Formation of a *p*-type quantum dot at the end of an *n*-type carbon nanotube

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We use field effect doping to study both electron- (n) and hole- (p) type conduction in a semiconducting carbon nanotube. We find that, in the n-type region, the ends of the tube remain p-type due to doping by the metal contacts. As a result, a $p-n$ junction forms near the contact, creating a small, p-type quantum dot between the $p-n$ junction and the contact. This zero-dimensional quantum dot at the end of a one-dimensional semiconductor is the reduced dimensional analog of the two-dimensional inversion layer that forms at the boundary of a gated three-dimensional semiconductor. © *2001 American Institute of Physics.*
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Semiconducting single-wall carbon nanotubes (SWNTs) have emerged as the prototypical one-dimensional (1D) semiconductor.[1,2] They were initially shown to operate as hole (p-type) field-effect transistor (FET) devices,[3,4] with the metallic contacts serving as p-type contacts to the 1D hole gas. Subsequently, electron-donating dopants such as potassium were used to create electron doped (n-type) devices and $p-n$ junctions.[5–8] The initial signatures of n-type behavior have been seen in previous experiments on strictly field-effect (gated) devices,[9] but there has not been a systematic study of both p- and n-type behavior using only field-effect doping.

Here we use a gate to study both p- and n-type transport in the same device. Transport in the p-type region at low temperatures shows Coulomb blockade behavior consistent with electrons confined to a 1D box by tunnel barriers at the end of the tube, with the states delocalized over the entire length of the tube.[10,11] In the n-type region, the conductance is much lower. Surprisingly, we observe Coulomb blockade corresponding to two dots, one with a very large charging energy. We attribute this behavior to the formation of $p-n$ junctions in the tube between regions doped p-type by the contacts and n-type by the gate. A small dot is formed in this p-type region between the contact and the $p-n$ junction.

The device consists of a SWNT grown by chemical vapor deposition (CVD).[12] After the growth step, appropriate tubes are located using an atomic force microscope (AFM). Electron beam lithography and liftoff are then used to pattern Au electrodes to the nanotube.[10] A schematic diagram of the resulting device is shown in the upper inset to Fig. 1. The lower inset to Fig. 1 shows the current (I) through the nanotube versus the gate voltage (V_g) and source drain bias (V). The large dark region in the center corresponds to the Fermi level in the band gap of the tube. The region on the left-hand side corresponds to p-type conduction, while the data on the right-hand side corresponds to n-type conduction. These regimes are illustrated schematically in Fig. 2.

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We begin by discussing the p-type region. At low temperatures, Coulomb oscillations are seen [Fig. 2(c)] with a period in gate voltage $\Delta V_g \sim 9$ mV. Using standard Coulomb blockade analysis of linear and nonlinear transport,[13] we can determine the charging energy, $U = 3$ meV, and barrier resistances, R(right-hand side) ~ 1 MΩ and R(left-hand side) < 100 kΩ. The capacitive couplings of the nanotube quantum dot to the gate, right-hand side and left-hand side electrodes are 18 aF, 15 aF, and 16 aF, respectively. These measurements indicate that the entire 1.5 μm long nanotube acts like a single quantum dot with tunnel barriers for entering and exiting the tube. This behavior has been seen previously in long metallic nanotubes.[10,11] Furthermore, the right-hand side tunnel barrier is observed to be the dominant one. Because of the small charging energy, at temperatures higher than 5 K, the Coulomb oscillations were washed away, and the linear conductance showed almost no gate dependence, except very near turn off. (Fig. 1)

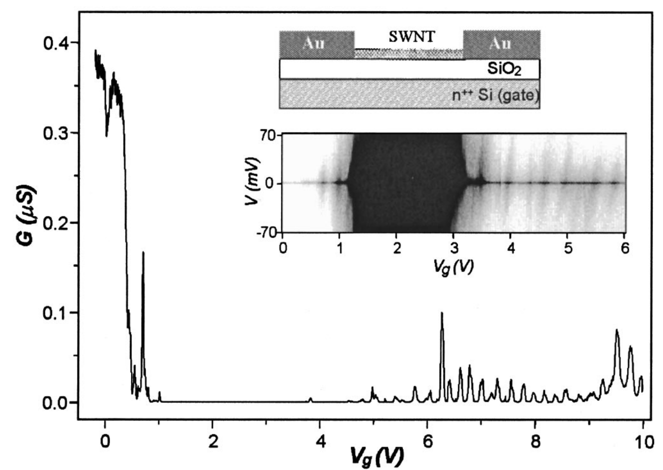

FIG. 1. Conductance as a function of the gate voltage (V_g) at 30 K is shown. Coulomb oscillation peaks are observed when $V_g > 3$ V (n type). Upper inset shows a schematic diagram of the device. The thickness of the insulating silicon oxide layer is 500 nm. Lower inset shows current as a function of the bias (V) and the gate voltage measured at 77 K. Current is zero for black regions and the maximum (100 nA) for white regions. A nonconducting band gap region (black) separates the p-type (left-hand side) and n-type (right-hand side) region.

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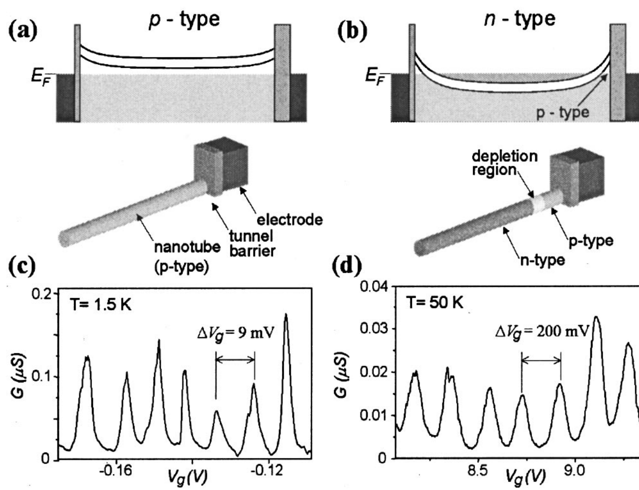

FIG. 2. Band diagrams and schematic pictures of a semiconducting nanotube device when it is field doped (a) p type and (b) n type are shown. Note that the right-hand side barrier is thicker than the other. (c) Coulomb oscillations are in the p-type regime at 1.5 K. The gate period is 9 mV. (d) Coulomb oscillations are in the n-type regime at 50 K. The gate period is approximately 200 mV.

We now turn to n-type operation. The device conducts in this region, but with a conductance that is a factor of 5–10 smaller. Most surprisingly, Coulomb oscillations with much larger gate voltage period, $\Delta V_g \sim 200\,\mathrm{mV}$, are observed, as seen in the main panel of Fig. 1. These oscillations are well defined at 30 K, long after the Coulomb oscillations observed in the p-type region have been washed out, and persist to $\sim 100\,\mathrm{K}$. This, combined with nonlinear measurements such as those shown in Fig. 3, yields a charging energy of approximately 50 meV. This indicates the presence of a quantum dot approximately ten times smaller than the one formed in the p-type region.

The n-type behavior just described can be easily understood using the band diagrams in Fig. 2. At large positive V_g, the center of the tube is electrostatically doped n type. However, the contacts still dope the ends of the tube p- type and screen out the effects of the gate. The net result is the formation of a small p-type quantum dot at the end of the nanotube. It is confined on one side by the tunnel barrier to the metallic electrode and on the other by the depletion region between the p- and n-type regions of the nanotube. In general, we expect the formation of two end dots, one at each end of the nanotube. However, the transport properties shown above can be understood by considering only one end dot. This is because the tunnel barrier to the right-hand side contact is much larger than the one to the left-hand side contact (as determined from measurements in the p-type region previously discussed). As a result, the p-type dot formed at the right-hand side high resistance contact dominates transport. The dot at the left-hand side contact is well coupled to the electrode and effectively behaves like an extension of the electrode under most circumstances.[14–16] From the measured charging energy and period in V_g, we estimate the size of the end dot to be $\sim 100\,\mathrm{nm}$. A theoretical estimate of the size of this dot would require detailed modeling, but this size is roughly consistent with the distance to the gate divided by the dielectric constant of SiO_2, $d \sim (500\,\mathrm{nm})/3.8 \sim 130\,\mathrm{nm}$.

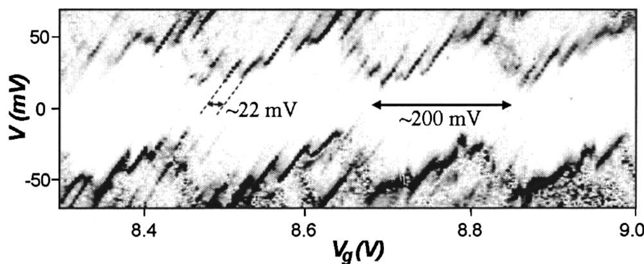

FIG. 3. Differential conductance plot as a function of V and V_g in the n-type regime is shown. The conductance is zero for white regions and the maximum conductance (black) is 0.1 μS. Two periodic features are present. There are Coulomb diamonds with a charging energy $\sim 50\,\mathrm{meV}$ and a gate period $\Delta V_g \sim 200\,\mathrm{mV}$. Along the edge of these diamonds, another periodic feature with $\Delta V_g \sim 22\,\mathrm{mV}$ period is observed. This corresponds to single-electron charging of the main nanotube dot.

We note that similar behavior—the formation of a large charging energy quantum dot—has recently been reported in two experiments on potassium doped devices.[7,8] The tentative explanation given was an inhomogeneous-doping-induced dot formed within the tubes. This explanation is highly unlikely in our case because no dopants were used in the experiment. Furthermore, local potential variations induced by chemical inhomogeneity or impurities are not likely to explain our data, for two reasons. The first is that the measurements in the p-type region show that there are no large scattering centers along the length of the tube. Second, the persistence of the Coulomb oscillations over a very wide range in V_g (see Fig. 1) is inconsistent with a quantum dot formed in a shallow potential minimum. Indeed, we believe that the physical origin of the dots observed in the previous experiments is the same as that found here. The contacts doped the end of the tube p- type, while the potassium doped the remainder n- type, forming an end dot. This model thus provides a simple and consistent picture of all of the experiments to date on n-type samples.

Other consequences follow from the picture of the nanotube in the n-type region represented in Fig. 2(b). In addition to the p-type dot at the end, we would expect a longer, n-type dot to be formed in the center of the tube. Indeed, low-T measurements reveal a clear signature of a second dot in series with the first. This is evident from the data in Fig. 3, where a gray scale plot of the differential conductance versus V and V_g at $T = 1.5\,\mathrm{K}$ is shown. The boundary of the large Coulomb gap associated with the end dot exhibits a sawtooth structure, and a series of lines are observed with a periodic spacing in $\Delta V_g \sim 22\,\mathrm{mV}$. Note that these lines are not parallel to the boundaries of the Coulomb blockade diamonds. This indicates that they are not excited states of the small dot, but rather associated with charging of a second, larger dot in series with the first. Transport through the device is thus dominated by Coulomb charging through two dots in series, with one dot approximately ten times larger than the other. The period in V_g of the larger dot is of the same order of magnitude of that observed in the p-type region, again indicating that it arises from the large n-type center portion of the tube.

Two quantum dots in series have been widely studied in previous experiments on lithographically patterned dots.[13] A number of phenomena, such as negative differential resis-

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tance (NDR) due to the alignment of the energy levels of the two dots, have been observed. We indeed observe dramatic NDR in this device (not shown), further supporting the overall picture outlined here. These results will be presented in a separate publication.

These experiments demonstrate that a zero-dimensional (0D) quantum dot can be electrostatically formed at the end of a one-dimensional (1D) semiconductor. This is the final step in a now well-established trend in semiconductor physics. Two dimensional electron gases at the boundary of three-dimensional semiconductors (e.g. metal–oxide–semiconductor FETs) are well known,[17] and are of tremendous fundamental and practical interest. 1D electron gases have also been created at the edge of two-dimensional systems.[18] Continuing this trend to 0D provides a simple and controlled way to create a very small quantum dot at the end of a 1D semiconductor. We expect that it will have applications in many areas, including high-temperature Coulomb blockade devices, the creation of multiple-dot structures, and scanned probe systems where a quantum dot is formed at the end of a nanotube AFM tip.

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