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Controlling the Electrical Response of Carbon Nanotubes Deposited on Diamond through the Application of Electric Fields

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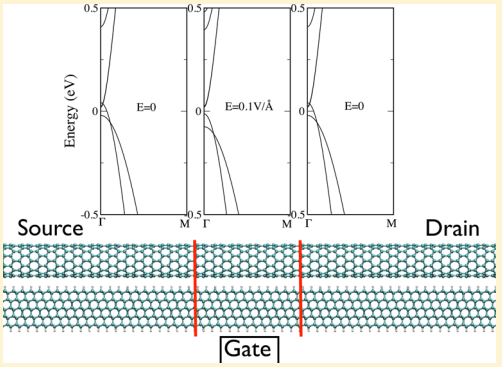
ABSTRACT: We apply first-principles methods to investigate the electronic properties of semiconductor carbon nanotubes deposited on hydrogen-terminated diamond surfaces. We found that the band gap of the diamond−nanotube system can be continuously varied (from 0 to 0.8 eV) through the application of an external electric field. The metal−semiconductor transition occurs for values of field between 0.03 and 0.035 V/Å, which could make viable the production of stable field-effect devices at nanometric scale. We also found that at zero value of electric field the nanotube electrical behavior can be modified by changing the diamond surface termination, which may be useful for producing ohmic metal−semiconductor contacts. On the other hand, at zero values of field, tubes deposited on nitrogen-doped diamond are metallic regardless of the surface termination. Thus, nitrogen doping could be useful in situations in which the atomistic details of the diamond surface are difficult to control.



INTRODUCTION

Because of their quasi-one-dimensional character and their unique electronic properties, carbon nanotubes present potential for application in nanoelectrectronic devices. In some cases, such a potential has been confirmed; for instance, flexible circuits, displays, RF-devices, and biochemical sensors have been reported.[1] An important advance in the field of carbon nanotube-based nanoelectronics was achieved at the beginning of the past decade when it was confirmed that carbon nanotubes can be used in field-effect transistors (FETs) that could outperform Si.[2,3] Ever since, the actual use of carbon nanotubes in nanoelectronics has met with difficulties in large-scale manufacturing techniques. A major challenge in the use of carbon nantotues in electronics is the metallic contact to semiconducting carbon nanotubes (SCNTs). If high-quality contacts are not provided, the SCNT-based devices could present wide Schottky barriers;[4,5] therefore, the transport properties are essentially determined by contact phenomena. First-principles calculations suggest that the contact morphology and the length of the contact region play an important role in the transport properties at the nanometric scale.[6,7] Such features are difficult to control in experiments. Therefore, high-quality metal−nanotube contacts are difficult to produce. In this sense, it is important to investigate alternative ways to form metal−semicondutor contacts in CNT-based systems.

In a recent experimental and theoretical work,[8] we showed that the nanotube−diamond contact causes significant modifications in the electronic properties of a semiconductor carbon nanotube. The two materials (SCNT and diamond) are crystalline and present distinct electronic structures, and the interface between them will define a heterojunction. Because one of the crystalline materials (SCNT) is one-dimensional, we will call the SCNT−diamond interface a 3D/1D heterojunction to distinguish it from the conventional heterojunctions formed by two bulk materials. The metallic behavior observed for the SCNT in contact with diamond results from the fact that the 3D/1D heterojunction is a broken-gap 3D/1D heterojunction, with the top of the highest valence band of diamond being above the minimum of the lowest SCNT conduction band. Thus, the charge transport occurs through an electron channel at the SCNT and a hole channel at the diamond surface. This phenomenon does not occur when the SCNT is put in physical contact with silicon.[8] Therefore, the same SCNT can present either semiconducting or metallic behavior depending on the type of substrate on which it has been deposited. If a region of a SCNT is deposited on silicon and another region is deposited on diamond, a metal−semiconductor contact is formed. In such types of contact, the complex metal−SCNT morphology mentioned above is avoided, which could eliminate the effect of contact phenomena on the transport properties of CNT-based devices.

In the present work we show, by means of first-principles methods, that the application of an electric field in the direction perpendicular to the diamond surface and tube axis in SCNT−

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hydrogen-terminated diamond interfaces can restore the CNT's semiconducting behavior. Therefore, it is possible to form a metal−semiconducting CNT contact with a single SCNT deposited on the diamond surface if a region under the influence of a electric field (or a gate potential) is provided. We observed that the size of the band gap of SCNT−diamond interface increases continuously with increasing field. The value of the electric field required to restore the tube's semiconducting behavior is between 0.03 and 0.035 V/Å. Because one of the dimensions of the nanotube−diamond system can be of the order of a few nanometers, the applied potential required to produce such a value of electric field can be of the order of 1 V (the same order of the gate potential applied in operational hydrogen-terminated diamond FETs[9]), which may make viable the production of FETs at nanometric scale. Some aspects of the contact morphology, such as surface termination (H or OH-terminated diamond) and the presence of substitutional nitrogen dopant atoms on the electronic structure, are also studied. Also, the effects of the thickness of the diamond film on the electrical behavior of the SCNT−hydrogen-terminated diamond interface is addressed.

METHODS

Our first-principles methodology is based on the density functional theory (DFT) as implemented in the SIESTA program.[10] We used the generalized gradient approximation (GGA) as parametrized in the Perdew−Burke−Ernzerhof scheme (PBE)[11] for the exchange-correlation functional. The ionic core potentials were represented by norm-conserving scalar relativistic Troullier−Martins[12] pseudopotentials in Kleinman−Bylander nonlocal form.[13] The fineness of the real-space grid integration was defined by a minimal energy cutoff of 150 Ry.[14] Other values of energy cutoff (200 and 250 Ry) were tested. However, we found that the electronic structure, the focus of the present work, shows no significant change. Along the tube axis, the difference between lattice parameters of the tube's unit cell (4.32 Å) and the diamond's unit cell (4.38 Å) is 1.3%, which leads to a small strain on the CNT. Nevertheless, such a value of strain has a small effect on the electronic structure of the (10,0) SCNT.[15] Besides, the same geometry and methodology were able to predict the existence of the broken-gap heterojunciton, which was confirmed experimentally.[8] The other dimensions of the supercell, 16.6 × 45 Å, used to represent the (10,0) SCNT on diamond (see Figure 1), were large enough to avoid interactions between SCNT and its periodic image. To sample the respective reciprocal Brilloin zone, a 16 × 4 × 1 Monkhorst−Pack grid was employed. In the case of the (20,0) tube, a 4.38 × 30.6 × 45 supercell was employed. In the case of nitrogen-doped diamond, the employed supercell was twice as large, along the tube's axis, as the described supercell. A larger cell was required to avoid interactions between the dopant atom and its periodic image. The geometries were fully optimized using the conjugate gradient algorithm[16] until all the force components were smaller than 0.04 eV/Å. The Kohn−Sham (KS) eigenfunctions were expanded as a linear combination of pseudo atomic orbitals of finite range (PAO). In the case of C atoms, the PAO basis set consists of double-ζ radial functions per angular momentum (DZ). In the case of N, O, and H atoms, the PAO basis set is composed of double-ζ radial functions per angular momentum plus polarization orbitals (DZP). The range of each atomic orbital was determined by a common confinement energy-shift of δE = 0.01 Ry.[17] The orbital confinement tends to shift the energy eigenvalues upward;[18] however, it does not change single-particle band gaps. The smearing of the electronic occupations is done using using an energy width of 5 meV.

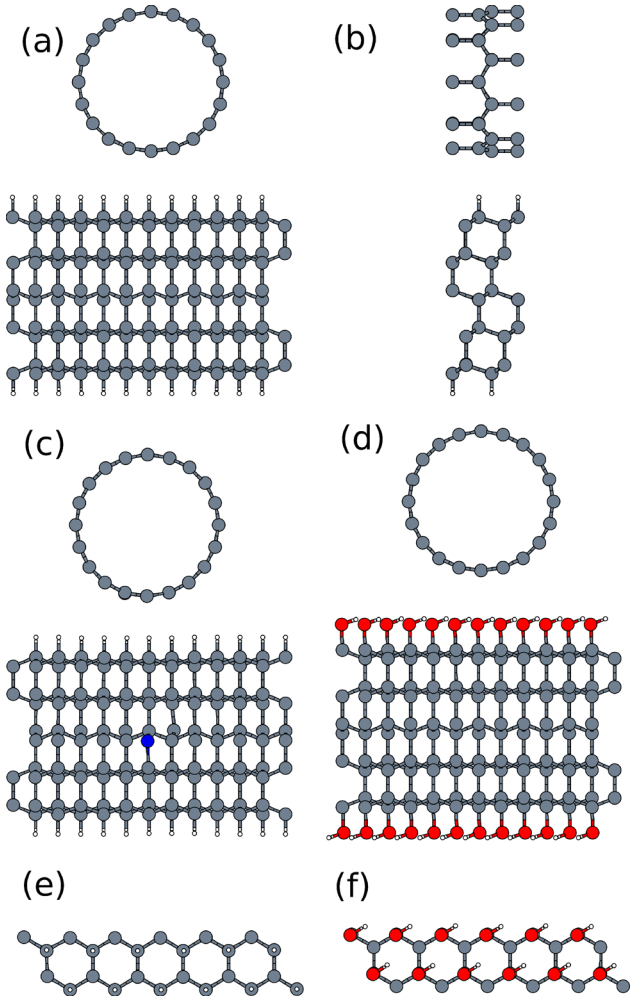

Figure 1. Geometry of the used supercells. Panels a and b show the front and side views of a (10,0) SCNT on hydrogen-terminated diamond, respectively. Panel c shows an N-doped system in which a carbon atom was replaced by nitrogen. Panel d shows the (10,0) SCNT atop OH-terminated diamond. Panels e and f show the optimized surface layer of H-terminated diamond and OH-terminated diamond, respectively.

RESULTS AND DISCUSSION

Panels a and b of Figure 1 show the front and side view of our model, respectively, representing SCNT on H-terminated diamond which consists of five layers of (111) diamond passivated with H at the ends plus a (10,0) SCNT. We found that the 3D/1D broken gap heterojunction is not formed if the diamond film is less the four layers thick. In the case of a SCNT deposited on graphane, a band gap of 0.75 eV, essentially the band gap of the (10,0) SCNT, is observed. The band gap decreases inasmuch as the number of layers increases from one to four, which suggests that the overlap between opposing surface orbitals affects the electronic structure. Other theoretical works indicate that a minimum of four layers is required to prevent the overlap between states of opposing surfaces in similar sp^3 films.[19,20] The band structure of the SCNT deposited on five-layered H-terminated diamond is

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shown in the left panel of Figure 2. It is useful to interpret such a band structure in terms of the superposition of the band

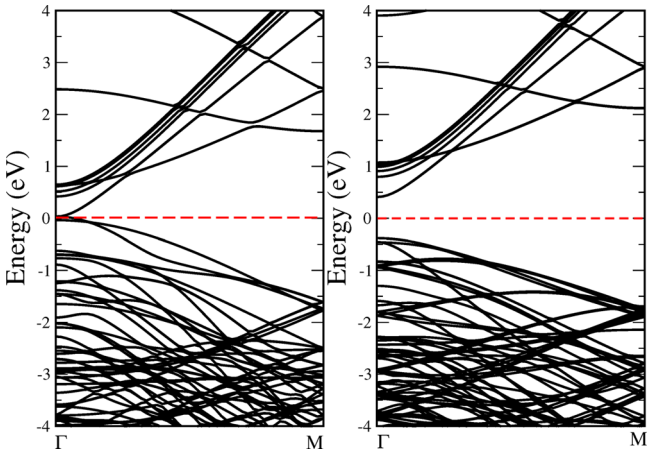

Figure 2. Left panel: band structure of a (10,0) SCNT atop H-terminated diamond. Right panel: band structure of a (10,0) SCNT atop OH-terminated diamond. In both panels the Fermi level was set to zero.

structure of its parts, the (10,0) SCNT and the H-terminated diamond. Such an interpretation is adequate because (except for the band alignment) the band structure of the parts remain essentially unaltered in the whole system.[8] The top of the diamond valence bands (bands with negative curvature) crosses the bottom of CNT conduction bands (bands with positive curvature). Because of the overlap of those bands, the hydrogen-terminated diamond transfer electrons to the tube forming an electron channel at the CNT and a hole channel at the diamond surface. Such a 3D/1D broken gap heterojunction has been confirmed by atomic force microscopy measurements in a recent theoretical and experimental work[8] which employed the same DFT-based methodology employed in this work. (It is well-known that GGA-PBE calculations underestimate the band gap of freestanding SCNTs. However, the calculations can produce reasonable results if the tube is near a surface. For instance, the band gap of a (10,0) CNT in contact with a metallic surface predicted by a recent GW calculation is 1.1 eV.[21] Such a value is in agreement with the band gap (or pseudoband gap, because it is below the Fermi level) of the tube in contact with hydrogenated diamond (0.9 eV) calculated using the same DFT methodology employed in this work.[8]) A natural question that arises from that result is can an electric field pointed from the diamond surface to the tube move the electrons back to the diamond and then restore the CNT semiconducting behavior? As will be shown, such a field can indeed restore the semiconducting behavior of the (10,0) and (20,0) nanotubes. Thus, it is possible to form a nanotube metal−semiconductor junction by the simple deposition of a semiconducting nanotube on hydrogen-terminated diamond, provided that there exists a region under the effect of an electric field. Fortunately, diamond itself is a very stable wide gap insulator and an excellent heat conductor, which makes it the ideal material to be used as insulating layer in field-effect devices. In fact, since the 1980s, field-effect transistors based on diamond have been produced,[3,9,22,23] and in recent years, efficient field-effect transistors based on hydrogen-terminated diamond have been produced also.[9]

The top panels of Figure 3 show that a constant electric field (along the direction perpendicular to the diamond surface and

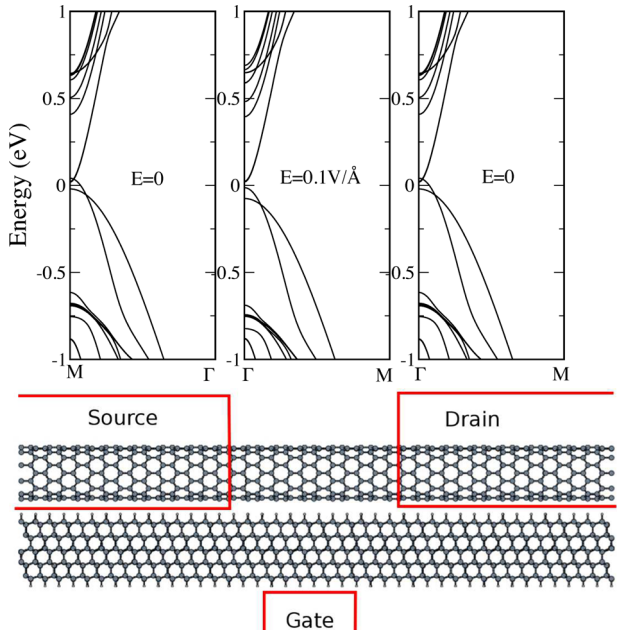

Figure 3. Top panels: band structure of a (10,0) SCNT atop H-terminated diamond. The middle panel shows the effect of an electric field along the z direction, perpendicular to the tube axis and to the surface. The bottom panel shows the geometry of metal−semiconducting junction made by SCNT atop H-terminated diamond. The SCNT presents a semiconducting behavior in the region under the influence of an electric field, which could be supplied by the gate potential, and a metallic behavior for the rest (in analogy with a FET, we call the metallic parts source and drain). The H-terminated diamond also works as an insulating layer between the gate and the conduction channel.

to the tube axis, namely z direction) can open a band gap in the heterojunction electronic structure. In the figure, positive values of electric field stand for fields pointing from the diamond to the tube. In the same figure, we show the geometry of a semiconducting nanotube deposited on hydrogen-terminated diamond working as a metal−semiconductor junction. In analogy with a FET, we call the metallic parts (below the left and right panels) source and drain. The electric field responsible for the semiconducting region (below the middle panel) can be supplied, in principle, by a gate potential in contact with the diamond that works as the insulating layer. A more detailed picture of the effect of the electric field on the heterojunction electronic structure can be seen in Figure 4, which shows the band gap as a function of the applied electric field. For small values of the field, the constant electric field can be seen as a perturbation to the system Hamiltonian ($H' = -qEZ$). The first-order correction to the energy eigenvalues is $-qE\langle Z\rangle$. Therefore, a linear dependence of the heterojunction band gap as a function of the applied electric field is expect for small values of field because the lowest unoccupied states (due to the SCNT) and the highest occupied states (due to the H-terminated diamond) are displaced along the z direction. Such a linear behavior can be seen in Figure 4 for values of applied electric field smaller than 0.2 V/Å for the (10,0) nanotube and for fields smaller than 0.045 V/Å for the (20,0) nanotube. For larger field values, a higher-order dependence is observed. It is possible to see in Figure 4 that the metal−semiconductor

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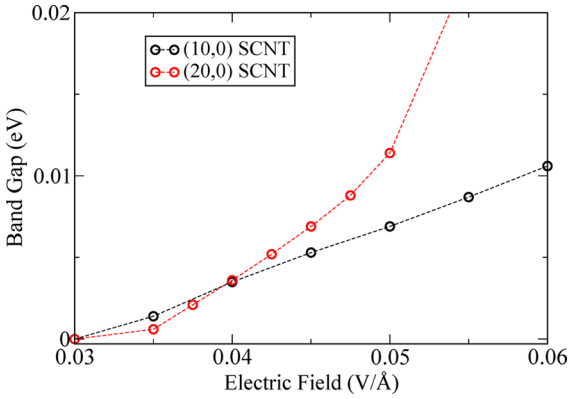

Figure 4. Band gap as a function of the applied transverse electric field. Metal−semiconductor transition occurs for values of field between 0.03 and 0.035 V/Å. For both studied tubes it is possible to see a linear behavior for small values of fields that is consistent with first-order perturbation theory.

transition must occur for values of applied field between 0.03 and 0.035 V/Å. Because the cell is only 45 Å thick along the z direction, a constant field of 0.03 V/Å implies a gate voltage of roughly 1.35 V is required to make a FET device based on SCNT−diamond heterojunction operational, which is the same order of gate voltages applied in real H-terminated FETs.[9]

In spite of the excellent agreement with experiments,[8] the model employed here to represent the diamond surface in Figure 1 is indeed a simplified view of the real diamond surface, which could present several kinds of defects, reconstructions, and different surface terminations.[24] Thus, the agreement with experiment indicates that the electronic structure of the bulk diamond and tube play the main role in the formation of the 3D/1D broken gap heterojunction and that the details of surface morphology are not so important. Such a hypothesis is worth addressing because surface characteristics can be difficult to predict and control. To address such a hypothesis, we first have changed the surface termination; the (10,0) SCNT was deposited on OH-terminated diamond. Such a choice was motivated by the premise that a very electronegative termination could prevent the electron transfer from diamond to the tube and then the formation of the 3D/1D broken gap heterojunctions. Then, we changed the diamond bulk; the (10,0) SCNT was deposited on nitrogen-doped diamond passivated with H or OH. This choice was motivated by previous scanning probe microscopy experiments[8] in which a nitrogen-doped tip (whose surface morphology was unknown) was employed. As will be shown, in the case of nitrogen-doped diamond, the 3D/1D broken gap heterojunctions are formed even if the surface termination is very electronegative, which is consistent with experiment.[8]

Because the electron transfer from diamond to the tube gives rise to the broken gap heterojunction, it is reasonable to think that an electronegative termination would prevent the formation of the broken gap heterojunction. Figure 1 shows the geometry of the (10,0) nanotube deposited on OH-terminated diamond. We found that a 3D/1D broken gap heterojunction is not formed in this case; instead, it can be seen that a band gap of roughly 0.8 eV in the band structure of a (10,0) nanotube is deposited on OH-terminated diamond (Figure 2, right panel). Such a result suggests that other electronegative diamond terminations, such as fluorine or oxygen, may also prevent the formation of broken gap heterojunctions. Thus, a metal−semiconductor junction could be formed using a single SCNT deposited on diamond provided that there exist regions passivated with hydrogen and passivated with electronegative species. In such a metal−semiconductor junction, the contact resistance may not exist.

Figure 1c shows an N-doped system in which a carbon atom was replaced by nitrogen. (To avoid interactions between nitrogen orbitals and orbitals of its periodic images, we used a supercell twice as large, along the tube direction, as those used to represent SCNT atop H and OH-terminated diamond.) The nitrogen atom introduces localized states in the large band gap of diamond which crosses the SCNT conduction bands. Such localized states can be recognized as the dispersionless band near the Fermi level in Figure 5, which shows the band

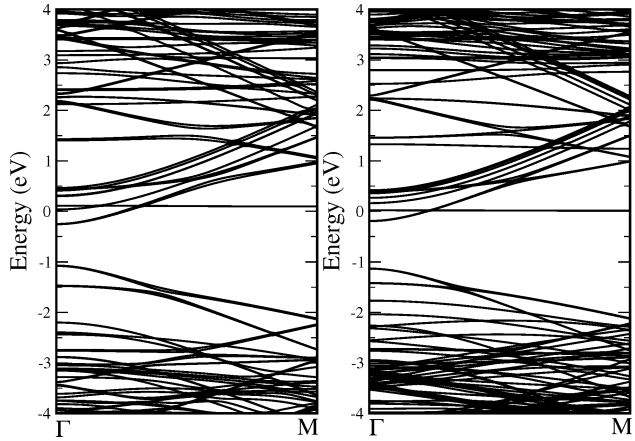

Figure 5. Left panel: band structure of a (10,0) carbon nanotube atop nitrogen-doped H-terminated diamond. Right panel: band structure of a (10,0) nanotube atop nitrogen-doped OH-terminated diamond. Both panels show a low dispersion nitrogen occupied state crossing the (10,0) nanotube conduction band near the Fermi level, which was set to zero.

structure of N-doped diamond terminated with either H and OH (left and right panels, respectively). Both panels show essentially the same band structure, which indicates that the surface termination does not strongly affect the electron states near the Fermi level. Instead, those states are determined by SCNT conduction states and nitrogen valence states. Such a result is consistent with experiment[8] and interesting for potential applications to devices because it suggests that the surface morphology, which can be difficult to control and predict, may not be crucial for the 3D/1D heterojunction electronic properties. Both SCNT−nitrided diamond studied junctions present free electrons in the nanotube and holes localized in the nitrogen impurities. Such a behavior is distinct from that of nondoped H-terminated diamond−SCNT junctions in which free charges of opposite signs exist in each side of the junction.[8]

CONCLUSIONS

In summary, we found that a small perpendicular electric field, above 0.03 eV/Å, can restore the semiconducting behavior of SCNT atop H-terminated diamond. Therefore, it is possible to form a 3D/1D metal−semiconductor junction with a single SCNT atop hydrogen-terminated diamond if an electric field is provided. In addition, we found that the size of the band gap changes continuously with the applied field, which is highly

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desirable for optical applications. In the case of SCNT deposited on nitrided diamond, 3D/1D broken band gap heterojunctions are formed for both investigated surface terminations (OH- and H-terminated diamond). For nondoped systems, the surface termination may prevent the formation of 3D/1D broken gap heterojunction if a full surface coverage with a very electronegative species is provided.

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Notes

The authors declare no competing financial interest.

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