Ab-initio Electron Transport Calculations of Carbon Based String Structures

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First-principles calculations show that monatomic strings of carbon have high cohesive energy and axial strength, and exhibit stability even at high temperatures. Because of their flexibility and reactivity, carbon chains are suitable for structural and chemical functionalizations; they also form stable ring, helix, grid, and network structures. Analysis of electronic conductance of various infinite, finite, and doped string structures reveal fundamental and technologically interesting features. Changes in doping and geometry give rise to dramatic variations in conductance. In even-numbered linear chains, strain induces a substantial decrease of conductance. The double covalent bonding of carbon atoms underlies their unusual chemical, mechanical, and transport properties.

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While the research in molecular electronics has been in progress since the 1960s, the problem of interconnecting those molecular devices has remained a real challenge. Recently, linear gold chains suspended between two gold electrodes have been produced [1]. Another ultimate one-dimensional nanowire, namely, a monatomic carbon linear chain (C-LC) has been observed at the center of multiwall carbon nanotubes [2]. Some carbon chain structures have been subjects of earlier theoretical studies [3–8].

This Letter predicts new stable structures of carbon-based strings and their unusual electronic transport properties. Carbon strings having impressive mechanical and electronic properties can form helix structures through bending, and also networks or 2D grids through T and cross-bar junctions. Interesting and potentially useful conductance variations can be achieved in these structures. In spite of the fact that the parent diamond crystal is a good insulator, an ideal C-LC is a better conductor than gold chain. Double-bond formation between adjacent C atoms underlies all these unusual properties of the carbon chain.

We carried out total energy and electronic structure calculations using a first-principles pseudopotential plane wave method [9] within density functional theory (DFT) and supercell geometries. Generalized gradient approximation (GGA) and local density approximation (LDA) have been used, and all the atomic positions and lattice parameters of string structures have been optimized. The analysis of quantum ballistic conductance has been performed using TRANSIESTA-C, a recently developed *ab-initio* transport software based on localized basis sets, DFT, and nonequilibrium Green's function (NEGF) formalism [10].

Among a large number of nanowire structures of carbon including planar zigzag, dumbbell, and triangular structures, C-LC (known as cumulene) is found to be the only stable structure [11]. Upon relaxation, all other structures are transformed to C-LC with a bond length of $c = 1.27$ Å. The C-LC is energetically very favorable as reflected by the cohesive energy of as large as 8.6 eV/atom (that is close to the calculated GGA cohesive energy in diamond structure, 9.5 eV/atom).

Structural and electronic properties of C-LC are essential for studying its transport characteristics (see Fig. 1). The σ-band below the Fermi level, E_F, is composed from $2s$ and $2p_z$ atomic orbitals. The doubly degenerate π-band formed from the bonding combinations of $2p_x$ and $2p_y$ atomic orbitals [3] crosses E_F at $k = \pi/2c$. Therefore the C-LC structure is vulnerable to Peierls distortion which may induce a metal-insulator transition. The existence and degree of such a distortion has been a subject of debate [8]. We calculated that the maximum energy gain (per atom) through the dimerization of the chain is just 2.7 (3.2) meV using LDA (GGA) at bond alternation parameter $\delta = 0.017$ Å. However, treating the GGA-calculated energy-change profile as an effective potential for the dynamics of a C atom in the chain, the zero-point energy of the atom in the double-well potential turns out to be much higher (51 meV) than the Peierls distorted ground state energy [see Fig. 1(b)]. As a result, the small distortion effect is insignificant and cannot be observed even at $T = 0$ K as calculated with GGA and LDA energies [12].

In addition to the σ-bond derived from the states of the σ-band, half-filled π-band states form a π-bond as shown in Fig. 1(c). This double-bond structure is responsible for the high stability and metallicity of ideal C-LC. Calculated longitudinal vibrational modes have higher frequencies than the doubly degenerate transverse modes as shown in Fig. 1(d). This indicates that the chain is stiff along its axis but flexible in the transverse directions. Accordingly, C-LC is suitable for deformations to form other string structures. The elastic response of the C-LC to different deformations is summarized in Fig. 1(e). As a measure of the elastic stiffness of the C-LC, the second derivative of the strain energy per atom with respect to the axial strain, $d^2E/d\epsilon^2$, is calculated to be 119 eV. This

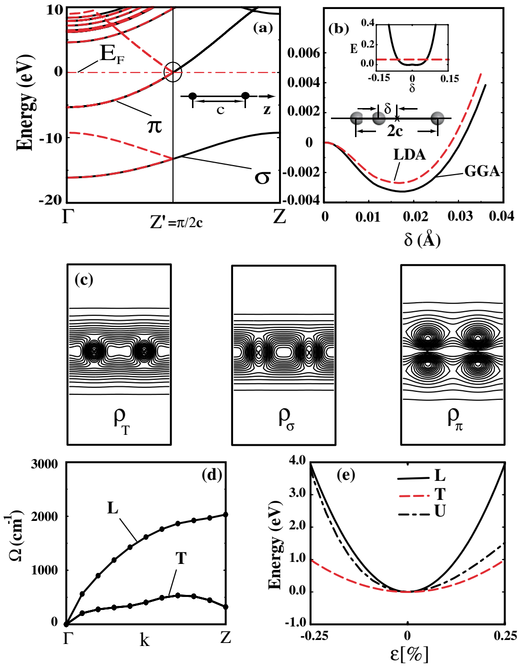

FIG. 1 (color online). (a) Energy band structure of C-LC. Zone-folded bands upon doubling the cell size from c to $2c$ are shown by dashed lines. (b) Variation of LDA and GGA total energies per unit cell of C-LC in the presence of Peierls distortion. The inset shows the zero-point oscillation energy of a C atom in the effective potential due to Peierls distortion. (c) Contour plots of total, σ-band, and π-band charge-densities in the plane passing through C-LC. (d) Longitudinal (L) and doubly degenerate transversal (T) branches of phonons. (e) Variation of total energy with the lateral (solid line), transversal (dashed line) displacements of a single C atom in a supercell of four atoms. Dot-dashed line (U) shows the variation of the total energy with uniform extension or compression of c from equilibrium.

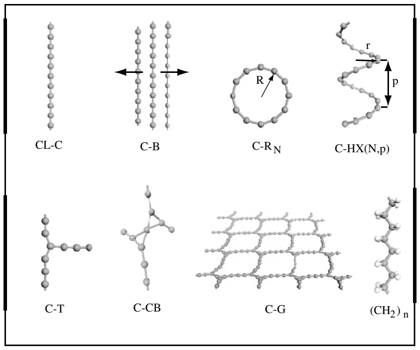

FIG. 2. Carbon-chain-based nanostructures: carbon linear chain (C-LC); bundle of several linear chains (C-B) with a repulsive interchain interaction; ring structure with N atoms (CR$_N$); helix of N atoms with pitch length p (C-HX(N, p)); T-junction of two chains (C-T); cross-bar structure of two chains (C-CB); planar grid structure (C-G); and C-LC functionalized with H-atoms ($(\mathrm{CH}_2)_n$).

value corresponds to a very high axial strength for the C-LC when compared to the corresponding values for carbon nanotubes, which are in the range 52–60 eV [13].

Even more interesting are structural and chemical functionalizations of carbon strings as illustrated in Fig. 2. Carbon rings, C-R$_N$, containing N atoms have a number of interesting features, and are closely related with the helix structure [7]. The helix structure by itself is denoted as C-HX(N, p) and can be generated from C-LC with different radii and pitch lengths p (in Å). Here, N is the number of C atoms in one pitch of the helix. The binding energies of helices are slightly smaller than that of the C-LC due to strain energy implemented by the curvature, such as for $p = 10$ Å fixed, E_b is 8.3 and 8.5 eV for $N = 10$ and 16, respectively. Finite helix structures are to be stabilized by fixing from both ends against a weak tendency of transforming to a LC. All C-HX structures we studied here have the bond alternation no matter what the value of N is, and are stable even at $T = 1200$ K. We believe that the C helix structure may be relevant to study chiral currents and to fabricate nanosolenoids. Further to circular ring and helix structures, the C-LC can branch off to form T and cross junctions. These junctions can form, since an additional C atom can easily be attached to any carbon atom of C-LC with a binding energy of 8 eV. For example, a T-junction is produced if a perpendicular chain develops from that adatom. At the junction, the double bond structure changes into planar sp^2-like bonding. In the case of cross-junction, two carbon atoms are attached to a single atom of C-LC. At the junction, a 3D sp^3-like bonding develops as shown in Fig. 2. These chains can further branch off to produce a grid of ($N \times M$) atomic rectangular cells [14], or a network structure. In principle, these grids or networks can be functionalized to generate 2D and 3D artificial crystals. Since the interconnects between the nodes are conducting, one can expect that carbon chain networks or grids can be useful for the integration in the molecular electronics.

Carbon chains are reactive owing to their double bond structure. Oxygen atoms can be chemisorbed to a single carbon atom (specified as top site) or form a bridge bond between two carbon atoms. Similarly, a single hydrogen atom can easily be adsorbed to a chain atom with $E_b = 3.6$ eV; it is larger than the energy associated with the chemisorption of H on single-wall carbon nanotubes [15]. The $(\mathrm{CH}_2)_n$ structure in Fig. 2 is a wide band-gap semiconductor.

Having revealed the atomic and electronic structures, we now turn to the prime objective of our study and examine how the conductance of these infinite and finite C-based string structures vary with geometry, elastic deformation, and doping. As usual, we have used an electrode-device-electrode geometry for conductance calculations. The conductance of the device has been calculated as $G(E) = (2e^2/h)\mathrm{Tr}(\Gamma_1 G^r \Gamma_2 G^a)$ ($G^{\{r,a\}}$: retarded and advanced Green's functions, $\Gamma_{1,2}$: coupling functions to the electrodes) after iteratively solving NEGF and DFT equations of the system [10]. In order to match the device potential and the surface potential of the semi-infinite electrodes, the device regions are defined to contain some portion of the electrodes. Here, we choose to use C-LC as the metallic electrodes. The atoms in the device region are subjected to geometry optimizations in supercells, keeping the electrode-atom positions fixed.

Earlier, conductance properties of short C chains have been reported. Using jellium electrodes it has been shown that the conductance of C atomic chains varies in an oscillatory manner with the number of atoms in the chain [16]. Larade *et al.* [17] predicted negative differential resistance for C chains coupled with Al electrodes. They also point out quantitative differences in odd- and even-numbered C chains [17]. We investigate effects of strain, impurities, and adatoms on conductance of C strings. Results of *ab-initio* electron transport calculations of C-LC, infinite and finite segments of C-HX with varying N and p are summarized in Fig. 3. The equilibrium conductance of ideal, undistorted C-LC is $2G_0$ due to the doubly degenerate π-band crossing the Fermi level. In case of bond alternation due to Peierls distortion there opens a gap around E_F. However, according to the present GGA results, the weak bond alternation should not be observable due to zero-point oscillations of the atoms. We also note that any defect (such as displacement of atoms from their equilibrium positions, etc.) in C-LC should lead to the localization of current transporting state, which is characterized by the localization length ξ. For a strictly 1D wire like C-LC, ξ is proportional to the elastic mean free path ℓ (ℓ itself depends on the type of defect and temperature). If the length L of the C-LC is larger than ξ, the resistance of the chain becomes $R \gtrsim \frac{h}{4e^2} + \frac{h}{e^2} e^{L/\xi}$ [18]. On the other hand, the opening of a conductance gap around E_F is related to the dimerization of carbon atoms, and that effect is seen to be reflected in the conductance plots of infinite carbon helix structures. The bending of the carbon chain into a helix also introduces some narrow conductance drops of integer number, which changes with the pitch length and radius of the helix. In case of finite-length solenoids, we considered single and double periods of helices placed in between two semi-infinite C-LC electrodes. The dimerization of atoms persists for finite-length helices. In Fig. 3(b) the set of curves presented for the conductance of finite-sized helices all display oscillatory behavior, the frequency of which depends on the radius and pitch length of the helix. Each peak corresponds to a molecular orbital level of the device (helix) aligned with E_F of the electrodes (C-LC). As the axial size of the helix is doubled, the number of the peaks in the conductance pattern is also doubled, pointing to the limiting case of infinite helix structure.

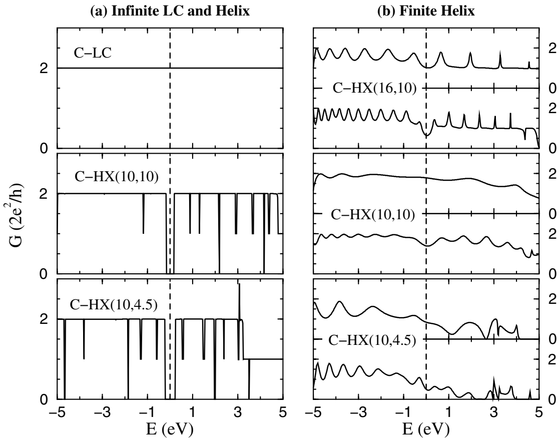

FIG. 3. Calculated conductance of various carbon chain structures in units of the conductance quantum ($G_0 = 2e^2/h$). (a) Infinite structures of undistorted C-LC and two helices C-HX(N, p) with different pitch lengths. (b) Finite-sized helices in between two C-LC electrodes. Each panel is divided into two; the top parts are for a single period of the helix and the bottom parts are for two periods. The Fermi levels are set to zero in all systems.

How the ballistic electron transport depends on strain, substitutional impurity, and external doping of C-LC is another interesting aspect of our study. When an axial tension F is applied to an N-atom C-LC, the chain elongates (the total length scales by $1 + \epsilon$, where ϵ is the strain), resulting with nonuniform bond lengths. For example, for $F = 7.78$ nN a 6-atom chain attains a strain $\epsilon = 0.15$ and a sequence of equilibrium bond lengths—1.56, 1.31, 1.59, 1.30, 1.59, 1.31, and 1.56 Å—when relaxed in between two C-LC electrodes. Resulting conductance spectrum of the strained chains displays oscillatory behavior with E. Figure 4(a) presents $G(E)$ of a C-LC device including $N = 5$ or $N = 6$ atoms subjected to different strains. The character of oscillations is dramatically different depending on N being odd or even (We have confirmed that chains with $N = 4$ and 7 comply with this trend.) If N is odd, the chain always has a peak conductance value of $2G_0$ at the Fermi level, whereas for even N, $G(E_F)$ corresponds to a dip of oscillations which drops considerably with increasing ϵ. This salient feature is related to the alignment of the molecular energy levels of the device region with the electrochemical potential of the electrodes. It turns out that E_F coincides with the HOMO (highest occupied molecular orbital) for odd-numbered chains, and with the center of the HOMO-LUMO (lowest unoccupied molecular orbital) gap for even-numbered ones. When geometrical optimization of the chain is omitted and the strain is assumed to be uniform, the conductance oscillations are still present but their amplitudes are smaller as shown in the insets of Fig. 4(a). The observation that even-numbered strained C chains have lower conductance values is compatible

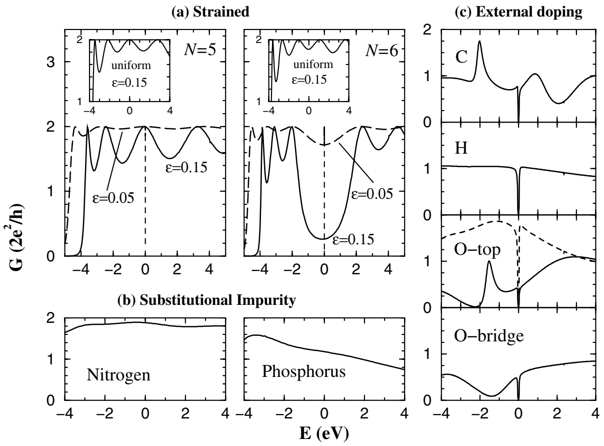

FIG. 4. Conductance variations of finite C-LCs modified by (a) strain under tension, (b) substitutional impurity atoms of N and P, (c) chemical doping with single C or H atom; single O atom at top site (dashed curve is obtained by deleting the adsorbed O but by maintaining the local distortion in C-LC caused by O); single O atom adsorbed at the bridge site. The Fermi levels are set to zero in all systems.

with the findings of Lang and Avouris for unstrained chains [16]. They report $G \cong 1.8G_0$ for C chains with $N = 5$ and 7 in between jellium electrodes. In our model, use of C-LC electrodes naturally corresponds to a "better contact" which leads to $G = 2G_0$. With our choice of electrodes, unlike the results in Ref. [16], the difference of N being odd or even in conductance of *unstrained* C chains does not manifest itself, because for all N the configuration is the same. Therefore, the odd-even N disparity we find in conductance of C chains is a pure strain-induced effect.

$G(E)$ is also affected by substitutional impurities as shown in Fig. 4(b). We considered 7-atom C-LCs containing a substitutional impurity atom of N or P at the center. While the decrease in conductance is minute for N-impurity, P causes a substantial decrease. Conductance variations $G(E)$ for C-LC externally doped by a single (C, H, and O) atom are illustrated in Fig. 4(c). The adatom deforms the C-LC by changing the type and the geometry of the local bonding at the adsorption site. For all cases, we see that $G(E)$ dips to zero at E_F. The dip is dominantly due to the deformation of the chain since it persists even if the adatom is removed but the distortion of the chain is kept the same. The $G(E)$ curve reflects the local electronic structure at the adatom site and is a fingerprint for the type of the adatom, as well as the adsorption geometry.

In summary, we showed that carbon atoms can form stable string structures with impressive physical properties. C-LC is flexible but has very high stiffness along the axial direction. Accordingly, carbon strings are suited for forming various stable nanostructures; they can be easily doped and functionalized by chemisorption of adatoms and molecules. Calculated conductance is found to be sensitive to deformation geometry and doping of the chain structure. Strained C chains show an odd-even N disparity. For interconnecting molecular devices, carbon atomic string structures can be a potential alternative to gold chain as well as to metallic carbon nanotubes. We believe that with their novel electronic, mechanical, and transport properties, carbon strings deserve further theoretical and experimental research to be a potential material for nanoscience and nanotechnology.

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[11] Planar zigzag chains have two C atoms per cell forming apex angles of either ~120° or 60°. Number of atoms per cell is 4 and 3 for the dumbbell and equilateral triangular structures, respectively. We also performed *ab-initio* calculations for finite C-LC having 5, 6, and 20 atoms in a supercell with an axial vacuum distance of 8 Å between the chains. Optimized structures are found to be stable.
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