Silicon nanowires terminated with methyl functionalities exhibit stronger Si–C bonds than equivalent 2D surfaces

Muhammad Y. Bashouti, Yair Paska, Sreenivasa Reddy Puniredd, Thomas Stelzner, Silke Christiansen and Hossam Haick*

Received 18th November 2008, Accepted 17th February 2009
First published as an Advance Article on the web 12th March 2009
DOI: 10.1039/b820559k

Silicon nanowires (Si NWs) terminated with methyl functionalities exhibit higher oxidation resistance under ambient conditions than equivalent 2D Si(100) and 2D Si(111) surfaces having similar or 10–20% higher initial coverage. The kinetics of methyl adsorption as well as complementary surface analysis by XPS and ToF SIMS attribute this difference to the formation of stronger Si–C bonds on Si NWs, as compared to 2D Si surfaces. This finding offers the possibility of functionalising Si NWs with minimum effect on the conductance of the near-gap channels leading towards more efficient Si NW electronic devices.

I. Introduction

Much effort has been devoted to the investigation of Si nanowires (Si NWs). However, information regarding the surfaces of oxide-free Si NWs is relatively scarce. Obviously, the chemical properties of Si NW surfaces are crucial to their stabilities and transport properties in nanoelectronic devices. Freshly prepared H-terminated Si NW surfaces have low surface recombination velocities but are not stable in air for more than a few days, because disordered oxide layers form. Hence, there is considerable interest in learning how to achieve Si NWs with high atmospheric stability, high conductance values, and low surface defect levels.

Recently, we have reported on Si NWs that were chemically modified by C₆H₅H₂₋₄CH₃ alkyl functionalities through a covalent Si–C bond. The resulting methyl-terminated Si NWs (hereinafter, CH₃–Si NWs) exhibited a tremendously enhanced stability (more than 336 h) against oxidation and higher oxidation resistance than equivalent Si NWs that were terminated with C₂H₅–C₆H₁₃ alkyl chains. Though the stability of CH₃–Si NWs is known, little is established about such chemistry for Si NW surfaces, and even less is known about the correlation between methyl modifications of Si NWs and the Si–C bond.

Here, we report on the functionalization of Si NW surfaces with CH₃–Si NWs and compare them with equivalent 2D CH₃–Si surfaces. We show that Si NW surfaces terminated with methyl groups, through Si–C bonds, provide similar surface coverage but stronger Si–C bonds than equivalent 2D Si surfaces. A preliminary mechanism explaining the performance of the Si–C bonds on Si NWs will be discussed.

II. Experimental

Synthesis of Si NWs

Si NWs were prepared by the vapour–liquid–solid (VLS) method using chemical vapor deposition (CVD) with silane on Si(111) substrates. For this purpose the substrates were etched in diluted HF to remove the native oxide and subsequently a 2 nm thick Au film was sputtered on the substrate and the sample was transferred into the CVD chamber. The substrates were annealed at ~580 °C and a pressure of ~5 × 10⁻⁷ mbar for 10 min. The temperature was then reduced to ~520 °C and a mixture of 5–10 sccm (standard cm³ min⁻¹) Ar and 5 sccm SiH₄ was introduced for 20 min at a pressure of 0.5–2 mbar for the nanowire growth.

Modification of Si NWs and 2D Si surfaces with methyl functionalities

After being cleaned with N₂ flow, H-terminated Si NWs were prepared by exposing the Si NWs to buffered HF solution (pH = 5) for 60 s and then NH₄F for 30 s. The samples were then removed and rinsed in water for <10 s per side to limit oxidation, dried in flowing N₂(g) for 10 s, and immersed in a saturated solution of PCl₅ in C₆H₅Cl (0.65 M) that contained a few grains of C₆H₅OOC₆H₅ to act as a radical initiator. The reaction solution was heated to 90–100 °C for 5–7 min. The reaction solution and rinsed in tetrahydrofuran (THF), followed by a rinse in CH₃OH and was then dried under a stream of N₂(g). The resulting (Cl-terminated) Si NWs were alkylated by immersion in 0.5 M alkyl Grignard in THF [CH₃–MgCl]. The reaction was performed for 5 to 4320 min (72 h) at 80 °C. At the end of the reaction time, the samples were removed from the reaction solution and rinsed in THF and CH₃OH. At the end of this process, the samples were dried under a stream of N₂(g). The alkylation process was gentle in the sense that it did not damage (or break) the Si NWs.

The substrates were annealed at

The Department of Chemical Engineering and Russell Berrie Nanotechnology Institute, Technion-Israel Institute of Technology, Haifa, 32000, Israel; E-mail: hhossam@technion.ac.il; Fax: +972 4 8295672

Institute of Photonic Technology e.V., Albert-Einstein-Str. 9, 07745, Jena, Germany

Max-Planck-Institute of Mikrostruktur Physics, Weinberg 2, 06120, Halle, Germany

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CH₃ terminations on 2D Si(100) and 2D Si(111) was prepared following the same procedure as mentioned above, but with one minor difference: the samples were chlorinated (i.e., immersed in a hot solution of PCl₅) for 60 min.

The resulting CH₃-terminated Si NWs—supported on Si(111) substrates (cf. ref. 7 and 10)—as well as 2D Si(100) and 2D Si(111) surfaces were characterized by high resolution X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectroscopy (ToF SIMS) analysis.¹¹

III. Results and analysis

The Si NWs investigated here were prepared using CVD, yielding undoped Si NWs with majority of (100) facets.¹⁰ TEM data indicated that these NWs were composed of smooth 50 ± 10 nm diameter Si cores coated with 3-4 nm SiO₂ skins, with lengths ranging between 2 and 4 μm.¹⁰ These Si NWs, and, for comparison, 2D Si(100) and 2D Si(111) substrates, were terminated with methyl (CH₃) functionalities using a two-step chlorination/alkylation route,¹²,¹³ as described in the Experimental section.

Fig. 1a shows the C1s XPS emission region of CH₃–Si NWs, fitted to three peaks: C-Si at 284.11 ± 0.02 eV, C–C at 285.20 ± 0.02 eV, and C–O at 286.69 ± 0.02 eV. Of these peaks, the C–Si peaks can be attributed to molecules bonded chemically to the Si surface. In contrast, the C–O peaks can be attributed to adventitious hydrocarbons containing oxygen that are bonded to either hydrogen or to carbon atoms that do not participate in the Si–C bond (i.e., physisorbed on top of the Si–C-bonded monolayer).¹²,¹³ The observation of a small oxygen (O1s) peak at 532.02 ± 0.02 eV suggests that the adsorbed adventitious hydrocarbons contain oxygen. It is reasonable to assume that these adventitious hydrocarbons could stem from wet chemical processing with THF solvent and the THF/methanol rinse after functionalization and/or from carbonaceous materials present in the laboratory environment. No SiO₂ was observed in the high resolution Si2p XPS scans, supporting the argument that the O1s signal was due to adventitious oxygen on the surface. The emission at 285.20 ± 0.02 eV can be ascribed to carbon bonded to either hydrogen or to carbon atoms that do not participate in the Si–C bond. The peaks were typically adjusted to produce fits that minimized the differences between the full widths at half-maximums (FWHMs).

Fig. 1b shows the coverage of methyl functionalities as a function of alkylation time. For Si NWs, 92 ± 3% of the maximum coverage was achieved after 20 ± 2 min alkylation. Longer alkylation periods, up to 24 h, changed the total coverage by 5 ± 3% only. Alkylation times of 24–72 h did not change the coverage on Si NWs further. Comparing the alkylation kinetics on Si NWs with 2D Si(100) showed two main notable differences: (I) 92 ± 3% of the maximum coverage on 2D Si(100) was achieved after 1000 ± 50 min alkylation; and (II) the reaction kinetics on 2D Si(100) at short and long alkylation times are rather different than on Si NWs. These differences in the kinetic behavior could be attributed mainly to differences in the surface energy. The cohesive energy becomes higher upon decreasing the dimensions of a given structure.¹⁴,¹⁵ Based on earlier work,¹⁴ it can be seen that 50 ± 10 nm (in diameter) Si NW surfaces has higher cohesive energy (~4.4 eV) than 2D Si(100) surfaces (~3.4 eV). Furthermore, the broadening of Si2p FWHMs in the case of Si NWs (data not shown), as compared to 2D Si(100) and 2D Si(111), suggests that wider distribution of Si–C bond strengths and/or angle variations of the organic ligands exists on the surface.¹⁵ We find the higher coverage on Si NWs, as compared to 2D Si surfaces, to be in good agreement with a previous study that reported higher coverage of H- and alkyl-terminations in porous silicon layers (PSL), as compared to flat 2D Si substrates.¹⁶

Since determining surface coverage requires accounting for escape length of photoelectrons and some other effects,¹⁷ an “impartial” indicator was required to examine the robustness of the data presented in Fig. 1b. With this in mind, ToF SIMS experiments, by which the methyl coverage is proportional to the SiCH₃⁺ (or CH₃⁺) fragments, were carried out. The results showed similar concentrations (within ±5% experimental error) of characteristic ToF SIMS fragments in both CH₃–Si NWs and 2D CH₃–Si(100) substrates (data not shown), marking the reliability of the XPS data presented in Fig. 1b.

Fig. 2a shows the SiO₂–Si2p peak area ratio for the CH₃–Si NWs and 2D CH₃–Si(100) surfaces upon exposure to ambient air over extended time periods. As shown in Fig. 2a, CH₃–Si NWs exposed to air over a period of more than one month showed ca. 3-fold less oxidation than the equivalent 2D

Fig. 1 (a) XPS of C1s region, showing C–Si, C–C and C–O peaks of freshly-prepared samples for CH₃–Si NWs at 24 h alkylation time. (b) Coverage of methyl groups (C1s/Si2p) of Si NW and 2D Si(100) as a function of alkylation time. Alkylation for 1440–4320 min (24–72 h) did not change the coverage on Si NWs or 2D Si(100) further, as compared to that achieved after 1440 min (24 h). For the sake of clear presentation, the results achieved in the 24–72 h alkylation time are not shown.

Fig. 2 (a) Ratio of the oxidized Si2p peak area to the bulk Si2p peak area for the methyl modification of Si NWs, 2D Si(100), and 2D Si(111), exposed to air over extended time periods.¹²,¹³,¹⁸ (b) Si–C decay as a function of exposure time for Si NW and 2D Si(100). The measurements were done three times for each sample and averages have been taken.
Si–CH$_3$ 0.239 
/C6 Si–C 0.142 
Si–O 0.037 
Si$_2$O 0.071 
Si$_2$OC$_2$H$_6$ 0.004 
SiO 0.071 

changes in the Si$_x$ by 36
furthermore, by tracking the Si–C bond signal upon exposure
the higher reactivity of Si NW atop sites (that is, all sites
of methyl functionalities, as compared to 2D CH$_3$–Si(100) surfaces, they showed ca. 2-fold higher oxidation than the CH$_3$–Si NWs.

The lower oxidation on CH$_3$–Si NWs, as compared to the 2D CH$_3$–Si surfaces, can be attributed to stronger Si–C bonds, due to the higher cohesive energy of the Si NW surfaces. This argument is supported by the (~0.11 eV) higher Si–C bond energy observed in the CH$_3$–Si NW (284.22 ± 0.02 eV) case, as compared to the 2D CH$_3$–Si ones (284.11 ± 0.02 eV), and, furthermore, by tracking the Si–C bond signal upon exposure to ambient conditions. The observation of ~0.11 ± 0.02 eV higher binding energy for a CH$_3$–Si NW, compared with equivalent 2D CH$_3$–Si(100) surfaces, could further support the higher reactivity of Si NW atop sites (that is, all sites (or atoms) that are located at the outer layer of the substrate’s surface). Indeed, the CH$_3$–Si NW results showed 22% decrease in the Si–C bond signal after 20 days, at the time the 2D CH$_3$–Si(100) samples showed >34% decrease of the same signal (Fig. 2b). These findings are in good agreement with those reported by Lee and co-workers on stronger H-terminations in Si NWs, as compared with 2D Si surfaces (cf. also ref. 22 and 23). These studies suggested that the robustness of the Si NW hydride is a consequence of bending stress, where re-bonding of dangling bonds at the edge of two adjoining facets of a Si NW takes place.5,22,23

To understand the relation between the strength of the Si–C bond and the oxidation resistance, ToF SIMS fragments of CH$_3$–Si NWs and 2D CH$_3$–Si(100) surfaces were collected after different exposure periods to oxidizing agents. Table 1 presents selected ToF SIMS spectrum peaks of CH$_3$–Si NW before and after 4 days exposure to pure (99.9999% purity) O$_2$(20%)–N$_2$(80%) environment containing 10–15% RH. As shown in Table 1, after 4 days of oxidation the Si$_x$ signal (where x = 1.2) of Si NW samples increased by 70–95 ± 10% while the concentration of Si–C and Si–CH$_3$ bonds decreased by 36 ± 2% and 15 ± 2%, respectively. The higher (absolute) changes in the Si$_x$ signal suggest that the molecule-free Si–Si bonds are more susceptible to breakage upon interaction with O$_2$ and/or H$_2$O molecules, than the Si–C bonds. The higher change in the Si–C (36 ± 2%) signal than that in Si–CH$_3$ (15 ± 2%) indicates that the Si–C bond is more easy to oxidise than the Si–Si bond directly beneath the –CH$_3$ group. These results indicate that the Si–Si back-bonds are broken first to form Si–O–Si back-bonds. After all of the Si–Si back-bonds are oxidized, the oxidizing species will start attacking the Si–C bonds. For 2D CH$_3$–Si(100) surfaces, the Si$_x$O signal (where x = 1.2) increased by 86–120 ± 10% while the concentration of Si–C and Si–CH$_3$ bonds decreased by 47 ± 2% and 21 ± 2%, respectively, after 4 days of exposure to the oxidizing atmosphere.

Comparing the relative changes obtained for 2D CH$_3$–Si(100) surfaces and CH$_3$–Si NWs calls for two main conclusions. The first is that CH$_3$–Si NWs are more stable than 2D CH$_3$–Si(100) surfaces, in consistency with the XPS observation reported earlier in this paper. The second is that the oxidation mechanism of 50 ± 10 nm (in diameter) CH$_3$–Si NWs is similar to that of 2D CH$_3$–Si(100) surfaces.

IV. Summary and conclusions

In summary, Si NW surfaces have been terminated with methyl groups, which sterically allows >85% Si–C terminations of atop sites. The results indicate that Si–C bonds on Si NWs are far stronger than similar bonds on 2D Si(100) and 2D Si(111) surfaces, in consistency with the XPS observation reported earlier in this paper. The strong covalent Si–C bond offers the possibility of functionalising Si NWs without affecting the conductance of the near-gap channels.1 In particular, this offers quasiballistic transport within several subbands below and above the Si NWs band gap.1 These effects are expected to become more significant as Si NWs become smaller in diameter, because the properties of the semiconductor surface begin to dominate the properties of the device as a whole, and, also, upon water exclusion at the nanometer scale.24

Acknowledgements

The authors acknowledge the Marie Curie Excellence Grant of the FP6, the BSF, and the RBNI for financial support. H.H. holds the Horev Chair for the Leaders in Science and Technology. S.C. acknowledges financial support by the Deutsche Forschungsgemeinschaft (DFG) under contract number CH159/1.

Notes and references

It is reasonable to assume that the supporting Si substrates of the Si NW samples have minor (or no) contribution to the obtained XPS and ToF SIMS signals. This argument was supported via a series of complementary experiments in which ToF SIMS depth profiles were obtained for fresh CH$_3$–Si NW samples. In these experiments (data not shown), sputtering up to 3–4 μm exhibited similar ToF SIMS values to those obtained for non-sputtered CH$_3$–Si NW samples (cf. Table 1). In contrast, sputtering 4–5 μm of the Si NWs layer (i.e., the estimated depth at which the signal from the 2D Si substrate starts to be dominant) exhibited values that are similar to the 2D CH$_3$–Si(100) surfaces (cf. Table 1).