Large electromechanical response in silicon nanowires predicted from first-principles electronic structure calculations

R. Rurali,[1] X. Cartoixà,[1] and D. S. Galvão[2]
[1]*Departament d'Enginyeria Electrònica, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain*
[2]*Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas, Caixa Postal 6165, CEP 13083-970, Campinas-São Paulo, Brazil*

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We study by means of first-principles electronic structure calculations the electromechanical response, i.e., the structural modifications upon charge injection, of ⟨100⟩ silicon nanowires. We show that, at variance with sp^2 carbon nanostructures, the response is remarkably linear, discriminates between injected charge of different signs, and is up to one order of magnitude larger than in carbon nanotubes.

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Silicon nanowires (SiNWs) are among the most promising building blocks for future nanoelectronics applications, because they can work either as the active region of the device or simply as interconnects.[1–3] Furthermore, differently from their bulk counterpart, wires grown along most of the crystallographic orientations have a direct band gap,[3–5] thus envisaging their use as optically active material for photonic applications.[6–9]

Recently, there has been a growing interest in the use of SiNWs as chemical sensors.[1,10,11] Additionally, the recent report of a giant piezoresistance effect[12] suggests that SiNWs are also suited for the design of highly sensitive mechanical sensors. Less attention has been devoted to the use of SiNWs as actuators, i.e., devices capable of transforming an electrical input into a different kind of signal, most typically a mechanical deformation. In this Brief Report we show that SiNWs belong to a different class of efficient electromechanical actuators, capable of elongating or contracting in response to charge injection.

Carbon sp^2 structures such as carbon nanotubes (CNTs) and carbon nanoscrolls (CNSs) have attracted great interest for their potential use as electromechanical actuators. The main reason is that in the high-injection regime the Coulomb repulsion—between opposite sides of the same layer (like in single-walled CNTs) or of different layers (like in CNSs or multiwalled CNTs)—is expected to dominate and to originate a larger response.[13–15] In CNTs, however, the response is rather moderate, amounting only to 0.2%–0.3%,[13] while CNSs exhibit a notable improvement regarding the radial response, reaching values of around 2%–2.5%.[16,17] Nonetheless, the major drawback of systems where the electromechanical actuation is driven by Coulomb repulsion is the fact that it is not possible to discriminate between injected charges of different signs, as in both cases the system tends to expand.

SiNWs, on the other hand, are not layered structures and thus the electromechanical response will not depend on Coulomb repulsion and will rely on a purely *electronic* actuation: in a simple molecule this is understood in terms of the bond order, i.e., the difference between electrons in bonding states and electrons in antibonding states. According to this simple picture, either forcing the population of an antibonding state or removing an electron from a bonding state results in a repulsion of the nuclei involved and thus in an extension of the bond. This simple model, however, already breaks down with slightly more complex molecular systems, e.g., *trans*-stilbene,[18] where the equilibrium geometry of the charged molecule is determined by an elongation and/or compression competition among different C-C bonds. The situation is further complicated in CNT[14,15] and graphyne[19] nanotubes, where the electromechanical response is highly nontrivial and the same charge injection can lead to expansion or contraction depending on the chirality.

We have performed density-functional theory calculations with the SIESTA package,[20] using norm-conserving pseudopotentials.[21] The one-electron wave function has been represented with a single-ζ polarized basis set, optimized following Anglada *et al.*[22] We have verified that this basis set reproduces structural properties of SiNWs accurately while keeping the computational complexity at a manageable size. We have used the generalized gradient approximation (GGA) due to Perdew, *et al.*[23] for the exchange-correlation functional. We have considered SiNWs of different characteristic thicknesses—10.5, 15.0, and 18.5 Å—where the surface dangling bonds have been terminated with hydrogens. Their respective unit cells contained 41, 65, and 93 atoms, while the lateral size was chosen to allow a buffer vacuum separation of ~20 Å. We have injected up to $\pm 0.06|e|$/at., relaxing both the atomic positions—until all the forces were reduced below 0.04 eV/Å—and the lattice vectors. A uniform neutralizing background was used to prevent the electrostatic energy from diverging, as customarily done in charged systems within periodic boundary conditions.[24,25] The Brillouin zone has been sampled with a converged grid of up to 12 **k** points along the wire growth axis according to the Monkhorst-Pack scheme.[26]

Figure 1, the main result of this work, shows the relative variation of the axial lattice parameter vs the injected charge per atom for the different wires studied. There are several remarkable features of the electromechanical response displayed, especially if compared to the known data of sp^2 carbon systems:[13,14] (a) the response is no longer monopolar, i.e., the wires extend upon electron injection and contract upon electron removal; (b) it is fairly linear over a wide range of injected charges; and (c) it is one order of magnitude more intense that in CNTs, and of the same order, though still larger, than the radial response of CNSs.[16]

A crucial characteristic of an electromechanical actuator

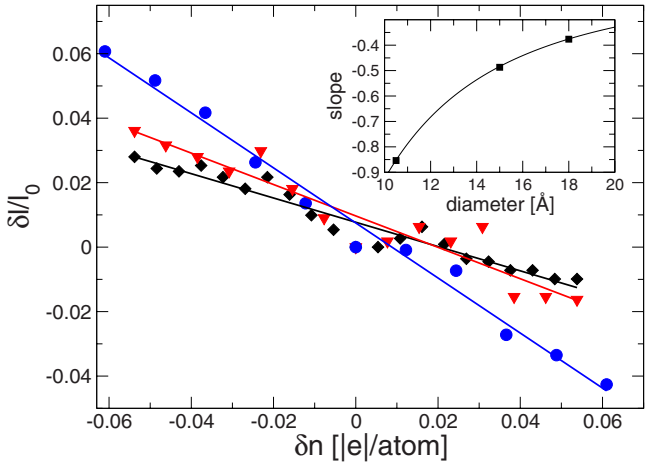

FIG. 1. (Color online) Relative variation of the lattice parameter l vs injected charge for ⟨100⟩ SiNWs of 10.5 (blue circles), 15.0 (red triangles), and 18.0 Å (black diamonds). Inset: electromechanical response of the wires as a function of their undistorted diameter. The line is a $1/d^2$ fit, d being the diameter, drawn to guide the eyes.

is the possibility to reliably induce a certain mechanical response upon charge injection. Tubular carbon nanostructures either exhibit a poor sensitivity or the response is related to the charge injection through a complicated relation which generally does not distinguish between electrons and holes. A linear response like in Fig. 1 provides a straightforward control on the wire which now can expand as well as contract, depending on the sign of the injected charge. Given the linearity of the response to charge injection, the electromechanical sensitivity is naturally defined as the slope of the $\delta l/l_0 \delta n$ fits in Fig. 1. It is interesting to note that it decreases as the wire grows larger. The diameter dependence is illustrated in the figure's inset.

A close look at Fig. 1 reveals that in the low charge injection regime ($-0.015 < \delta n < 0.015$) SiNWs expand for both signs of the charge, as electrons are either removed from bonding states or added into antibonding states. On the other hand, in the high-injection regime the overall geometry is determined by a subtle interplay between the energy of the neutral, distorted system, and the electronic energy of the added charges, which can drive the system to a noticeable deformation (see Fig. 2). A method proposed by Gartstein *et al.*[15] maps how changes in bond lengths in a nanostructure reflect in the elastic energy and, through a simple tight-binding Hamiltonian, the band gap and band curvature. After a minimization of the total energy with respect to the bond lengths, the equilibrium geometry for a given charge injection can be obtained. They performed their analysis for carbon nanotubes CNTs, showing that bonds with different orientations can display different bonding and/or antibonding characters, driving the system to a spontaneous breaking of the symmetry. This class of rich behavior, also well known for conductive polymers,[27] is highly structure dependent and cannot be captured by simple electrostatic and/or bond order arguments. An analogous analysis for our SiNWs is out of the scope of this work, due to the increased number of non-

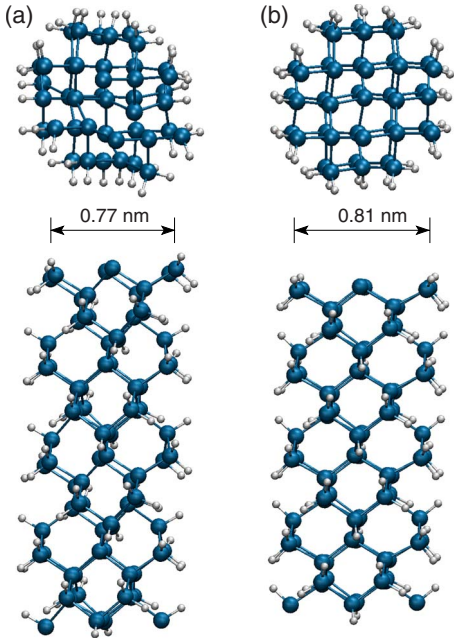

FIG. 2. (Color online) Top and side views of the thinnest SiNW studied with an injected charge δn of (a) −0.06 and (b) $+0.06|e|$/at. An estimation of the wire diameter shows that an axial elongation (contraction) is associated with a radial contraction (elongation). Due to the strong asymmetry, the wire diameter has been averaged at four different Si planes and without taking into account the hydrogens.

equivalent atoms in the nanowire unit cell with respect to that of CNTs. Being not hollow, the nanowires will be much less sensitive to Coulomb-related effects, and the linearity of the response in the studied charge injection range is not masked. Since the system now becomes metallic, e.g., the Fermi level crosses the conduction and/or valence band, the excess charge will accumulate at the wire surface, as shown in Fig. 3, where the variation of the atomic charge with re-

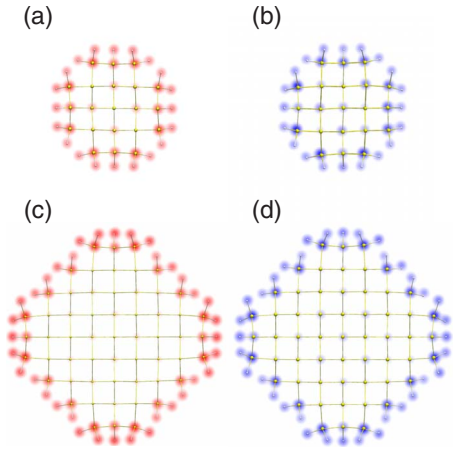

FIG. 3. (Color online) Variation of the Mulliken population with respect to the neutral wire for the 10.5 and 18.0 Å SiNWs for −0.02 [(a) and (c)] and $+0.02|e|$/at. [(b) and (d)]. In the charged systems electrons are preferentially added and/or removed at the surface atoms.

spect to the neutral wire is plotted. Integration of the electronic density of states in the conduction band indicates that the levels of charge injection here studied can be achievable by the application of a few volts of bias over the nanowire. These results indicate that this effect is more widespread than previously thought and it might be common to a wider class of nanostructures.

In conclusion, we have shown that ⟨100⟩ SiNWs exhibit a large and linear electromechanical response. The amount of the response is attributed to the lower strength of the Si-Si bond with respect to the C-C bond. On the other hand, the linearity appears to be an effect intertwined with the geometry of sp^3 systems. Finally, the bipolarity of the response, i.e., the ability of discriminating charge of different signs, results from the absence of a significant Coulomb component of the response, which dominates the behavior in layered carbon nanostructures. We hope that the present work will stimulate further experimental works to test our predictions.

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