Electronic properties of silicon nanotubes with distinct bond lengths

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We analyze the band structure of a silicon nanotube with sp^3 bonds and variable bond lengths. This nanotube has many similarities with a carbon nanotube including a band gap at half-filling and conducting behavior which is dependent on structure. We derive a simple formula which predicts when the nanotube is metallic. We discuss our results in the context of a nanotube subject to small applied strains as this provides a means of distorting bond lengths in a predictable way and may be tested experimentally. The effects of strain on nanotube conductance have important implications for sensor technology.

PACS number(s): 71.10.Fd, 71.10.Pm

There exists a wide variety of nanotubes which can be constructed from inorganic materials such as silicon,[1] boron nitride,[2–5] and tungsten disulfide.[6] While the vast majority of nanotube research concentrates on carbon nanotubes (CNTs), there is some evidence that inorganic nanotubes may be better suited to certain tasks. For example, silicon nanotubes (SNTs) may be preferable to CNT as hydrogen storage devices[7] and boron nitride nanotubes have several potential applications in electronics because, unlike CNT, the band gap is not structure dependent and may be tuned to a desired width using an electric field.[8] In this Brief Report we look at the conducting properties of a SNT derived from simple analytic band-structure calculations. Numerical studies have indicated that SNTs are possibly metallic[11] and in most cases our calculations agree with this conclusion. In some cases, however, an energy gap is formed and this may lead to semiconducting behavior.

Typically, a CNT forms sp^2 bonds which result in a hexagonal lattice structure. In SNT sp^2 bonds are possible but sp^3 bonds are energetically favorable and so a square or at least quadrilateral lattice is more likely than a hexagonal lattice.[9–15] Therefore, we consider a SNT constructed from rolling up a two-dimensional quadrilateral lattice. The quadrilateral lattice allows for some interesting band-gap behavior which is not dissimilar to what is observed in hexagonal CNT lattices. We find that in the general case the dispersion is gapped at zero energy, except at eight points, while a CNT has six gapless points. In the special case of a parallelogram lattice the band gap vanishes and the dispersion is continuous.

We assume that each quadrilateral in the two-dimensional lattice is identical, although possibly rotated, as shown in Fig. 1. The nearest-neighbor bonds are described by four vectors $\boldsymbol{\sigma}_{1,2,3,4}$ with the constraint $\boldsymbol{\sigma}_4 = \boldsymbol{\sigma}_1 - \boldsymbol{\sigma}_2 + \boldsymbol{\sigma}_3$. We denote the hopping strength across $\boldsymbol{\sigma}_l$ by t_l. Clearly this lattice is very similar to an irregular hexagonal lattice which may describe a CNT but with an additional bond along $\boldsymbol{\sigma}_4$, and therefore we will use notation which is commonly used for CNT. The quadrilateral lattice can be described by two identical irregular triangular sublattices offset by $\boldsymbol{\sigma}_1$ and with lattice vectors $\mathbf{c}_1 = \boldsymbol{\sigma}_1 - \boldsymbol{\sigma}_2$ and $\mathbf{c}_2 = \boldsymbol{\sigma}_1 - \boldsymbol{\sigma}_3$. When rolling up the two-dimensional lattice to form a nanotube, we define the x axis as being around the circumference C and the y axis as the longitudinal direction. We define a vector $\mathbf{C} = n\mathbf{c}_1 + m\mathbf{c}_2$

$= (n+m)\boldsymbol{\sigma}_1 - n\boldsymbol{\sigma}_2 - m\boldsymbol{\sigma}_3$ with integer $n, m \geq 0$ for which the x component defines the circumference $C = (n+m)a_1 - na_2 - ma_3$ and the y component is constrained by $(n+m)b_1 - nb_2 - mb_3 = 0$, where $\boldsymbol{\sigma}_l = (a_l, b_l)$.

We will first discuss the special case of a SNT constructed from a parallelogram lattice. We calculate the dispersion relation and find that this nanotube is most likely metallic. Although this case is rather simple we present it for completeness as it is distinctly different from the general case of a quadrilateral lattice. On deriving the dispersion for the general case we find that a gap opens up about zero energy. In most cases the Fermi energy will lie outside this gap and the SNT will be metallic. If the SNT is doped to half-filling, i.e., one electron per lattice site, the resultant particle-hole symmetry ensures that the Fermi energy is at zero and so must lie within the gap. In this case the SNT behaves much like an undoped (half-filled) CNT with conducting behavior directly related to its lattice structure. The irregular lattice structure of a SNT can either form naturally or be due to some applied strain. As an applied strain will distort the lattice in a predictable manner and because it can be experimentally verified, we discuss the effect of a small external strain on the conductance of a SNT which is doped to half-filling. We assume that the strain is either longitudinal or torsional and that it is applied evenly across the lattice so that the lattice continues to comprise equal quadrilaterals. We also assume that the strain is not large enough to cause buckling. We find that distorting the SNT can cause it to oscillate through several metal-insulator transitions, though the energy gaps of the semiconducting phases may be very small.

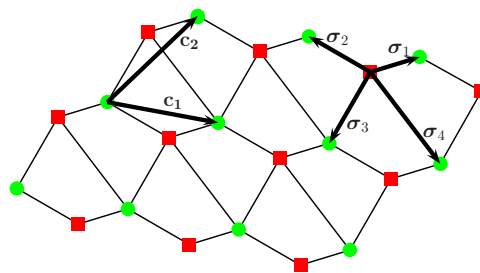If the quadrilaterals in Fig. 1 are parallelograms then each

FIG. 1. (Color online) An irregular quadrilateral lattice with the two sublattices represented by circles and squares.

lattice site is identical and we do not have two distinct sublattices. Because of this the general quadrilateral case does not reduce to the parallelogram case and we must consider them separately. For parallelograms only two vectors $\boldsymbol{\sigma}_{1,2}$ are required as $\boldsymbol{\sigma}_1=-\boldsymbol{\sigma}_3$ and $\boldsymbol{\sigma}_3=-\boldsymbol{\sigma}_4$. If we define $\mathbf{c}_1=\boldsymbol{\sigma}_1-\boldsymbol{\sigma}_2$ and $\mathbf{c}_2=\boldsymbol{\sigma}_1-\boldsymbol{\sigma}_3=2\boldsymbol{\sigma}_1$, in analogy with the general case, then the vector $\mathbf{C}$ must be modified $\mathbf{C}=n\mathbf{c}_1+m\mathbf{c}_2/2=(n+m)\boldsymbol{\sigma}_1-n\boldsymbol{\sigma}_2$ so that the circumference of the rolled-up lattice is $C=(n+m)a_1-na_2$ and $(n+m)b_1-nb_2=0$ for integer $n,m\geq 0$. Following the terminology in Ref. 16, there are two special cases for nanotubes constructed from parallelogram lattices: the prismatic case is $n=0$ for which only one lattice vector $\boldsymbol{\sigma}_1$ is required to define the circumference and the antiprismatic case is $m=0$ for which both lattice vectors contribute equally to the circumference. All other cases can be defined as chiral.

As a first approximation we consider an interactionless Hubbard Hamiltonian

$$H=-\sum_{l=1}^{2}\sum_{xy} t_l[c^\dagger(x,y)c(x+a_l,y+b_l)+\text{H.c.}], \quad (1)$$

where (x,y) represents every lattice site and H.c. is the Hermitian conjugate. The operators $c(\mathbf{r})$ and $c^\dagger(\mathbf{r})$ are annihilation and creation operators, respectively, at the site $\mathbf{r}=(x,y)$. On rewriting the operators in terms of their momentum-space Fourier transform,

$$H=-\sum_{k_x,k_y}[2t_1\cos(\mathbf{k}\cdot\boldsymbol{\sigma}_1)+2t_2\cos(\mathbf{k}\cdot\boldsymbol{\sigma}_2)]c^\dagger(\mathbf{k})c(\mathbf{k})$$
$$=\sum_{k_x,k_y}\epsilon(\mathbf{k})c^\dagger(\mathbf{k})c(\mathbf{k}), \quad (2)$$

where the momentum is $\mathbf{k}=(k_x,k_y)$ and $\epsilon(\mathbf{k})$ is the dispersion in momentum space.

When rolling up the two-dimensional lattice the x component of the momentum must be quantized by $k_x=2\pi p/C$ for integer p. Let us say the Fermi energy is ϵ_F with corresponding Fermi momentum $\mathbf{k}_F=(k_{xF},k_{yF})$. In a completely clean SNT there will be no free electrons and the Fermi momentum will lie below the dispersion $\epsilon(\mathbf{k})$ so the lattice will be semiconducting. A small amount of doping[17] will introduce free carriers into the lattice, shifting the Fermi momentum, and because the dispersion is continuous in both dimensions it should be possible to find a Fermi momentum $\mathbf{k}_F$ for a given Fermi energy ϵ_F for which $\epsilon(\mathbf{k}_F)=\epsilon_F$ and $k_{xF}=2\pi p/C$, i.e., the system is gapless and therefore metallic.

In the general quadrilateral case the two-dimensional lattice comprises two sublattices and the dispersion relation is distinctly different from the simple parallelogram lattice case. The interactionless Hubbard Hamiltonian is

$$H=-\sum_{l=1}^{4}\sum_{xy} t_l[c_2^\dagger(x,y)c_1(x+a_l,y+b_l)+\text{H.c.}], \quad (3)$$

where the subscript of c_j defines the sublattice. In Fig. 1 $j=1$ is represented by circles and $j=2$ is represented by squares. On writing the operators in momentum space,

$$H=-\sum_{l=1}^{4}\sum_{k_x,k_y}[A_l(\mathbf{k})c_2^\dagger(\mathbf{k})c_1(\mathbf{k})+A_l^*(\mathbf{k})c_1^\dagger(\mathbf{k})c_2(\mathbf{k})] \quad (4)$$

with $A_l(\mathbf{k})=t_l e^{-i\mathbf{k}\cdot\boldsymbol{\sigma}_l}$. The dispersion relation is $\epsilon=\pm|\Sigma_l A_l|$,

$$\epsilon(\mathbf{k})=\pm\sqrt{\left(\sum_l t_l\cos\mathbf{k}\cdot\boldsymbol{\sigma}_l\right)^2+\left(\sum_l t_l\sin\mathbf{k}\cdot\boldsymbol{\sigma}_l\right)^2}. \quad (5)$$

This dispersion, unlike the parallelogam lattice dispersion, is not continuous over its full range as a gap has opened up about $\epsilon=0$.

Like the two-dimensional hexagonal lattice of an unrolled CNT, the energy gap does not appear across the entire $\epsilon=0$ range and there are several points $\mathbf{k}_0=\pm(k_{x0},k_{y0})$ where the dispersion on the quadrilateral lattice can be zero $\epsilon(\mathbf{k}_0)=0$. In the hexagonal lattice there are six such points, but in the quadrilateral lattice we find eight. After some algebra it can be shown that

$$k_{x0}=\frac{(b_1-b_4)[C_{12}-2q_{12}\pi]\mp(b_1-b_2)[C_{14}-2q_{14}\pi]}{(b_1-b_2)(a_1-a_4)-(b_1-b_4)(a_1-a_2)},$$

$$k_{y0}=-\frac{(a_1-a_4)[C_{12}-2q_{12}\pi]\pm(a_1-a_2)[C_{14}-2q_{14}\pi]}{(b_1-b_2)(a_1-a_4)-(b_1-b_4)(a_1-a_2)},$$
$$(6)$$

with $q_{12},q_{14}=0,1$ and

$$C_{12}=\cos^{-1}\left(\frac{t_1^2+t_2^2-t_3^2-t_4^2}{2(t_3t_4-t_1t_2)}\right),$$

$$C_{14}=\cos^{-1}\left(\frac{t_1^2+t_4^2-t_2^2-t_3^2}{2(t_2t_3-t_1t_4)}\right). \quad (7)$$

The solution in Eq. (6) takes the upper sign when $(t_3t_4-t_1t_2)(t_2t_3-t_1t_4)<0$ and the lower sign in the opposite case. For either of these solutions to exist, we require that C_{12} and C_{14} are both real. In a hexagonal lattice the six zeros $\mathbf{k}_0$ are known as Dirac points because the dispersion can be written as $\epsilon(\mathbf{k}_0+\mathbf{k})=v|\mathbf{k}|$ for small $\mathbf{k}$ and constant v. In general the zeros of the quadrilateral lattice are not Dirac points.

On rolling up the quadrilateral lattice to form a nanotube k_x becomes quantized, $k_x=2\pi p/C$ for integer p. When ϵ_F is far from the energy gap the SNT will generally be metallic (if free carriers are available) as it is always possible to find $\mathbf{k}_F$ which satisfies both $\epsilon(\mathbf{k}_F)=\epsilon_F$ and the quantization requirement. The situation is much more interesting if the SNT is doped[18–21] to half-filling so that $\epsilon_F=0$. Now the SNT will only be metallic if $k_{x0}=2\pi p/C$ for integer p. On solving this condition for p while making use of the constraints $(n+m)b_1-nb_2-mb_3=0$ and $\boldsymbol{\sigma}_4=\boldsymbol{\sigma}_1-\boldsymbol{\sigma}_2+\boldsymbol{\sigma}_3$ we find that when

$$p=[(n+m)C_{12}\pm mC_{14}]/2\pi \quad (8)$$

is an integer the SNT is metallic if C_{12} and C_{14} are both real. The $\pm$ sign follows the same rule as the $\mp$ sign in Eq. (6). With Eq. (8) we have shown that the conducting properties of a half-filled SNT are only dependent on the hopping strengths and the (n,m) structure, which is also the case in a
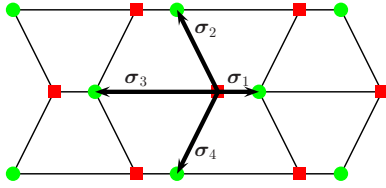
FIG. 2. (Color online) A prismatic trapezoidal lattice.

CNT. One situation where a SNT is always metallic is when $n=0$ (prismatic) and $t_2=t_4$, as this ensures $C_{12}=C_{14}$ with the lower sign and $p=0$.

Provided the curvature is not large $t_l \propto \sigma_l^{-2}$. Large curvature ruins this simple relationship through hybridization effects. So, assuming the nanotube circumference is not small we can write Eq. (8) solely in terms of the bond lengths. In most circumstances the bond lengths of a SNT will be different, but this difference will be very slight. One way in which to enhance these differences is to subject the SNT to a small applied strain.

The application of strain presents an ideal way in which to compare theory with experiment as one can distort the bonds of the nanotube in a predictable way and a wide range of different lattice structures can be obtained. However, if we begin with an unstrained parallelogram lattice and subject it to longitudinal and torsional strains we will distort the lattice but it will remain a parallelogram with a gapless dispersion and no changes in electronic properties will be observed. Therefore, we illustrate how strain may effect the electronic properties of a SNT by using the simplest nonparallelogram lattice, a prismatic $n=0$ SNT, which is constructed from a trapezoidal lattice, as shown in Fig. 2 with $\boldsymbol{\sigma}_1=\sigma(1-\delta a,0)$, $\boldsymbol{\sigma}_2=\sigma(-\delta a, 1+\delta b)$, $\boldsymbol{\sigma}_3=\sigma(-1-\delta a,0)$, and $\boldsymbol{\sigma}_4=\sigma(-\delta a,-1-\delta b)$ for some constant length σ. The dimensionless constants δa and δb define the distortion in the lattice prior to any external strain. This initial lattice is such that $\sigma_2=\sigma_4$ so $t_2=t_4$ and, as discussed previously, this SNT must be metallic. If we apply a small strain along the longitudinal axis the y components of $\boldsymbol{\sigma}_{2,4}$ will increase at the same rate (but in the opposite direction) and $\boldsymbol{\sigma}_{1,3}$ will remain constant. In this scenario we still have $t_2=t_4$ so the SNT remains metallic, provided C_{12} and C_{14} continue to be real.

If torsional strain is applied to the SNT the changes in $\boldsymbol{\sigma}_{1,2,3,4}$ can be represented by the dimensionless variables δx and δy. After the application of torsional strain $\boldsymbol{\sigma}_2=\sigma(-\delta a-\delta x, 1+\delta b+\delta y)$ and $\boldsymbol{\sigma}_4=\sigma(-\delta a+\delta x,-1-\delta b-\delta y)$ while $\boldsymbol{\sigma}_{1,4}$ remain constant. We can relate δx and δy to measurable parameters such as the change in length of the nanotube and the torsional angle ϕ which defines the rotation of one end of the tube relative to the other end. In general the length is $L=(nq_n+mq_m)(b_2-b_3)/(n+m)$ for integers $q_m,q_n \gg 1$, so the change in length can be written as $\Delta L=L_0\delta y/(1+\delta b)$, where L_0 is the initial length of the tube. Similarly, one can find the torsion angle, $\phi=(2\pi L_0/C)\delta x/(1+\delta b)$.

Figure 3 is a contour plot of integer p and shows that the application of torsion on a SNT at half-filling may cause it to oscillate through several metal-insulator transitions. Similar behavior has been observed in CNT.[22] The values of $\delta a \neq 0$ and δb do not have a significant effect on the shape of the contours of integer p as can be seen by comparing Fig. 3(a)
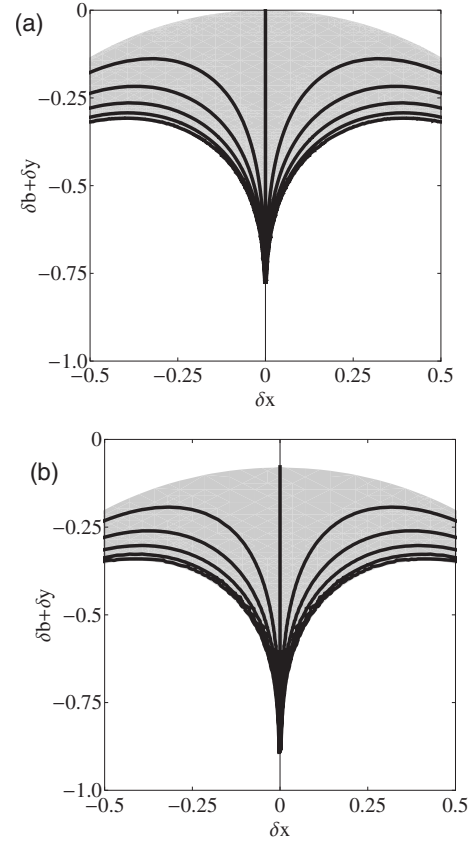

FIG. 3. The shaded area is where p is real and the lines are where p is an integer, i.e., where the SNT is metallic for the trapezoidal SNT with $n=0$, $m=12$ and (a) $\delta a=0.0001$, (b) $\delta a=0.2$.

with Fig. 3(b) which are essentially the same but shifted relative to one another. When $\delta a=0$ the situation is different as the lattice reduces to a square, and so this half-filled SNT is always metallic.
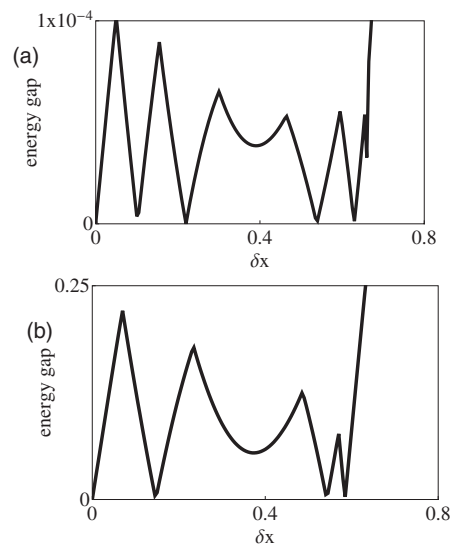

FIG. 4. The energy gap for the trapezoidal SNT with $n=0$, $m=12$, $\delta b=-0.25$, $\delta y=0$, and (a) $\delta a=0.0001$, (b) $\delta a=0.2$. The energy gap is measured in units of the proportionality constant g which is defined by $t_l=g/\sigma_l^2$.

In Fig. 4 we plot the energy gap for the two SNTs considered in Fig. 3. For $\delta a = 0.0001$ the contour plot in Fig. 3(a) clearly shows several metal-insulator transitions, but Fig. 4(a) shows that the energy gap is very small and will possibly not be distinguishable from the metallic $\delta a = 0$ case. As δa increases the energy gaps of the insulator phases tend to increase. Therefore, to experimentally distinguish the insulator phases from the metallic we would require that the bond lengths prior to the application of strain are significantly different. If this is possible we may be able to tune the band gap through the application of torsional strain. This ability to control electronic properties through mechanical means may

find applications in several technologies, such as sensors and transistors.

In summary, we have studied the band structure of a quadrilateral lattice in order to determine whether or not a SNT is always metallic. In the majority of cases, provided there are free electrons in the lattice, the SNT is metallic. However, when an element of disorder is introduced through variable bond lengths a gap opens up about zero and not unlike the energy gap observed in CNT. This energy gap is dependent on the SNT structure.

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