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Transition of Single-Walled Carbon Nanotubes from Metallic to Semiconducting in Field-Effect Transistors by Hydrogen Plasma Treatment

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ABSTRACT

We report hydrogen plasma treatment results on converting the metallic single-walled carbon nanotubes to semiconducting single-walled carbon nanotubes. We found that the as-grown single-walled carbon nanotubes (SWNTs) can be sorted as three groups which behave as metallic, as-metallic, and semiconducting SWNTs. These three groups have different changes under hydrogen plasma treatment and successive annealing process. The SWNTs can be easily hydrogenated in the hydrogen plasma environment and the as-metallic SWNTs can be transformed to semiconducting SWNTs. The successive annealing process can break the C−H bond, so the conversion is reversible.

Since Iijima discovered the carbon nanotube in 1991,[1] carbon nanotubes have attracted more and more attention because of their unique one-dimensional structure and attractive electrical, mechanical, and chemical properties, out of which many promising technological applications have been demonstrated. One of the most important applications is to form electronic devices such as field-effect transistors based on carbon nanotubes (CNTFETs)[2] and single-electron transistors.[3] But there are two key problems that block serious consideration of CNTs in nanoelectronics. One is to realize the integration of these devices at wafer scale, and the other remains in the growth area, such as the yield of a mixture of metallic and semiconducting single-walled carbon nanotubes (SWNTs) by many synthesis methods.[4−6]

The metallic SWNT can be used as an interconnection element but not desired for CNTFETs potential application. Many efforts have been carried out to selectively deposit semiconducting or metallic SWNTs for device application. Some approaches are to sort and separate these two types of nanotubes by selectively functionalizing CNTs.[7] But this method is not compatible with the integrated circuit process, and the effect of the chemical solution is uncertain. It will change the intrinsic properties of CNTs. Other efforts have been done on selective growth of semiconducting SWNTs(S-SWNTs),[8,9] electrical breakdown of metallic CNTs,[10,11] or converting the metallic CNTs to semiconducting CNTs through electron irradiation.[12,13] But the mechanism of electron irradiation changing the electrical property of SWNTs is not clear and the size of the electron beam is so small that this method cannot be used for real device application. Another reported approached is that the metallic CNTs can be easily etched and only semiconducting CNTs retained under hydrogen plasma treatment.[14−16] But when the metallic SWNT was etched, one cannot ensure that

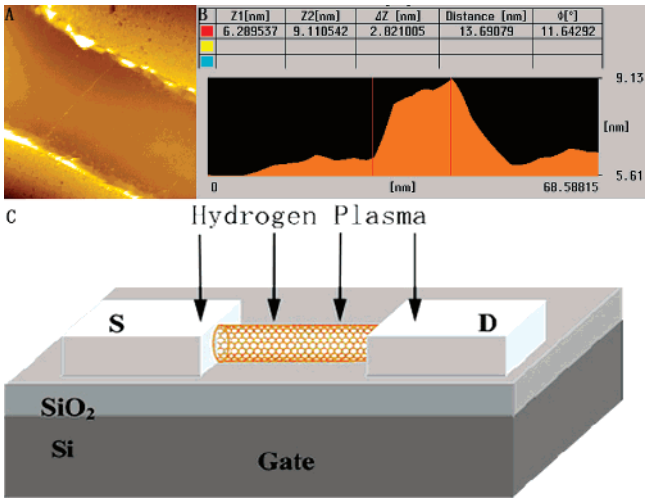

Figure 1. (A) An AFM image of a SWNT between the electrodes. (B) Height profile shows the diameter of the SWNT. (C) Schematic of hydrogen plasma treatment on the device.

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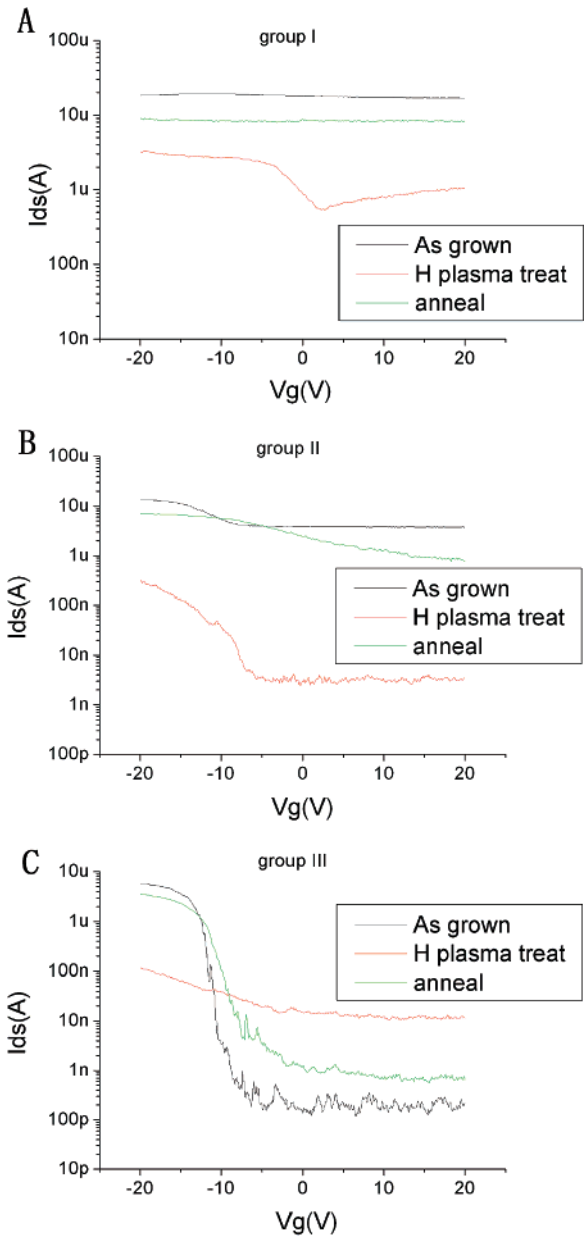

Figure 2. Current (I_{ds}) vs gate voltage (V_g) characteristics (V_{ds} = 1 V) for three different SWNT device groups before and after hydrogen treatment and annealing process: (A) a typical result for group I, retained as a metallic SWNT after H plasma treatment; (B) a metallic SWNT converts to semiconducting SWNT after hydrogen treatment and changed back to metallic SWNT after annealing at 700 °C; (C) the effect of hydrogen plasma and annealing process on an as-grown semiconducting SWNT, a typical result for group III.

S-SWNTs remain defect free. And when the metallic SWNTs were removed, the yield of the SWNT-based devices was obviously descended.

Here we report our experimental result on hydrogen plasma treatment on SWNTs. By carefully controlling the hydrogen plasma, we found that the as-grown metallic SWNTs can be converted to semiconducting CNTs and this conversion is reversible by a standard annealing process. The reversible property of these CNTs showed that it is the hydrogenation that caused this change and the CNTs were

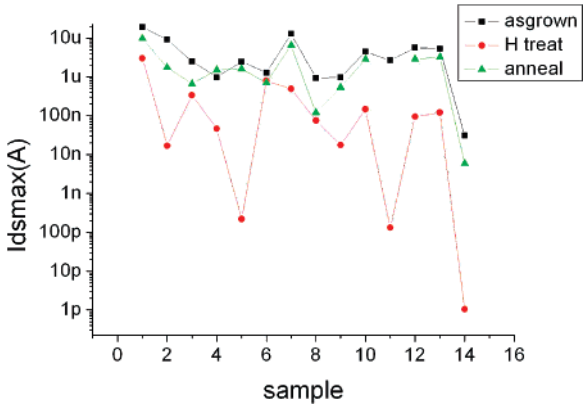

Figure 3. The maximum current, I_{dsmax}, which identifies the current-carrying ability when the CNTFETs are ON for different samples before hydrogen treatment, after hydrogen treatment, and after the annealing process.

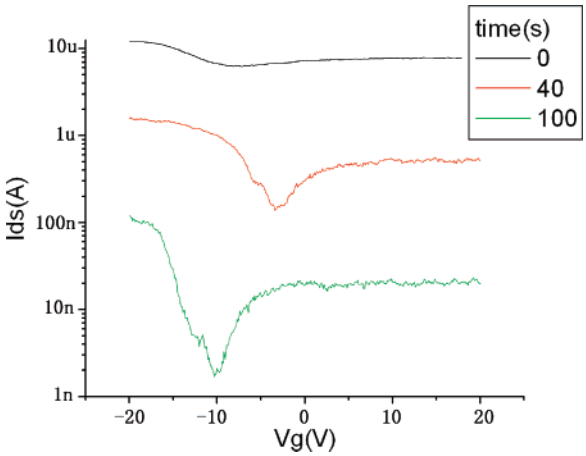

Figure 4. Current (I_{ds}) vs gate voltage (V_g) characteristics (at V_{ds} = 1 V) of the sample after different hydrogen plasma process time (rf power 60 W, H_2 400 sccm, pressure of the chamber 70 Pa).

not destroyed, or in other words defects were not introduced by this controllable process.

The SWNT devices we used in this work were obtained through the following steps. Catalyst islands, with a bilayer structure of MgO(10 nm)/Fe(1 nm), were fabricated by photolithography, E-Beam evaporation, and a lift-off process on p-doped silicon substrate with a thick layer of thermally grown silicon dioxide, on which 100 μm strips were first patterned by wet etching of SiO_2 to serve as gate structure. A low-pressure chemical vapor deposition (CVD) system was employed to grow the SWNTs, which were confirmed by atomic force microscopy (AFM) with a diameter distribution of 0.5−2.8 nm (parts A and B of Figure 1). Finally a third photolithography step was carried out to pattern the source and drain electrodes on top of the catalyst island, followed with a metal deposition and lift-off process. An annealing process was first carried out to make the SWNTs have a better electrical contact with electrodes. Then the devices were treated by hydrogen plasma as shown in Figure 1C in a commercial plasma-enhanced chemical vapor deposition chamber. At last the samples were annealed in a low-pressure system with argon protected at 600−700 °C for half an hour. The electrical properties of these devices were measured with

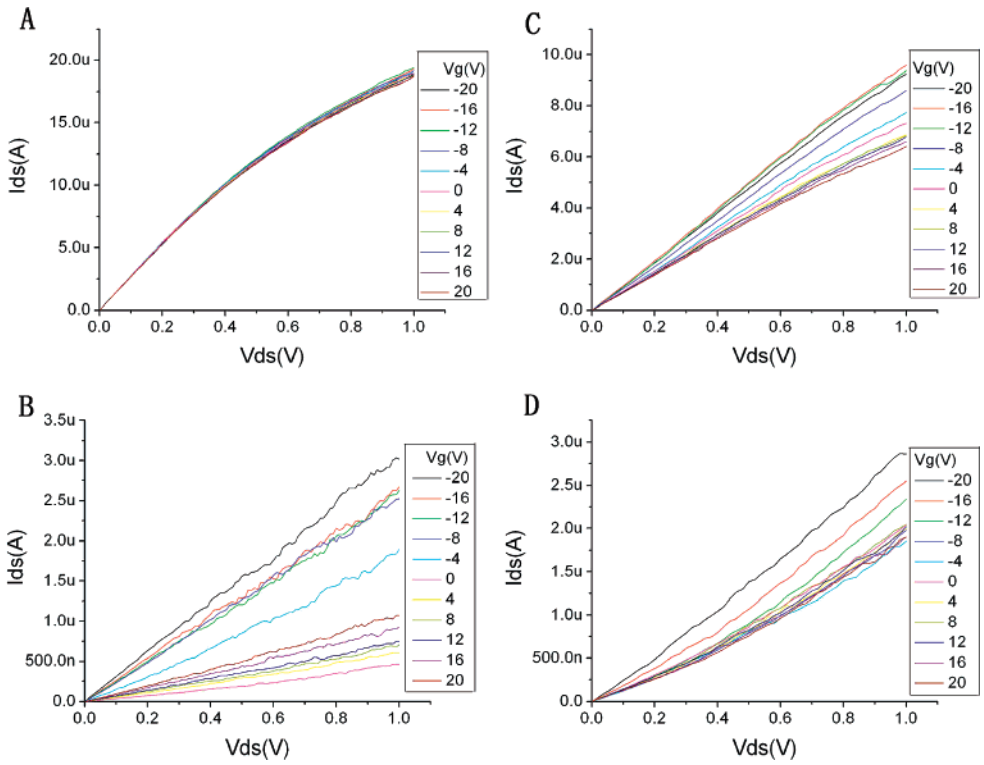

Figure 5. Current (I_{ds}) vs bias voltage (V_{ds}) characteristics for two samples under different hydrogen plasma power condition: (A, C) the $I-V$ curve of the as-grown SWNTs; (B) the $I-V$ curve of the SWNT in sample A treated at 200 W for 20 s; (D) the $I-V$ curve of the SWNT in sample C treated at 60 W for 20 s.

Agilent 4156 and Keithley 4200 on a Cascade four-probe station before plasma treatment, after treatment, and after annealing as comparison.

The electrical properties of as-grown SWNTs were different from each other. Among the hundreds of devices we have measured, we found the devices can be divided into three groups: (a) For the first group, there's almost no gate modulation effect in the as-grown SWNT, which is at a given bias voltage (1 V in our study) and gate voltage sweeping from −20 to 20 V the maximum current (I_{dsmax}) and the minimum current (I_{dsmin}) are almost the same. The SWNTs in this group are obviously metallic SWNTs. The electrical results show the hydrogen treatment has less effect on these CNTFETs. The on/off ratio (I_{dsmax}/I_{dsmin}) had some changes but remained smaller than 3 after treatment. The successive annealing process in Ar atmosphere at 600 °C retracted their on/off ratio to their initial value. Figure 2A gives a typical $I_{ds}-V_{gs}$ characteristic for such kinds of SWNTs. (b) For the second group (as shown in Figure 2B), the on/off ratio of the as-grown SWNT is smaller than 10 but bigger than 3. The hydrogen treatment showed a very obvious effect with on/off ratio changed to 100−1000, which realized a conversion from metallic SWNT to semiconducting SWNT. And the successive annealing process at 600 °C kept this conversion result with on/off ratio as 100−1000. Only when we further increased the annealing temperature to 700 °C did the SWNT change back to metallic SWNT. (c) For the third group (Figure 2C), the as-grown SWNTs behave like semiconducting SWNTs. The hydrogen treatment to this group showed a little bit different effect. The treatment lowered their on/off ratio from >100 to >10. But the successive annealing process repaired the semiconducting SWNT by raising their on/off ratio to >1000.

Moreover the current-carrying ability of all these three groups was weakened by hydrogen treatment but can be recovered by the successive annealing process. Figure 3 shows the maximum current I_{dsmax}, which identify the current-carrying ability when the CNTFETs are in the on state, for different samples before hydrogen treatment, after hydrogen treatment, and after annealing process. We can see some of the samples have a large current drop after hydrogen treatment, which almost makes us believe that the device was destroyed by the hydrogen plasma, but the successive annealing process still can revive them. This result and the successive AFM investigation showed that the CNTs in our experiment have not been etched by the hydrogen plasma, no matter if the CNT has a large diameter (such as 2.8 nm) or a small diameter (such as 0.5 nm). This may due to the controllable plasma power and relative short treatment time we used.

According to the diameter and chirality, SWNTs have different structures with different electrical properties. Because of the π-bond of the SWNT, the SWNT can be easily hydrogenated, which is more stable.[17−19] An annealing process can break the C−H bond at 600 °C or at a higher temperature.[20] According to the calculation results,[17] the hydrogenation brings an important change of the SWNT. As the sp^2 C−C bond changed into an sp^3 C−C−H bond, the structure and energy level of the SWNTs changed.[17,18] For example a bare (9,0) SWNT is metallic with no gap in its bond structure. But when it absorbs hydrogen atoms, a different percentage of hydrogen coverage and hydrogen

position can cause different gaps in the bond structure. Hydrogen plasma offers hydrogen atoms around the SWNTs, which make the SWNTs easily absorb some hydrogen at room temperature.[20] So hydrogen plasma treatment can cause the electrical properties of CNTs to change.[7] Our electrical measurement results of the first and second groups are consistent with these theoretical results that metallic SWNTs would open a gap when they absorb hydrogen atoms. But for the third group in our experiments, the semiconducting SWNT behaves a little bit abnormally, as if their gap would become smaller when they absorb hydrogen atoms. A further study including theoretical calculation is undergoing about this phenomenon.

On the other hand, there may be another reason that causes the electrical property change of the SWNTs. Hydrogen plasma also has a physical impact effect on the SWNTs which can cause defects of the SWNTs. Defects can change the structure, and these changes can cause a great change of the electrical properties of SWNTs. But the main energy of the hydrogen in the plasma is 0.3 eV,[21] and the energy of the C−C bond is 3.6 eV. So the physical impact of the hydrogen plasma could not break the C−C bond. To prove this we performed a nitrogen plasma treatment as a contrast. Electrical measurement results showed that the nitrogen plasma did not cause any change even when we used a higher rf power (110 W) and a longer time (40 s) which can make a stronger bombardment than hydrogen atoms. So hydrogen absorption played an important role in our experiment. We believe that it is the hydrogenation that brings the important changes of electrical properties of these SWNTs.

It is reasonable to believe that by changing the rf power of hydrogen plasma and the time of treatment we can control the percentage of the hydrogen coverage. So the converting from metallic SWNTs to semiconducting SWNTs is controllable. Figure 4 shows the results of the sample that has been treated by H plasma at different process times. A longer process time will make the ON current of the SWNT device lower. Denser plasma should also have larger effect. Figure 5 shows the results of two samples that have been treated by hydrogen plasma with different rf powers. Parts A and B of Figure 5 show sample 1 before and after hydrogen plasma treatment separately, and parts C and D of Figure 5 show the results of sample 2. The current (at $V_{ds} = 1$ V) of the as-grown sample 1 is around 20 μA and on/off ratio is near 1. After 200 W/20 s of H plasma treatment, the current (at $V_{ds} = 1$ V) becomes 3 μA and on/off ratio is near 20. However, the current (at $V_{ds} = 1$ V) of the as grown sample 2 is around 10 μA and on/off ratio is near 1.2. After 60 W/20 s of H plasma treatment, the current (at $V_{ds} = 1$ V) becomes 3 μA and on/off ratio is near 1.5. So in this way we can control the electrical property of the SWNTs by adjusting the rf power and process time. We can adjust the gap to make it larger by a hydrogenation process and smaller by an annealing process.

In summary, we found that the as-grown SWNTs can be sorted into three groups which behave as metallic, as-metallic, and semiconducting SWNTs. These three groups have different behavior under hydrogen plasma treatment and the successive annealing process. The SWNTs can be easily hydrogenated in the hydrogen plasma environment. By controlling the rf power and process time of the hydrogen plasma, we can adjust the percentage of the hydrogen coverage; thus the gap of the SWNT could be created and enlarged. By the successive annealing process, the C−H bond could be broken; thus the gap could be eliminated.

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Supporting Information Available: TEM images of SWNTs fabricated under different conditions and Raman spectra showing SWNT samples with different diameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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