Controlled growth and electrical characterization of bent single-walled carbon nanotubes

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ABSTRACT

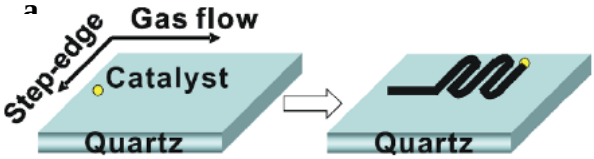
Single-walled carbon nanotubes (SWNTs) are grown with bent structure by controlling the interaction of gas flow and nanosized step-edges of single-crystal quartz. The frequency of bending is tailored by adjusting the angle between flow direction and step-edges on quartz substrate and the electrical resistance increases with the number of bends. The increase of resistance can be attributed to the introduction of hetero-junctions and topological defects at the turning points. Our results suggest the possibility of growing SWNTs with multiple bent geometries in a simple one-step process and integrating them into all-nanotube devices with different morphologies and tuned electronic properties.
Keywords: Bent SWNT, electrical property

INTRODUCTION

The unique electrical and mechanical properties of single-walled carbon nanotubes (SWNTs) make them one of the most promising candidates for next generation nanoelectronics. [1] For better utilization of SWNTs, it is very crucial to control the nanotubes growth direction (vertical, horizontal) and their morphologies (e.g., straight, junction, coiled). Horizontally aligned SWNTs growth has been demonstrated by applying electric field during growth, [2] using fast heating method [3] and ultra low gas flow method. [4] Recently, significant advance has been achieved in the horizontally aligned SWNTs growth on certain types of single-crystal substrates, including quartz [5,6] and sapphire. [7,8] Experimental and theoretical results have demonstrated that SWNTs can be synthesized along the thermally generated nanosized step-edges on the single-crystal substrates. Complex geometries, such as crossbar structure, have also been achieved by multi-step transfer of aligned SWNTs onto other substrates [6] or by applying electric-field during nanotube growth. [8] However, it is still challenging to achieve complex geometries for as-grown SWNTs. To integrate SWNTs into nanoelectronic circuit or nanoelectromechanical systems (NEMS), it is highly necessary to grow SWNTs with complex morphologies and functionalities. In this study, we demonstrate bending of SWNT during growth and the corresponding electrical characterization. The bend of SWNTs is controlled by using the combined effect from substrate step-edges and gas flow. The degree of bending is tailored by adjusting the angle between flow direction and step-edges on quartz substrate. SWNTs can be bent during growth using a simple one-step process without any further transfer process or external field assistance. The existence of negative curvature fullerene based units in bent SWNT morphologies necessitates the presence of topological defects - in the form of pentagons, heptagons and octagons - at the junction regions for maintaining a low energy sp^2 configuration. [9] With the presence of these intrinsic defects, chirality of bent SWNTs is changed across the junction and is expected to have unique electrical characteristics. This simple strategy sheds light on the complex geometry control of SWNTs and tailoring electrical property of SWNTs. This strategy can be extended for various nanowires or nanotubes on different single-crystal substrates.

EXPERIMENTAL DETAILS

The SWNTs were grown by thermal chemical vapor deposition (CVD) at 900 °C with CH_4 and H_2 (10-1400 sccm) as carbon feedstock and iron thin film (~0.3 nm) as catalyst. An ST-cut single-crystal quartz wafer was used as substrate and annealed at 900 °C for 8 hr to form nanosized step-edges. The angle between gas flow and step-edges was preset before CVD growth. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to study the morphology of SWNTs. The bent SWNTs were connected to Pd (50 nm) contacts by using electron beam lithography to study the electrical conductance change accompanying the multiple bends.



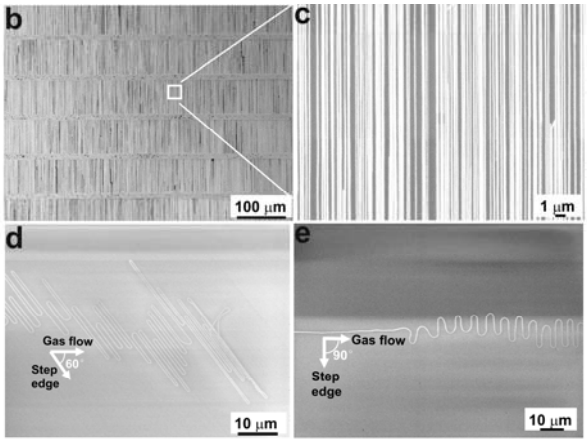


Figure. 1. (a) Schematic of bent SWNTs growth by tailoring the direction of step-edges and gas flow. (b, c) SEM images of highly aligned SWNTs grown at medium flow rate of 500 sccm. (d, e) SEM images of bent SWNTs grown at low flow rate of 10 sccm with different angles. The frequency of bending increased as the angle decreased.

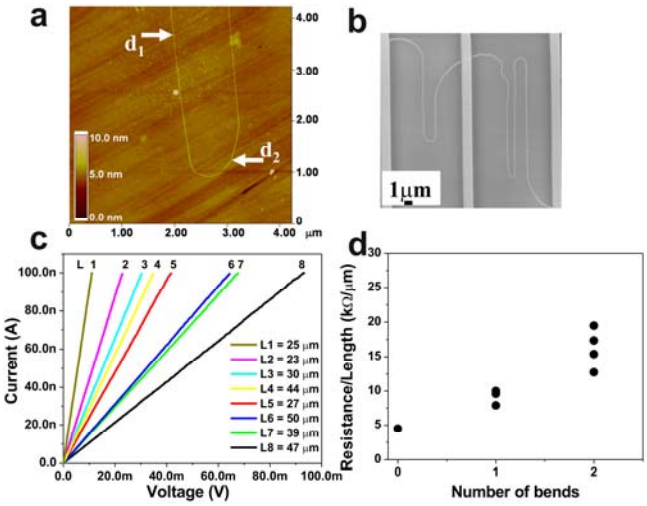


Figure. 2. (a) AFM image of a bent SWNT segment and a change in SWNT diameter is observed at straight and bent area ($d_1 < d_2$). (b) SEM image of a typical test device with one and two bends between Pd electrodes. (c) Current-voltage (*I-V*) characteristics from an individual bent SWNT with multiple bends. L1-L8 represents the total length of SWNTs between two consecutive Pd electrodes. (d) Resistance/Length versus number of bends to compare the resistance of SWNT segments with different morphologies.

RESULTS AND DISCUSSION

The growth mechanism of flow guided SWNTs growth is proposed as "kite mechanism" in which SWNT and catalyst are lifted up by gas flow and float over the substrate surface while growing.[3,4] However, the growth of SWNTs on quartz is more complex due to the interaction between gas flow and step-edges. Depicted in the schematic of figure 1(a) is our approach to bend an SWNT into zigzag shape by utilizing the interaction of gas flow and step-edges. We found that the gas flow effect on bending SWNTs is trivial at medium flow rate. Over the medium flow rate of 500 sccm, SWNTs are aligned by step-edges only, forming almost perfectly aligned SWNTs along the step-edges direction on the quartz substrate. Figure 1(b) and figure1(c) show the SEM images of aligned SWNTs arrays grown at medium gas flow rate of 500 sccm. Well aligned SWNTs start from one catalyst stripe and stop growing when the SWNTs meet the next catalyst stripe. However, the gas flow effect starts to play an important role when the flow rate is reduced to below 100 sccm. The growth process of bent SWNTs can be divided into the following steps. At low gas flow, the SWNTs and catalysts are lifted up and floating along the gas flow direction.[4] Once the SWNTs touch the quartz surface, due to the strong van der Waals force with substrate, the SWNTs start bending towards step-edges direction. However, the shear force from gas flow, due to the viscous force from gas flow, produces a torque on the SWNTs and dominates over the van der Waals force with substrate. Then the SWNTs start bending towards gas flow direction again. This process repeats many times and leads to the formation of bent SWNTs. This growth mechanism is proposed via experimental observation and need further investigation. Figure 1(d) and figure 1(e) show the SEM images of bent SWNTs grown at low gas flow rate of 10 sccm with different angles (θ) between gas flow and step-edges directions. The frequency of bending can be tuned by adjusting θ, which results in the change of average number of bends from 1 / μm (figure 1d) to 0.3 / μm (figure 1e) as θ changes from 60 º to 90 º. And the radius of curvature increases from 0.5 μm to 1.4 μm accordingly.

Figure 2 (a) demonstrates the AFM image from bent SWNT segment. By evaluating the AFM height profile, it is found that a diameter change occurs from 1.3 nm (d_1) at the straight segment to 2.0 nm (d_2) at the bent area. This observation is in good agreement with the recent report by Ding et al.,[10] in which a diameter change is found in a "sickle" shaped SWNT due to the variation of catalyst particle size. However, in our case, when the SWNTs touch the substrate and grow along step-edges direction, the catalyst nanoparticle may skid on the surface of substrate and change its properties including size, composition, and morphology.[11] As a result, the diameter of SWNT varies nearby the bent area. Note that when the SWNT is floating in the gas, the temperature difference between the gas flow and substrate[4] may cause different carbon solubility in the catalyst nanoparticle, which may be another reason for the observed diameter variation. As the bandgap of SWNTs is inversely proportional to the SWNT diameter,[1] the straight and bent SWNT segments may form hetero-junctions with different bandgaps. Yao et al have demonstrated the diameter variation of SWNTs by temperature oscillation during growth which forms intramolecular junction in SWNTs.[12] Our results provide another possible approach to form multiple

hetero-junctions by tailoring the bending of SWNTs. The electrical properties of bent SWNTs are exploited using two-terminal current-voltage (*I-V)* measurement at room temperature. The SEM image of a typical test device is shown in figure 2(b). Palladium contacts are employed to ensure an ohmic contact because of its high work function (ϕ_{Pd}~5.1 eV).[13] Since the contact resistance between Pd and SWNTs ranges from 5 to 10 KΩ,[14] whereas the resistance of bent SWNT segments between two consecutive Pd electrodes is quite large (200 KΩ - 1 MΩ), the contact resistance is only 1-5 % of the intrinsic resistance in SWNT and thereby only adds a negligible contribution to the total resistance. From figure 2(c), it is clearly seen that the measured current does not scale with the SWNT length, which indicates that the morphology of SWNT may play an important role. To better understand the electron transport in bent SWNTs, resistance per unit SWNT length (R (L)) is calculated to compare the resistance of SWNT segments with various morphologies. The SWNT segments with one and two bends have an average R (L) of 9 KΩ/μm and 16 KΩ/μm, respectively, which is 1.5-3 times higher than straight one (figure 2(d)). An electron mean free path of 1.4 μm can be estimated for the straight SWNT segment, [15] whereas the mean free path decreases to ~300 nm for the SWNT segment with two bends. The resistance increase and mean free path decrease can be attributed to the introduced electron scattering at hetero-junctions and topological defects at the bent area.[9]

CONCLUSION

In conclusion, this study demonstrates an easy and reliable method to bend SWNTs during growth by the interplay between van der Waals force with substrate and shear force from gas. At the bent area, a diameter change is observed due to the catalyst property change and the different carbon solubility in catalyst by temperature gradient. A resistance increase is observed with the number of bends in bent SWNTs due to the additionally introduced hetero-junctions and topological defects. With the understanding of the growth mechanism of bent SWNTs, it is possible to achieve more complex geometries and to build an all-nanotube device by integration of SWNTs having different functionalities into complex circuit.

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