Preserved Conductance in Covalently Functionalized Silicon Nanowires

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We study by means of *ab initio* simulations the Landauer conductance of covalently functionalized silicon nanowires. We show that in the case of alkyl side chains, the most common linkers, silicon nanowires remain quasiballistic over a large energy range. More reactive side molecules, such as alkenyl or phenyl conjugated radicals, amino and alkoxide groups, are less favorable as they induce resonant backscattering in the valence bands mainly. Such results provide strong support for the use of selectively functionalized nanowires in (opto)electronic devices and molecular sensors.

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Chemical functionalization offers an important means to manipulate and tailor the properties of carbon nanotubes (CNTs) and nanowires (NWs). From CNTs separation, selection, and self-assembling [1], to the modification of the electronic properties of the conducting channel, or of the contact resistance, in a CNT or NW-based field-effect transistor (FET), a large body of work devoted to understanding the effect of functionalization has received, at least at the experimental level, considerable attention in the past few years. In particular, the use of functionalized semiconducting NWs in rectifying optical and chemical or biological molecular sensor devices has been explored recently by several groups [2–10].

An important limitation related to the functionalization of CNTs is that the interaction of the side molecules with the sp^2 graphitic network may considerably reduce the mobility of the charge carriers. This is particularly true in the case of covalent functionalization whenever the conjugated π network is strongly perturbed [11]. In the case of nanowires, doping of the canal significantly reduces the conductance as well [12–14]. Other indications from theoretical work suggest further that surface roughness may strongly affect the conductance of narrow channels [15]. However, concerning the effect of functionalization on transport properties, there is no theoretical study available to date, despite the large number of experimental realizations.

In the present Letter, we show that the covalent functionalization of silicon nanowires (SiNWs) by alkyl chains, the most standard linkers, hardly affect the conductance of the near-gap channels. The absence of backscattering is particularly impressive in the conduction bands where the transport remains ballistic within several subbands. Other possible side chains, including alkenyl or phenyl conjugated radicals, alkoxide or amino groups, are also explored. For such systems, the conductance of the conduction bands remains unaffected, but resonant backscattering reappears in the valence bands. Our results suggest that SiNWs functionalized with alkyl spacers, or possibly other side groups in the case of n-type doped wires, will remain ballistic over a large bias or gate voltage range, enabling an efficient use of functionalized wires in devices.

Conductance calculations have been performed using a density functional based (DFT) *ab initio* implementation of Landauer formalism using the TABLIER code [13]. We start with a DFT study [16] of the equilibrium structure and electronic properties of our functionalized wire using long unit cells (13 periods of the bare wire primitive cell, amounting to 520 atoms) with one functional group per supercell. The ground state calculations are performed with the SIESTA package [17]. We adopt a single-zeta plus polarization basis for Si atoms, while a double zeta basis was chosen for first-row elements. The finite range of the basis orbitals yields a block-tridiagonal Hamiltonian. This form allows an efficient recursive evaluation [18] of the left and right electrode surface Green's function, of the related self-energies $\hat{\Sigma}_{L(R)}$ electrodes (semi-infinite pristine SiNWs here), and of the central device Green's function $\hat{G}_D$. The transmission can be calculated in a standard way [19]: $T(\epsilon) = \mathrm{Tr}[\hat{\Gamma}_L \hat{G}_D^a \hat{\Gamma}_R \hat{G}_D^r]$, with $\hat{\Gamma}_{L(R)} = \mathrm{Im}[\hat{\Sigma}_{L(R)}]$.

The literature on the covalent functionalization of flat silicon surfaces [20] and SiNWs [2,3,5,7,10] point out a few important classes of reactions. The most important routes for covalent functionalization are the hydrosilylation of H-terminated Si surfaces or the alkylation of halogen-terminated surfaces, leading to the formation of Si-C bonds connecting the silicon surface atoms to saturated alkyl radicals. Such chains are called spacers or linkers. They are usually terminated on the other end by an active chemical group (photoactive function, molecular

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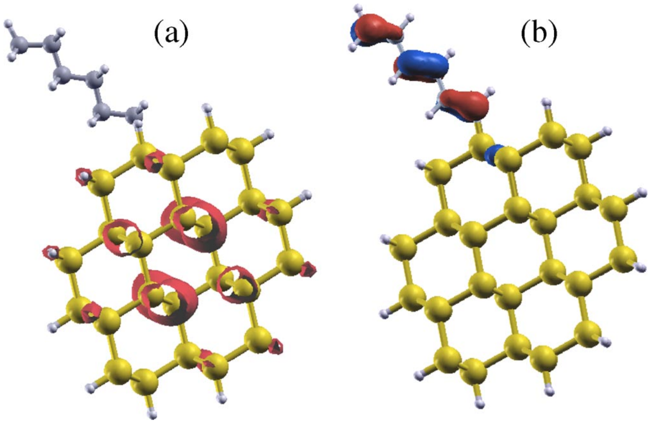

FIG. 1 (color online). (a) Symbolic representation of the hexane radical (hexyl) functionalized SiNW. A plot of the integrated charge density for states with energy in the range of Fig. 2 is provided (contour at 10% of the maximum density value). (b) Symbolic representation of the alkenyl ($n = 6$) functionalized wire with a plot of the side chain "HOMO" level [see peak at ~ -0.8 eV in Fig. 3(c)].

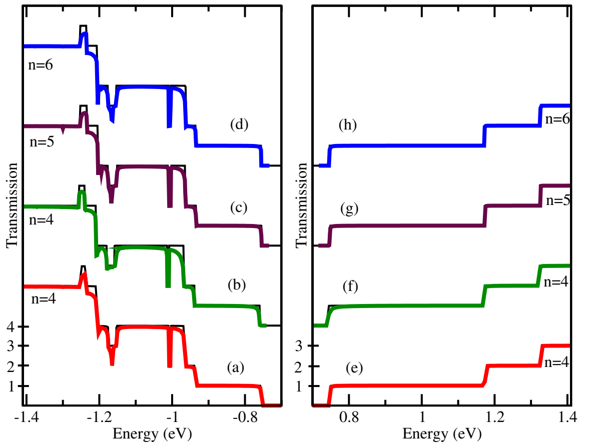

FIG. 2 (color online). Transmission for alkyl-functionalized SiNWs. The index (n) indicates the number of carbon atoms in the alkyl chain. In (a) and (b), the ($n = 4$) butyl chain is grafted on the {111} and {100} facets of the wire.

recognition receptor, etc.), which is thus spatially separated from the SiNWs. Similar reactions can lead to the grafting of carbon-based π-conjugated oligomers such as alkenyl chains or phenyl rings. Other chemical bonds can be formed, such as Si-O through the alkoxylation of hydrogen or halogen-terminated surfaces or Si-N through the reaction of an amino group on a chlorine-terminated surface [20].

We study a prototype hydrogen-passivated $\langle 110 \rangle$ SiNW with a diameter of 13 Å [21]. Since alkyl chains are the most common linkers used to functionalize H-terminated Si wires or surfaces, we first replace one hydrogen by an $R = -(\mathrm{CH}_2)_n$-H alkyl radical, with n the number of carbon atoms in the lateral chain (see Fig. 1).

The conductance of alkyl-functionalized nanowires is presented in Figs. 2(a)–2(d) and Figs. 2(e)–2(h) for the valence and conduction bands, respectively. In the case of a butyl ($n = 4$) lateral chain, both functionalization of the {111} [Figs. 2(a) and 2(e)] and {100} facets [Figs. 2(b) and 2(f)] are studied [22]. Black lines indicate the standard plateau of the perfect NW conductance (in units of $G_0 = 2e^2/h$) while thick color lines indicate the effect of grafting one molecule. As clearly evidenced in Figs. 2(e)–2(h), the functionalization has absolutely no effect on the transmission in the conduction bands over a large energy range. A similar conclusion applies to the first plateau below the Fermi level. While some reduction in transmission can be observed at lower energy (around ~ -1.17 eV), the effect is rather small, especially compared to CNT functionalization [11] or NW core doping [12] where a drop of 50% to 100% of the conductance could be observed at resonant energies [23].

In order to understand the present results, we plot in Fig. 3(b) the functionalized SiNWs density of states (eDOS) projected onto the side chains' orbitals in the case of an hexyl radical ($n = 6$) that we compare in Fig. 3(a) to the total eDOS of the corresponding isolated hexane chain [24]. The band gap of the SiNWs is indicated by the two vertical thick lines. Clearly, the highest-occupied (HOMO) and the lowest unoccupied molecular level of the grafted alkyl chains fall well below and above the SiNWs band gap, respectively. Integrating the charge density over the energy range covered by the conductance plot in Fig. 2, we find hardly any contribution from the side chain [Fig. 1(a)]. As a result, weak hybridization and no

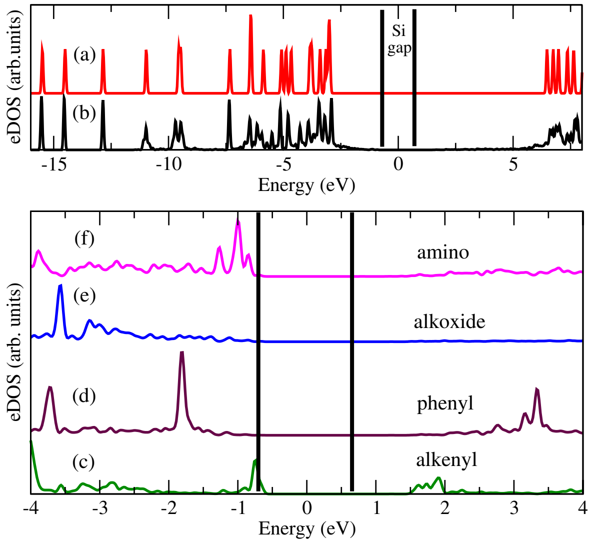

FIG. 3 (color online). (a) eDOS for the hexane ($n = 6$) isolated molecule. (b)–(f) Local density of states projected on the side chains' orbitals: (b) hexyl, (c) alkenyl, (d) phenyl, (e) alkoxide, and (f) amino radicals. The two thick vertical lines indicate the SiNWs' band gap. Note that the two graphs are not to scale. eDOS in the lower panel have been normalized to the number of valence electrons in the side chain for the sake of comparison.

resonant backscattering are expected to take place in the functionalized wire. Identical results apply to the various chains studied above [25].

The large decoupling in energy between alkyl molecular levels and the SiNWs states around the band gap ensures that no resonant backscattering is to be expected. Further, the analysis of the scattering potential induced by the side chain, defined by the variations of the total electronic potential inside the SiNW upon grafting of the alkyl group, is found to be extremely shallow. The on-site Si-s and Si-p self-consistent Hamiltonian matrix elements show indeed a maximum variation of ~0.1 eV for the Si atom directly connected to the carbon chain, while further away in the SiNW, the on-site energies do not differ by more than 0.01 eV with respect to equivalent Si atoms located far away from the akyl group along the nanowire. Such values indicate, in particular, that the Si-C and Si-H bonds have similar polarization, resulting in little additional charge transfer upon functionalization. The very shallow character of the scattering potential can be compared, e.g., to boron or phosphorus doping for which the substitutional impurity builds a potential well of the order of a few eVs [12]. As a result, nonresonant scattering is also weak in alkyl-functionalized SiNWs [26]. Since the mean-free path scales quadratically with the scattering potential strength (through the Fermi golden rule), very long wires need to be considered to witness drops of conductance similar to that induced by dopants [14].

This quasiballistic behavior of alkyl-functionalized SiNW is not uniquely related to the chemical inertness of the alkane molecules. In the case of the CNTs, it has been shown that engaging a carbon π orbital in a covalent bond, independently of the chemical nature of the grafted group, significantly reduces the conductance, an effect that can easily be mimicked by simply removing the π orbital from a given carbon atom in a simple $\pi - \pi^*$ model [11]. In the case of the SiNWs, the functionalized Si atom just remains sp^3 hybridized. Further, while charge carriers are confined to the "surface" in the case of CNTs, they are delocalized over the whole Si core in the nanowire case. Our conclusions should therefore apply even more strongly in the limit of larger wires.

Functionalizing SiNWs without affecting significantly their conductivity is an important result as it suggests that heavily functionalized SiNWs can be used in transport devices such as FETs. Contrary to nanotubes where most covalent grafting routes severely degrade the carriers' mobility, the conductance in SiNWs is expected to remain large even in the limit of a substantial number of grafted linker molecules. The possibility of integrating SiNWs' channels with a large number of active side chains per unit surface should significantly enhance the sensitivity of SiNW-based sensors or photoactivated devices. Together with selectivity, this is certainly a central issue conditioning the future of such devices.

Another important consequence of the present findings is that the mechanisms involved in SiNW-based molecular sensors cannot be attributed to a change of carrier mobility upon binding of the side chains. This provides weight to a scenario where adsorbed molecules act as "chemical gates" by transferring charge to the SiNW substrate [6,7], an effect that changes the current either through the opening of new conduction channels and/or tuning of the contact Schottky barrier by a change in the Fermi level position and work function.

We finally extend this study to less common functional groups. We provide in Fig. 4 the conductance associated with our prototype SiNW functionalized with π-conjugated -(CH)$_n$-H alkenyl chains, with $n = 4$ [Figs. 4(a) and 4(g)] and $n = 6$ [Figs. 4(b) and 4(h)] carbon atoms, a phenyl radical (C_6H_5) [Figs. 4(c) and 4(i)], an -OC_3H_7 (alcohol radical) alkoxide group [Figs. 4(d) and 4(j)], and an amino -NH_2 group [Figs. 4(e) and 4(k)]. Again, there is no reduction of the conductance in the first unoccupied plateaux. However, in the case of the valence bands, the physics of resonant backscattering reappears, in particular, in the case of the conjugated alkenyl [Fig. 4(a)] and amino [Fig. 4(e)] groups with a drop to zero of the conductance at specific energies (see stars on graph).

This effect can again be clearly seen on the local density of states provided in Figs. 3(c)–3(f). In the case of the alkenyl group [green lines in Figs. 3(c) and 4(b)], the molecular HOMO level [Fig. 1(b)] lays just below the top of the valence bands, explaining the drop of conduc-

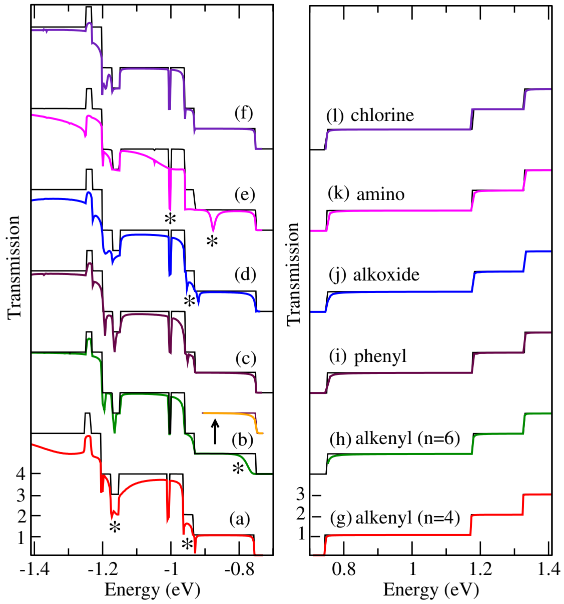

FIG. 4 (color online). Transmission for SiNWs functionalized with conjugated (a),(g) -$(CH)_4$-H, (b),(h) -$(CH)_6$-H alkenyl radicals, (c),(i) a phenyl group, (d),(j) a -OC_3H_7 alkoxide group, (e),(k) an amino group, and (f),(l) a residual chlorine atom. The color code corresponds to that of Fig. 3 (lower panel). The stars indicate some typical resonant backscattering drop of conductance. The effect of passivating the Si-connected C atom of the -$(CH)_6$-H alkenyl group by a hydrogen is indicated (see arrow).

tance in Fig. 4(b) in this energy range (see star) [27]. Similarly, the states present below the top of the valence bands in the amino case (pink line in Fig. 3(f)] can explain the large drop of conductance observed just below the band gap [pink line in Fig. 4(e)]. However, in all cases, no molecular derived levels can be seen above the Fermi level for several subbands, the alkenyl case being here the less favorable. Interestingly, residual chlorine atoms, which are expected to be left in the case of functionalization by alkylation of halogen-terminated Si surfaces, do not induce significant backscattering as shown in Figs. 4(f) and 4(l).

In conclusion, we have shown that the functionalization by alkyl chains, the most standard linkers, hardly affect the conductivity of SiNWs. In particular, the transport remains quasiballistic within several subbands below and above the SiNWs band gap. Functionalization by more active side groups, such as alkenyl, phenyl, amino, or alkoxide groups, is shown to be less favorable as resonant backscattering reappears in the valence bands, even though in the conduction bands the conductance is hardly affected. The present results are a strong indication that selective functionalization is a viable route for tailoring the properties of SiNWs in (opto)electronic devices and chemical or biological sensors.

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[23] The drop of transmission at ~ -1.01 eV is present in the perfect wire and is related to a small gap opening between two bands (forbidden crossing).
[24] The isolated alkane and grafted alkyl-chain *e*DOS have been aligned on the lowest occupied level at ~ -15.5 eV (well below the Si occupied bands).
[25] The band gap of the infinite alkane chains is $E_g = 8.8$ eV (DFT-LDA value). As such, the present results generalize to longer chains not studied here explicitly. We note that the "Kohn-Sham" DFT band gaps are known to be underestimated ($\sim$1.5 eV DFT-LDA value here). It has been shown in Ref. [21] that in this size range, the SiNW DFT band gap should be corrected by no more than 1–2 eVs. As such, the alkane chains' band gaps still remain much larger, accounting further for the fact that their band gap is underestimated as well within DFT.
[26] This shallow scattering potential is found to assume positive values in the SiNW core, explaining that mostly holes (valence channels) are slightly affected.
[27] The saturation of the Si-bonded carbon atom by an additional hydrogen, isolating the resonant chain from the SiNW, is enough to restore the ballistic behavior at the top of the valence bands [see arrow in Fig. 4(b)], illustrating the role of saturated linkers.