.V., Albert-Einstein-Str. 9, 07745 Jena, Germany, and Max-Planck-Institute of Mikrostructure Physics, Weinberg 2, 06120 Halle, Germany

Received October 8, 2008; E-mail: hhaick@technion.ac.il

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 SiO<sub>2</sub>) 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.<sup>1</sup> Recently, we have reported on Si NWs that were chemically modified by CH<sub>3</sub> functionalities through a covalent Si–C bond.<sup>2</sup> The resulting CH<sub>3</sub>–Si NWs allowed formation of air-stable Si NW Field Effect Transistors (FETs) having on–off ratios in excess of 10<sup>5</sup> over a relatively small gate voltage swing (±2 V).<sup>2</sup> Though CH<sub>3</sub> termination gives full coverage of the Si atop sites,<sup>3</sup> 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 CH<sub>3</sub>–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 CH<sub>3</sub>–CH=CH–Si NWs exhibit superior oxidation resistance over Si NWs that are modified with CH<sub>3</sub>– or CH<sub>3</sub>–C≡C– functionalities, which give nearly full coverage of the Si atop site too.

The Si NWs investigated here were composed of 50 ± 10 nm diameter Si cores coated with 3–4 nm native SiO<sub>2</sub> skins (see Supporting Information, Figure 1S) and contained pronounced low index facets, such as (111), (100), and (112).<sup>4</sup> These Si NWs were terminated with methyl (CH<sub>3</sub>–), propenyl (CH<sub>3</sub>–CH=CH–), and propynyl (CH<sub>3</sub>–C≡C–) functionalities using a chlorination/alkylation route,<sup>5</sup> 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 propenyl-terminated Si NWs. The Si2p spectrum shows Si2p<sub>3/2</sub> and Si2p<sub>1/2</sub> 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);<sup>5</sup> (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

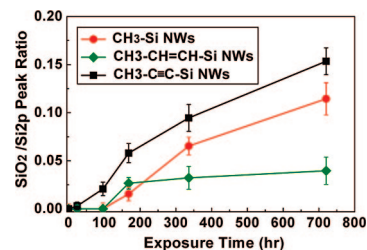


Figure 1. Ratio of the SiO<sub>2</sub> to Si2p peak areas for the different surface modifications of Si NWs, exposed to air over extended time periods.

the C–Si to the Si2p signal (C–Si/Si2p) of each alkyl group was measured relative to the C–Si/Si2p ratio for the CH<sub>3</sub> termination, which was found to provide nearly full coverage of the Si atop sites of 2D Si(111).<sup>3</sup> CH<sub>3</sub>–CH=CH–Si NW surfaces showed a C–Si/Si2p ratio of 103 ± 5% relative to that of CH<sub>3</sub>–Si NW surfaces indicating that the CH<sub>3</sub>–CH=CH–Si NW can be packed at very high density. Similarly, the C–Si/Si2p ratio for CH<sub>3</sub>–C≡C–Si NWs produced 97 ± 5% relative to that of CH<sub>3</sub>–Si NW surfaces. Fourier transform infrared (FTIR) spectroscopy on CH<sub>3</sub>–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).

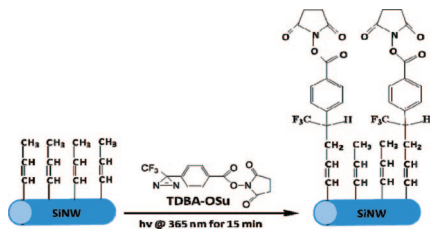
Figure 1 shows the ratio of the SiO<sub>2</sub> to Si2p peak areas for the functionalized Si NWs upon exposure to ambient air. As shown in the figure, the oxidation of CH<sub>3</sub>–CH=CH–Si and CH<sub>3</sub>–Si NWs started only after ~100 h of exposure. Following this exposure period, the SiO<sub>2</sub>/Si2p ratio of CH<sub>3</sub>–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 SiO<sub>2</sub>/Si2p; ~0.15 monolayer of oxide) to the value at ~150 h. In contrast, the oxidation of CH<sub>3</sub>–Si NWs increased continuously after ~100 h of exposure, reaching 0.115 ± 0.017 SiO<sub>2</sub>/Si2p (~0.50 monolayer of oxide) after ~720 h, without showing any indication for stabilization. The oxidation of CH<sub>3</sub>–C≡C–Si NWs increased continuously at higher rates than the other two samples, reaching 0.154 ± 0.014 SiO<sub>2</sub>/Si2p (~0.67 monolayer of oxide) after ~720 h of exposure. The high stability of the CH<sub>3</sub>–CH=CH–Si NW can be attributed to the π–π interactions between the adjacent molecules.<sup>6</sup> In the case of CH<sub>3</sub>–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 atop Si site (beneath the molecule) and interact with oxidizing agents (water, O<sub>2</sub>, etc.). It is noteworthy to point out that modification of Si NWs with (simple) C<sub>2</sub>–C<sub>6</sub> alkyl chains showed C–Si/Si2p peak ratios of (49–68) ± 5% relative to that of CH<sub>3</sub>–Si NW surfaces and a 3–5-fold higher oxidation rate than that of CH<sub>3</sub>–Si NWs.<sup>7</sup>

Figure 2 below and section 2.3 of the Supporting Information give an overview of a representative example for subsequent covalent functionalization of CH<sub>3</sub>–CH=CH–Si NWs. In this

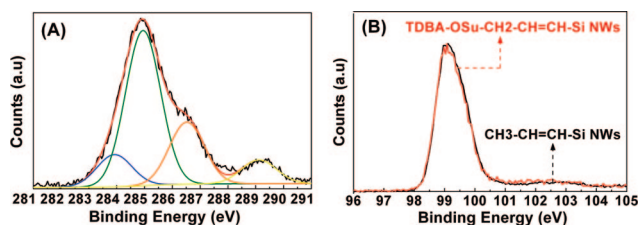
<sup>†</sup> Technion - Israel Institute of Technology.

<sup>‡</sup> Institute of Photonic Technology e.V.

<sup>§</sup> Max-Planck-Institute of Mikrostructure Physics.



**Figure 2.** Schematics for the subsequent functionalization of the  $\text{CH}_3\text{-CH=CH-Si}$  NW with photoactive aryldiazirine cross-linker (TDBA-OSu).



**Figure 3.** XPS scan for (A) C1s and (B) Si2p regions of propenyl-terminated Si NWs before and after functionalization with TDBA-OSu. 2D  $\text{CH}_3\text{-CH=CH-Si}$  (111) samples exhibited similar XPS spectra to those of  $\text{CH}_3\text{-CH=CH-Si}$  NWs.

approach, a photoactive aryldiazirine cross-linker, 4'-[3-trifluoromethyl-3*H*-diazirine-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 exits with amino reactive groups at the other end.<sup>8</sup>

The wide scan XPS spectra for Si NWs terminated with  $\text{CH}_3\text{-CH=CH-}$  and TDBA-OSu- $\text{CH}_2\text{-CH=CH-}$  are shown in Figure 3S of the Supporting Information. After attaching TDBA-OSu on  $\text{CH}_3\text{-CH=CH-Si}$ , the F1s peak appears around 680.0 eV due to the trifluoromethyl group of the TDBA-OSu cross-linker. The small N1s peak is also visible in the XPS survey spectrum at 402.4 eV due to the low atomic ratio of nitrogen in TDBA-OSu. Overall, these results show that the TDBA-OSu is covalently attached to the  $\text{Si-CH=CH-CH}_3$  surface.

The C1s signal of the TDBA-OSu- $\text{CH}_2\text{-CH=CH-Si}$  NW surfaces can be deconvoluted into four peaks (Figure 3A), as follows: (i) a peak at 284.0 eV for carbon atoms that are covalently bonded to silicon (C-Si); (ii) a peak at 285.0 eV for carbons in the aliphatic hydrocarbon chain; (iii) a peak at 286.6 eV for  $\alpha$ -carbons adjacent to the carbonyl carbon atoms; and (iv) a peak at 289.1 eV for the carbonyl carbon atoms. The ratio between these four peaks (1.4:6.5:2.6:1), before and after 10 min of sonication, was found to be equivalent to  $\sim 50\%$  density of reactive amino groups on the surface. XPS spectra of the Si2p region showed no surface oxidation before and after the secondary functionalization process (Figure 3B), indicating that the propenyl monolayer was not damaged during the secondary functionalization and has no degradation effects on the stability of the TDBA-OSu- $\text{CH}_2\text{-CH=CH-Si}$  NWs. The reactive nature of resulting surfaces makes them a promising launching pad for further subsequent experiments. To illustrate this point, *para*-phenylenediamine (PPD) was deposited on TDBA-OSu- $\text{CH}_2\text{-CH=CH-Si}$  NWs (see Supporting Information, section 2.4). The XPS spectra of PPD-TDBA-OSu- $\text{CH}_2\text{-CH=CH-Si}$  samples, before and after 10 min of sonication, indicated that the  $\text{CH}_3\text{-CH=CH-Si}$  layer was intact and that the TDBA-OSu and PPD functionalities were covalently bonded to Si NW surfaces (see Supporting Information, Figure 3S). It should be noted that reacting  $\text{CH}_3\text{-Si}$  NWs with TDBA-OSu according to the abovementioned scheme has shown no evidence for the presence of subsequent covalent functionalization.

For the sake of comparison, a similar set of experiments was performed on 2D Si(111), as described in section 2 of the Supporting Information. Generally speaking, *freshly prepared* molecularly modified 2D Si(111) surfaces, before and after subsequent functionalization, exhibited XPS spectra similar to those obtained for Si NWs (see Figure 3 above and Supporting Information, Figures 2S and 3S). In contrast, 2D Si(111) surfaces terminated with  $\text{CH}_3\text{-CH=CH-}$  or  $\text{CH}_3\text{-C}\equiv\text{C-}$  functionalities exhibited higher oxidation resistance than equivalent Si NWs (cf. Figure 1 above and Figure 4S of the Supporting Information). This difference might be attributed to the finding that distinctive Si facets adsorb monolayers at different packing densities.<sup>9</sup> In this context, it should be mentioned that the 2D Si(111) surfaces have a higher concentration of (111) facets than Si NWs, which (in addition to the (111) facets) contain (100) and (112) too.<sup>4</sup> 2D Si(111) surfaces terminated with  $\text{CH}_3\text{-}$  functionalities exhibited lower oxidation resistance than equivalent Si NWs (cf. Figure 1 above and Figure 4S of the Supporting Information). As yet, the origin of these differences is still puzzling and more studies are needed to elucidate this topic.

In summary, functionalization of Si NWs with  $\text{CH}_3\text{-CH=CH-}$  groups gives nearly full coverage of the Si atop sites. The resulting Si NWs provide high stability against oxidations and, at the same time, reactive functionality for further chemical modifications. In contrast,  $\text{CH}_3\text{-C}\equiv\text{C-}$  and  $\text{CH}_3\text{-}$  functionalities, which give nearly full coverage of the Si atop 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"<sup>10</sup> 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>.

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