Radial breathing mode in silicon nanowires: An *ab initio* study

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(Received 12 February 2010; revised manuscript received 14 April 2010; published 25 May 2010)

We study by means of first-principles calculations the phonon spectrum of silicon nanowires oriented along the ⟨110⟩ direction with a diameter ranging from 1.0 to 2.4 nm. We analyze in particular the evolution of the radial breathing mode frequency as a mean to calibrate experimentally the diameter through Raman analysis. Remarkably, the results of elastic theory analysis are very reliable even in the limit of ultrathin wires with significant deviations from the cylindrical shape.

DOI: 10.1103/PhysRevB.81.193410 PACS number(s): 72.25.−b, 72.10.Fk, 73.63.Fg

The compatibility of silicon nanowires (SiNWs) with silicon based technology is certainly an important factor explaining the large amount of work devoted to the synthesis and characterization[1] of these semiconducting 1D systems with promising applications in electronic,[2] optoelectronic or photovoltaic[3] devices, molecular recognition, and sensing[4] or thermoelectricity.[5]

An important tool for the characterization of wires is provided by the analysis of phonon modes. The wealthiness of information drawn from such measurements has been largely exemplified in the case of carbon nanotubes with a particular emphasis on the study of the diameter dependent Raman-active radial breathing mode.[6] While much *ab initio* simulations have addressed topics related to structural, electronic, or transport properties, studies of vibrational modes with first-principle approaches remain limited to a recent study of the phonon band structure of SiNWs,[7] complementing previous analysis based on empirical potential calculations of the optical modes[8] and Raman active modes.[9]

In the present Brief Report, we study by means of *ab initio* calculations the radial breathing mode of small free-standing hydrogen-passivated SiNWs grown along the ⟨110⟩ direction. The diameter of the studied SiNWs ranges from 1.0 to 2.4 nm. We provide in particular a scaling law as a function of the NWs radius for the radial breathing mode (RBM) frequency and compare the associated radial displacements with elastic theory analysis.

Our calculations are performed within the density-functional theory using pseudopotentials and the PBE exchange-correlation functional.[10] For wires up to 62 atoms per cell, we performed plane-wave-based calculations with the PWSCF package[11] with a kinetic energy cutoff of 25 Ry using ultrasoft pseudopotentials. These calculations were repeated using the SIESTA code[12] with a double-zeta polarized basis for Si and double-zeta basis for H. The reduced size of the localized basis allowed further to study a larger wire comprising 144 atoms per cell with a diameter of 2.4 nm. The sampling of the one-dimensional (1D) Brillouin zone (BZ) was performed with 16 k points. Cell sizes along the wire axis and atomic positions were relaxed with a 0.1 eV/Å threshold criteria. A minimal distance of 10 Å was kept between periodic image wires in the transverse direction.

We plot in Figs. 1(a)–1(d) the symbolic representation of the wires studied in the present work. Since the wires are not perfectly cylindrical, the diameter is defined following Niquet and co-workers in Ref. 13 as the diameter of the cylinder of length ℓ with a volume equal to $\Omega = N_{sc} a^3/8$, where N_{sc} and ℓ are the SiNW unit cell number of atoms and length, and a the bulk Si lattice parameter. Surface dangling bonds are passivated by hydrogen atoms.

Phonon modes at zone center were obtained by diagonalizing the dynamical matrix.[14] An analysis of the calculated phonon eigenvectors at zone center easily allows to recognize the RBM mode for each wire. We plot in Fig. 2(a) the evolution of the RBM frequencies as a function of diameter. Both plane wave and localized-basis calculations yield very similar results, indicating the reliability of the "less con-

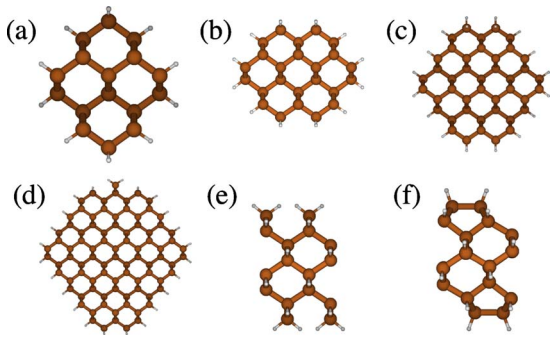

FIG. 1. (Color online) Symbolic representation of the wires studied in this work with diameters of (a) 1.03, (b) 1.26, (c) 1.67, and (d) 2.39 nm. In (e) and (f), side view of the 1.03 nm diameter wire with unreconstructed and reconstructed (period doubled) surface, respectively.

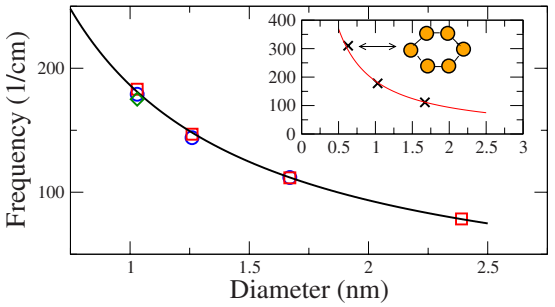

FIG. 2. (Color online) Evolution of the frequency as a function of diameter for the RBM mode. The SIESTA results are in red (open squares) and the PWSCF one in blue (open circles). The full line is the $\omega_{\mathrm{RBM}}(d)$ fit (see text). The green diamond corresponds to the reconstructed wire in Fig. 2(f) (PWSCF). Inset: results of Ref. 7 (crosses) compared to our fit in full line. The smallest wire cross section is drawn symbolically (no hydrogen).

verged" local basis approach. The frequency evolution can be nicely fit by an inverse power law,

$$\omega_{\mathrm{RBM}}(d) = \frac{1}{Ad+B} \quad \text{with} \quad \begin{cases} A = 5{,}3 \times 10^{-3} \ \text{cm/nm} \\ B = 4{,}0 \times 10^{-5} \ \text{cm} \end{cases}$$

The small value of the B/A ratio indicates that for wires a few nm in diameter, a $1/d$ law fits very well the RBM frequency as predicted by elastic theory analysis.[9] Such a good agreement is quite striking given (a) the very small size and (b) the severe deviation from the ideal cylindrical shape of our wires. As a matter of fact, looking at the effect of a period-doubling surface reconstruction for our smallest wire [compare Figs. 1(e) and 1(f)], we observe that the RBM frequency is hardly affected (see green diamond Fig. 2), indicating again that the RBM frequency is very robust against details of the atomic structure. Our functional form $\omega_{\mathrm{RBM}}(d)$ fits further very well the results of Ref. 7 (see inset Fig. 2) using the same diameter definition. Quite surprisingly, in the ultrathin limit of the "two-atoms across" wire treated in Ref. 7 (see inset drawing), which we excluded from the set of data points fitted, the agreement with the elastic theory law is still very good.

In the well-known case of the nanotubes, for which a large bulk of Raman studies of the RBM mode have been performed over the years, the deviations from elastic theory in the small diameter limit were also observed to be rather small despite the strong effects of curvature on some of the nanotubes properties.[15,16] Such conclusions apply however to pristine tubes since, e.g., coating of tubes by weakly bound (physisorbed) molecules was shown to quench the RBM mode.[17] In the present case of SiNWs, we can expect our results to be significantly altered upon functionalization by large molecules or coating by an all-around insulating gate.

In the larger size limit, for a wire of $d=5$ nm, the fit yields a frequency of 38 cm^{-1}, in remarkable agreement with the 40 cm^{-1} value obtained by Thonhauser and Mahan for ⟨111⟩-oriented wires using a semiempirical Stillinger-Weber potential.[9] Again, such good agreement can be interpreted as the signature of the reliability of isotropic elastic theory analysis. The present results strongly suggest that

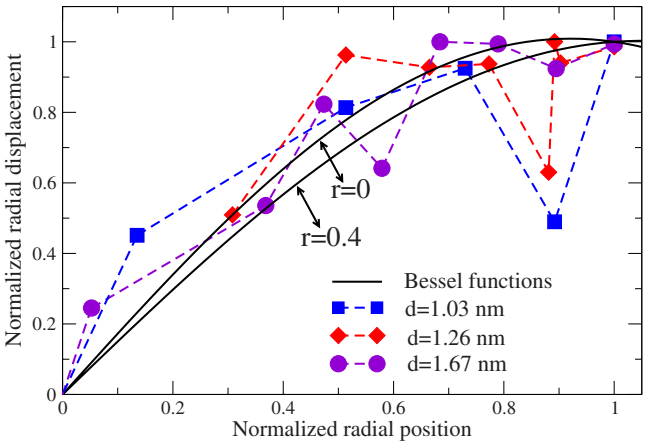

FIG. 3. (Color online) Normalized radial displacement of Si atoms for the RBM mode. Changing symbols (colors) indicate wires with varying diameter. The two full lines are the results of isotropic elastic theory with the elastic constants related r parameter spanning the range of acceptable values (see text).

the RBM analysis is an excellent tool, even in the 'ultimate" size limit ($d \geq 0.5$ nm), to obtain information on the nanowires mean diameter. While SiNWs can be grown in many directions, the success of the isotropic elastic theory analysis, and the good agreement between our fit of ⟨110⟩ wires data with the frequency of the 5 nm thick ⟨111⟩ wire, suggest that the RBM frequency should mainly depend on the diameter, but only weakly on the crystallographic direction of wire growth.

We finally analyze the radial displacement associated with the RBM modes (see Fig. 3). To represent all wires on the same graph, the radial position of the atoms is normalized by the wire radius and the radial displacement is divided by the maximal radial displacement. The results are compared to standard elasticity theory[9] and we plot in full line the normalized elastic displacement $J_1(\alpha r/R)/J_1(\alpha)$ where J_1 is the first-order Bessel function of the first kind. The coefficient α such that $\alpha^2 = 8(1-r)/(2-r)$ is related to the shear modulus μ and the first Lamé parameter λ through $r = \mu/(\lambda+2\mu)$. Taking $0 < r < 0.4$ as suggested in Ref. 9, one obtains the two limiting full line curves in Fig. 3. Even though significant deviations exist as compared to any smooth continuous curve that would yield elastic theory analysis (depending on the r value), the deviations start to be reasonable even for the rather small $d=1.67$ nm diameter wire. The better agreement between *ab initio* calculations and elastic theory analysis for phonon frequencies as compared to individual atom displacements can be justify by the fact that the energy change upon phonon distortion is averaging over all atomic displacements. Similar conclusions can be drawn in, e.g., the analysis of the strain energy and atomic displacements around a dislocation in an extended solid.[18]

In conclusion, we have studied the zone-center phonon modes of small SiNWs with diameter ranging from 1.0 to 2.4 nm. We find that the radial breathing mode frequencies follows quite robustly the elastic theory analysis, in spite of the

variations from cylindrical shapes in the small diameter limit, and rather independently of the computational technique adopted, provided presumably that the elastic constants are well reproduced. This suggests that RBM measurements are a very reliable tool to identify nanowire diameters down to the ultrathin limit.[19]

The calculations have been performed at the French CNRS National Computing Center (IDRIS, Orsay) and the CIMENT supercomputing center in Grenoble. This work was partly supported by the French National Agency for Research (ANR) through the contract QuantaMonde Grant No. ANR-06-NANO-069-02.

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