Carbon Nanoribbons: An Alternative to Carbon Nanotubes

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***Abstract*—The electronic and vibrational properties of carbon nanoribbons (CNRs) are analyzed and compared to carbon nanotubes (CNTs). Transport properties are analyzed from the perspective of use in an FET device. The required sizing and consequent processing requirements are discussed. The overall properties of the CNRs and CNTs are found to be similar, with the primary difference being the more restrictive size vs. bandgap behavior of the CNRs.**

Keywords-component; graphene; carbon nanoribbon; carbon nanotube; bandgap; mobility

I. INTRODUCTION

Carbon nanoribbons, essentially a monolayer of graphite patterned into a narrow strip, have recently been proposed [1] as an attractive alternative to CNTs While the CNTs have many highly desirable electronic properties (such as exceedingly high mobility and potentially excellent short channel effects in FETs due to the small "depth" / length aspect ratio), no method of assembling large-scale circuits comprised of CNTs has yet been devised. The main difficulty is the fact that CNTs are created prior to integration and need to be placed in correct positions in the circuit. This is contrary to the conventional planar process in Si, in which devices are formed on the entire wafer at once by lithographic means. CNRs offer the promise of lithographic patternability, while providing electronic properties similar to those of CNTs. Furthermore, the electronic properties of the CNRs are lithographically tunable, selecting metallic vs. semiconducting CNRs, by the orientation of the edge termination (for a semiconducting armchair CNR, see Figure 1). Thus, the channel, source and drain regions are formed by a single patterning step, requiring only the addition of the gate stack and contacts to complete the transistor. A schematic of such a transistor is shown in Figure 2. The required sizes and orientations result from the basic CNR properties, as discussed in the following sections.

II. ELECTRONIC PROPERTIES

The bandstructure of CNRs is computed using the conventional nearest-neighbor Tight-Binding method, with a p_z-orbital-derived Bloch wavefunction basis, similar to the method frequently used for CNTs[2,3]. The overlap element is retained, resulting in the generalized eigen problem. The p_z basis is sufficient even for narrow ribbons, since the small-

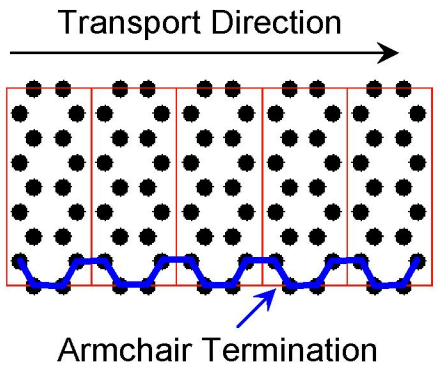

Figure 1 Section of CNR is shown, with points representing atoms of carbon. Only one unit cell is actually simulated, with periodic boundary conditions applied in the transport direction (CNT also has periodic boundary conditions applied along the edge).

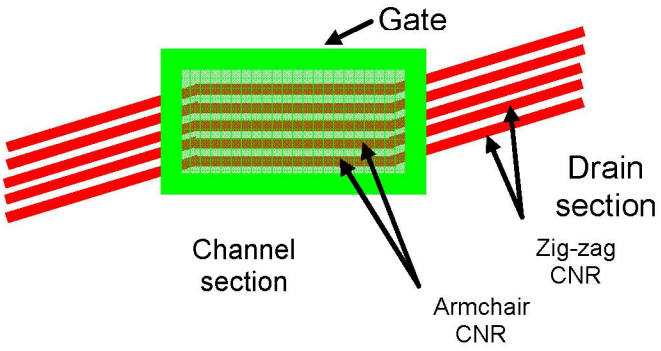

Figure 2 Top-down schematic of CNR transistor, with CNRs forming both channel and SD regions.

curvature approximation usually made for CNTs is strictly valid for CNRs. The absence of curvature implies that the p_z portion of the TB Hamiltonian is decoupled from the sp^2 in-plane part, and can be treated separately. Since the bottom of the conduction band and the top of the valence bands are formed using precisely the p_z set of states, which are in turn decoupled from the rest of the Hamiltonian, only the p_z portion is used for computations. The key ingredient for CNR computation is the treatment of the boundary conditions. Whereas the CNT has periodic boundary conditions in both the transport and "width" directions, the CNR has periodic boundary conditions only in the transport direction. No special boundary condition is asserted on the wavefunctions in the

transverse directions; the edge atoms are simply assumed to have fewer coupling neighbors. In order to facilitate computations with this boundary condition, the zone-folding approach is not used, resulting in a larger (but still very manageable) eigenvalue problem. Note that this approximation ignores the interaction of the carbon atoms with the Si-C substrate (used to form the graphene layer), which is assumed here to be weak.

Computed CNR bandstructures are shown and compared to those of CNTs in Figure 3. There are obvious qualitative similarities: both metallic and semiconducting bandstructures are manifested, the semiconductor bandgap depends on the size of the structure, and the conduction and valence bands are not symmetric (due to the inclusion of the overlap parameter).

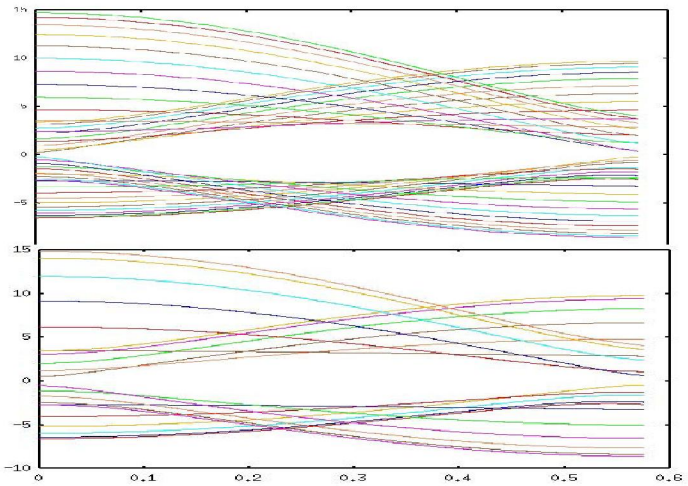

Figure 3 CNR (top) and CNT (bottom) electron bandstructures are shown, for the (10,0) chirality.

There are also notable differences, however. Firstly, the two-fold degeneracy of the CNT states is removed – the lowest subband of the conduction and valence bands are non-degenerate in the CNR. Secondly, the lowest subband of the CNR has appreciably higher curvature than the corresponding CNT subband (for the semiconducting cases).

The most striking difference between the CNT / CNR bandstructures, however, is the much smaller bandgap of the CNRs. This is illustrated in Figure 4, where the bandgap of CNRs and CNTs is shown as a function of size. The much smaller CNT bandgap can easily be understood qualitatively, as shown schematically in Figure 5. The electronic wavefunctions of CNTs must obey periodic boundary conditions (PBCs), matching both value and slope at the tube "edge". Thus, the lowest energy state must have the qualitative shape of the sinusoidal (red) wavefunction. The CNR has no such restriction, and consequently permits a wavefunction qualitatively similar to the semi-circular (black) curve. The latter will obviously have lower energy (the reduced curvature results in lower expectation value for kinetic energy). Thus, the CNR permits states lower in energy than the CNT. This is a basic property of periodic vs. non-periodic structures, and is not subject to modeling details.

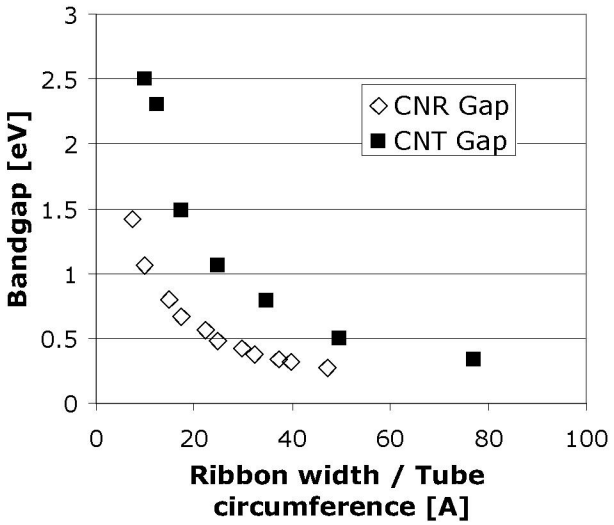

Figure 4 The dependence of bandgap on size for CNRs and CNTs is shown. *Copyright 2006, American Institute of Physics [8].*

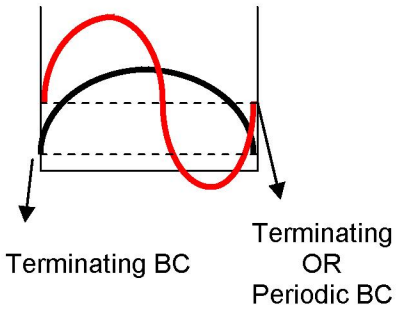

Figure 5 A schematic of ground state wavefunctions in CNRs (terminating) and CNTs (periodic) is shown.

The small bandgap of the CNR has important technological consequences, since it limits the band-to-band source-to-drain tunneling and ambipolar conduction (sufficiently short devices will be SD tunneling limited). As shown on Figure 4, achieving Si-like bandgaps requires 1 nm or smaller CNRs, with 0.5 eV bandgaps achievable at ~2 nm. Such minuscule sizes bring into question the feasibility of large-scale integration, possibly defeating the promise of lithographic patternability.

III. VIBRATIONAL PROPERTIES

Transport in a perfect CNR (or CNT, for that matter) will be determined by phonon scattering, since vibrational distortions of the lattice cannot be removed at finite temperature. The continuum approach of computing phonon dispersion relations becomes invalid for narrow structures; the length scale for lateral variations in the displacement field must be many atomic distances in size, a condition that is clearly violated for a structure that is only a few atoms across. Thus, an atomistic approach is needed.

We employ the semi-classical force-constant method, This is essentially an application of Newton's second law, with a

tensorial force-constant coupling each atom pair [3]. The total force on any given atom is obtained by summing the contributions of all neighbors within a given radius (fourth-nearest neighbors are included). A propagating wave form of the solution is then assumed in the transport direction (1-dimensional transport and k-vector for the CNR and CNT), which leads to a generalized eigenvalue problem for the frequency, at any given wave vector. The problem is then solved for a set of wavevectors in the Brillouin zone, resulting in the complete dispersion relation (phonon bandstructure). Furthermore, the eigenvectors (multiplied by the wavevector-dependent phase factor) represent the atomic displacements of the various modes. The treatment of the CNT and CNR is virtually identical; all atoms experience a force coupling to all neighbors within a 4th-nearest neighbor radius. For the CNT, this means that periodic boundary conditions are applied. For the CNR, the edge atoms simply have fewer coupled neighbors No displacement boundary conditions are applied; these arise naturally from the solution of the eigen problem. The force constants are assumed not to change near the edge of the ribbon. This is an approximation, of course, but a reasonable one for a first order calculation (more detailed calculations would need to comprehend the influence of the substrate, as well as any other surrounding topography).

The resulting bandstructures for the CNR and CNT are shown in Figure 6. While they appear quite different at first glance, there are notable similarities in the low-frequency acoustic modes. Specifically, the two in-plane modes (modes with linear dispersion relation near the origin of the plot) and the lowest frequency transverse mode (parabolic near the origin) are quite similar. Higher order modes have reduced frequency and lifted degeneracy in the CNR. The similarities and differences of the two dispersion relations are best understood by examining the atomic displacements.

Since the force-constant tensor does not couple in-plane displacements with out-of-plane forces (and vice versa), the in-plane and out-of-plane motions are decoupled. Thus, modes are either entirely in-plane, or entirely out-of plane. For the CNR, this arises naturally, for the CNT, it is due to the neglect of curvature. The second two modes of the CNR and CNT are shown in Figures 7. The in-plane displacements are indicated by arrows, whereas out-of-plane displacements are indicated by discs. In the CNR, the absence of PBCs in the lateral direction permits an additional degree of freedom for the atomic displacements of the edge atoms, which can move in opposite directions (not possible in CNTs). This results in additional phonon modes for the CNR.

IV. Transport Properties

The key property that makes the CNT attractive for an FET devices is its high mobility. While the CNR is qualitatively similar to the CNT, it is not necessarily clear that it will have similarly high mobility. We compute the low-field phonon-limited mobility for both the CNR and CNT using the Born Scattering approach, similar to that outlined in [5] and [6]. The overlap matrix elements are computed using direct integration of the previously computed electron and phonon wavefunctions. The selection rules are limited to forward momentum and conservation only (angular momentum would apply for the CNT as well, but not the CNR). The overall mobility value is obtained using the Kubo-Greenwood formula.

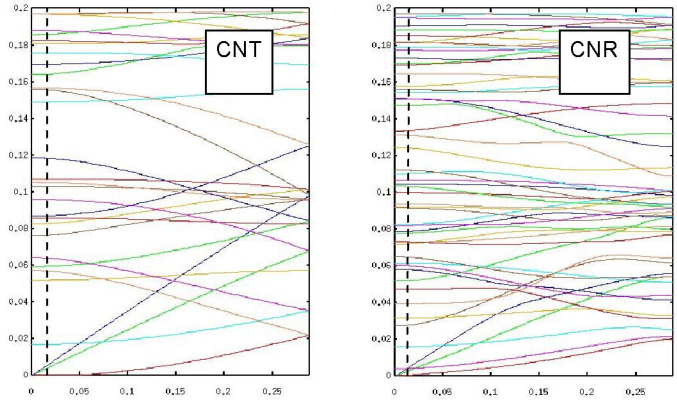

Figure 6. The phonon dispersion relations for a (7,0) CNT (left) and (7,0) CNR right are shown, in the first Brilloiun zone. The lowest energy modes are similar, degeneracy lifting and energy reduction is evident for the higher modes.

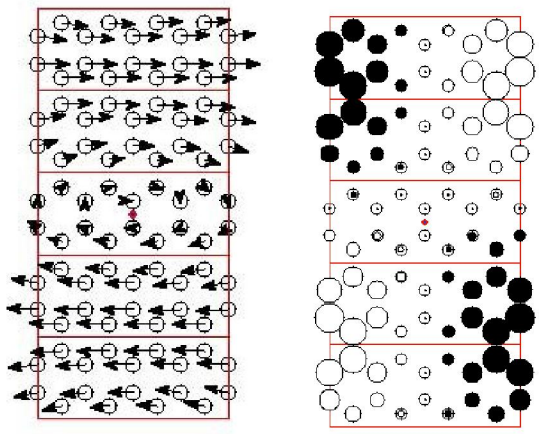

Figure 7. The 3rd and 4th phonon modes of the (7,0) CNR. Note that the 4th (out-of-plane) mode clearly has non-periodic boundary conditions, not possible in the CNT. *Copyright 2006, American Institute of Physic [8].*

The results of the mobility computation as a function of CNR / CNT size are summarized in Figure 8. As previously reported (both theoretically and experimentally), the CNT mobility degrades with decreasing CNT diameter. The CNR mobility behaves similarly, and the effect is understood as a consequence of increasing wavefunction confinement with decreasing structure size. Also apparent is the fact that the CNR mobility is in fact higher than the CNT mobility, at equal size (the perimeter of the CNT equals the width of the CNR). This can be primarily attributed to the significantly smaller transport effective mass of the CNR. As previously discussed, the CNR has a lower energy / higher velocity ground state than the CNT. The phonon modes primarily responsible for low-field mobility are quite similar between the two, and are therefore not a significant differentiator of the CNT / CNR.

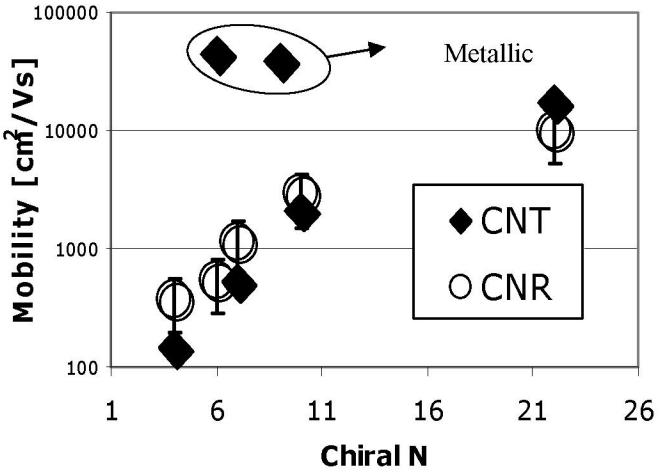

Figure 8. Comparison of CNT and CNR mobilities. All structures are semiconducting except where indicated otherwise.

The mobility shown in Figure 8 corresponds to the low-vertical field mobility. In general, we expect the phonon-limited mobility to be strongly modulated by the vertical field, as evidenced by the inversion layer of the planar MOSFET, Si nanowire, or FinFET device. The CNT and CNR, however, exhibit a very weak field dependence of mobility, with a nearly constant mobility from 0 field to the MV/cm field range. The mobility does not change significantly until the vertical field approaches the 10 MV/cm range. Given that the primary reason for the field-induced variation of inversion layer is the modulation of the spatial confinement of the carriers, it is not surprising that the CNTs and CNRs show very little field dependence; their out-of-plane confinement is essentially unchanged with the applied field. This intuitive assertion is supported by field-dependent bandstructure calculations [7].

Whereas the vertical electric field has little influence on the bandstructure and mobility of CNRs and CNTs, the lateral field modulates it quite strongly. This is quantified using the MC method, and the results are shown in Figure 9. The behavior of the CNT mobility has already been reported in [6], where scattering from the conduction band ground state to the first excited state resulted in mobility degradation, at a faster rate than what scattering-limited velocity saturation would predict. The CNR behavior is very similar, with the electron transfer to higher subbands occurring at lower energies, and the mobility consequently degrading at lower fields.

While the equal-size mobility of the CNR is higher than that of the CNT, it is perhaps more meaningful to compare the mobilities at equal bandgaps. The size of the bandgap determines the available range of voltages for a device operating in the ambipolar mode, as well as the ultimate limit for device scaling due to S/D tunneling. This comparison is illustrated in Figure 10 . This implies that the CNR is operating with stronger lateral confinement, which overwhelms the superior group velocity of the smaller CNR. As the bandgap approaches 0 (graphene), the mobilities of the CNR and CNT become similar, but at more technologically relevant bandgaps of > 0.5 eV, the CNR mobility is hardly superior to that of Si. The nearly ballistic regime often cited for CNTs is available to CNRs only for bandgaps < 0.25 eV.

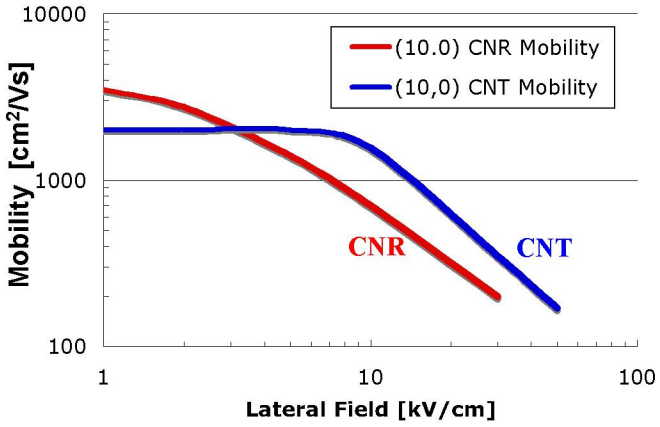

Figure 9. Comparison of CNT and CNR mobilities vs. lateral field (from Monte Carlo, similar to the approach of [6]). At matched size, CNR low-field mobility is higher, but the high-field degradation starts at lower field values.

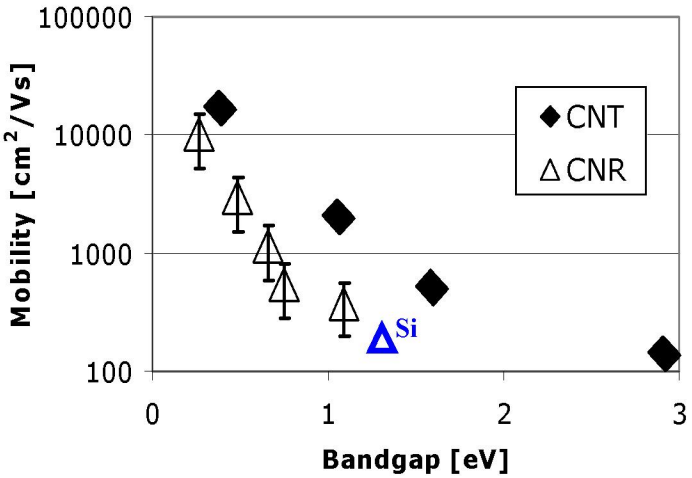

Figure 10. Comparison of CNR and CNT mobilities at matched bandgap. Due to the reduced CNR bandgap, CNTs have considerably higher mobilities at matched bandgap. *Copyright 2006, American Institute of Physics [8].*

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