The Influence of the Asymmetric Metal Electrodes on the Self-assembly of Single-walled Carbon Nanotubes by AC Dielectrophoresis

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Abstract: There are two procedures in the single-walled carbon nanotubes (SWCNTs) DEP (dielectrophoresis) assembly process, including the DEP and suspension removal. This paper mainly pays attention to the effects of the suspension removal procedure on the assembly efficiency. We found that the interaction energy between the SWCNTs and electrode metal materials plays a major role in preventing the arriving SWCNTs from getting off the electrodes when the suspension is blown-off, which will impact the DEP assembly yield of SWCNTs further. Three kinds of metal materials having various interaction energy with SWCNTs with the order of Ti>Hf>Al were chosen as the electrode materials and then the SWCNTs DEP assembly experiments were carried out. Our results show that the assembly yields exhibit the accordant order with that of the interaction energy of Ti>Hf>Al, which demonstrates our deduction.

1. Introduction
After the past two decades of intensive research on their intrinsic features and diverse application potential, carbon nanotubes (CNTs) have evolved into studious application exploitations, especially for the CNT-based electronic devices, including transistors, chemical and biological sensors, diodes, and so forth. Because of the wide application in photovoltaic and betavoltaic microcells, infrared detectors and microwave rectifiers, SWCNT-based diodes have attracted immense research attention. They mainly have three structures, such as doped p-n junction, split-gates, and Schottky barrier (SB). Among them, the SB diode with an asymmetric configuration of “high-work-function (φh) metal/SWCNT/low-work-function (φl) metal” has the advantages of very simple fabrication and is doping-free resulting in avoiding the failure induced by dopant diffusion or freeze whether in high or extremely low temperatures. For the widespread application of SWCNT-based devices, one of the crucial obstacles of the state of the art is how to make the large-scale assembly of SWCNTs precise, efficient and compatible with conventional micro-fabrication technologies as well. Although the chemical vapor deposition (CVD) can achieve direct growth of SWCNTs on substrates [1], the high growth temperature makes it incompatible with the current complementary metal-oxide-semiconductor (CMOS) technologies [1]. Post-synthesis assembly techniques are the promising alternative to the CVD technique owning to their very simple set-up and operation at room temperature [2-4]. DEP is advantageous over other post-processed techniques because it allows controlling the position and density of the assembled SWCNTs between pre-fabricated electrodes and
has no post-etching or transfer printing processes, which may introduce defects in the SWCNTs and degrade their electrical properties. A lot of research have investigated the dependence of the assembly yield of SWCNT depends its conditions, including AC bias voltage and frequency [5-6], assembly time [7], electrode geometry [8] and solution concentration [9]. In our SWCNT assembly experiments for asymmetric-work-function metal electrodes, different electrode-metal materials result in greatly differing assembly yields. However, to date no report concerns the matter of electrode-metal materials on the yield both in theory or experiment. In this paper, we qualitatively analyzed the interaction forces on the SWCNTs that occur throughout the DEP process, especially taking into account the suspension-removal procedure during the DEP process. We found that the interaction force between the SWCNTs and metal materials is the main factor preventing the arriving SWCNTs from leaving the electrodes during the suspension-removal procedure. Next we experimentally examined the influence of different electrode-metals on the DEP assembly of SWCNTs and the results prove our qualitatively deduction.

2. THEORY AND CONSIDERATION

The conventional DEP assembly process can be divided into two steps, i.e. SWCNTs self-assembly and the suspension blowing-off. In the first step, SWCNTs dispersed in the suspension move, reach and bridge the two opposite tips of the electrode at last. There are mainly three forces acting on the SWCNTs during this procedure, such as DEP force, hydrodynamic forces of electro-thermal flow and AC electro-osmosis flow, and adhesive forces as shown in Figure 1. The first two are long-range forces, which determine the moving direction and speed of the SWCNTs in the suspension [4-8]. The z-direction of the forces push the SWCNTs toward the tip of the electrodes, and the x- and y-direction make the SWCNT align with the gap direction. When two ends of SWCNTs approach the electrode surface at the distance of nanometer scale, the DEP and hydrodynamic forces decline abruptly because of the electrical field reduction and the short-range adhesive force like van der Waals one becomes dominant(Figure 1(b)). Then, the second step starts, i.e. the solution with those SWCNTs left should be blown off by nitrogen gas as fast and clean as possible. It is unavoidable that some of the assembled SWCNTs will be taken out at the same time. Just before the blow-off, although the two ends of SWCNTs are in contact with metal, the major part of the arrived SWCNTs are still floating in the suspension over the gap area with the distance to the substrate approximately equal to the thickness of the electrode about 100 nm in this paper. Therefore, the adhesive force between the arrived SWCNTs and the electrode-metal material plays an essential role in fixing the SWCNTs to resist the blowing force, especially at the starting moment. So, it can be deduced that electrode metal materials should impact the SWCNTs assembly yield.
Figure 1 The main forces acting on the SWCNTs: (a) before the SWCNTs contact with the electrode, (b) after the SWCNTs contact with the electrode. Red arrows indicate the hydrodynamic forces pattern. FDEPx, and FDEPz are the x-, and z-direction forces of DEP. F_AF is the contacting force between the metal and SWCNTs.

There are two categories of interaction energy between the contacting materials. One is the physisorption which bring about relatively weak adhesive force, i.e. van der Waals forces. The contacting force between SWCNTs and Al is this kind. In addition, the strong oxidation in air will weaken the binding affinity of Al with SWCNTs further [11]. The other is the chemisorption caused by covalent bonds which is much stronger than the former. For SWCNTs, it is generated by sp2→sp3 transition of metal and adjacent C-atoms, such as SWCNTs-Pt and SWCNTs-Ti [11]. It has been reported that interaction energies of transition metals enhance with the number of vacancies in d orbital. If the vacancy is the same, the closer to the nucleus the d orbital is, the higher the interaction energy is, [14]. We can confer that the 3d metal of Ti possesses higher interaction energy than the 5d metal of Hf, even though they have the same number of vacancies in d orbital. Therefore, the descending order of the adhesive forces between SWCNT and the different metals is Ti>Hf>Al which were chosen as the electrode materials in our following experimental.

3. STRUCTURE AND EXPERIMENTAL
The tip-to-tip finger-electrode pairs (Figure 2) where the SWCNTs will be bridged, are 30 μm in length, 3 μm in width, 2 μm gap of opposed finger tips and 5 μm lateral interval of the fingers, which were optimized by our previous experimental study [9]. Because of our emphasis on asymmetric-work-function metals, Pt was chosen as the φh-metal and Ti, Hf and Al as φl-metals. The Ti/Pt (20 nm/150 nm) and 170 nm thick Ti, Hf and Al were respectively sputtered and patterned by lift off processes in turn on the n-type<100> silicon wafer with 300 nm thermal oxide. The SWCNTs powder of high purity (>90%) was dissolved in N, N-Dimethylformamide solvent with the concentration of 0.5 μg/ml by ultrasonic dispersion for 2 hours. An AC voltage was loaded and then, a drop (~3 μl) of SWCNTs suspension was dripped onto the sample by capillary tube. After several tens of seconds it was blow-dried using nitrogen gas. Different DEP conditions were also investigated with three groups as: (1) AC voltage (Vpp): 1 V, 5 V, 10 V at 5 MHz and 30 s; (2) AC frequency: 1 MHz, 5 MHz, 10 MHz at 5 V and 30 s; (3) Assembly time: 30 s, 60 s, 90 s at 5 V and 5 MHz. Subsequently, the number of the assembled SWCNTs was counted by a high resolution scanning electron microscope (NanoSEM). These experiments are designed to comprehensively observe the effects of different metal electrodes and DEP conditions on assembly yield rates.
4. RESULTS AND DISCUSSION

We counted the number of SWCNTs assembled between each pair of electrodes by high resolution scanning electron microscope (NanoSEM). 360 pairs of electrodes were used to estimate the yield in every condition. The total-assembly yield rate (P) is the ratio of the number of electrode pairs assembled by SWCNTs to 360, and the single-assembly yield rate (Ps) is the ratio of the number of electrode pairs bridged by only one bundle of SWCNTs to 360 and the multi-assembly yield rate (Pm) is that of electrode pairs bridged by more than one bundles of SWCNTs.

Figure 3 P for Pt-Ti, Pt-Hf and Pt-Al samples at different AC voltages (a), frequencies (b) and assembly times (c).

Both Figure 3(a) and 3(c) show that the P increased with both of voltage magnitude and DEP assembly time because more SWCNTs can be transported to the gap and assembled then, which is in agreement with other experiments and theoretical work [4-9]. As we know, in the range of 1 to 10 MHz, the total number of SWCNTs assembled depends very little on the frequency [6]. However, we found that the P measured at 1 MHz is significantly higher than those at 5 MHz and 10 MHz (Figure 3(b)). Figure 4 is the SEM images of assembled SWCNTs of Pt-Ti in three different frequencies. It can be seen that there were many tangled SWCNTs between the gaps of the electrodes with large particles at 1 MHz, while the assembled SWCNTs highly oriented between the gaps with few particles at 5 MHz and 10 MHz. Therefore, it is evident that these large particles at 1 MHz pin the arrived SWCNTs on the electrode and helped them not to be blown off by the nitrogen gas.
Figure 4 SEM image of the SWNTs assembled on Pt-Ti electrodes at various frequencies of 1 MHz (a), 5 MHz (b) and 10 MHz (c).

Figure 5 shows the Pm of the three types of devices of Pt-Ti, Pt-Hf and Pt-Al under different assembly parameters. The Pm also displays the same order with P, i.e. Pm (Pt-Ti) > Pm (Pt-Hf) > Pm (Pt-Al). We observe that the slopes of Pm increase significantly with an increase in the interaction energy between metal and SWCNT as well. We will explain this phenomenon later.

Figure 5 Pm for samples at different AC voltage (a), frequency (b) and assembly time (c) respectively.

Figure 6 Ps samples at different AC voltage (a), frequency (b) and assembly time (c) respectively.

As for Ps shown in Figure 6 the data basically conform to the order of Ti>Hf>Al as P and Pm. However, there are abnormal phenomena under every kind of assembly conditions as shown in Figure 6 (a) – (c). One type of these is the decrease of Pt-Ti Ps at 10 V in (a) and in (c) and the Ps of Pt-Ti is lower those that of Pt-Hf and even Pt-Al. It can be found that the Ps exhibits an upper limit value about 40% regardless of assembly conditions or electrode materials. This is most likely due to the structure and dimension of electrodes, which conforms the electric field distribution and change during the assembly process. Davis et al. [15] reported that the electrode width is the determining factor for the number of SWCNTs assembled. If the electrode width is sufficiently narrow (< 200 nm), the second bundle of SWCNTs cannot assemble between the same pair of electrodes due to the repulsion force generated by the first assembled SWCNT [13]. Therefore, it can be inferred that the electrode width of 3 μm in this paper, which is much larger than the 200 nm, leads to the 40% upper limits of Ps.
Because of the relatively weak interaction force with SWCNTs of Hf and Al, the Ps of the Pt-Hf and Pt-Al electrodes is much lower than 40% so that it can keep increasing with the voltage and assembly time. While, the strongest interaction force with SWCNTs of Ti makes its Ps the first one to reach the upper limit value of 40% at Vpp=5 V, f=5 MHz, t=30 s. Then, it starts to decline dramatically when the voltage is higher than 5 V and the assembly time is longer than 30 s respectively resulting in those abnormal non-order data in Figure 6 (a) and (c). In addition, when total yield rate is low, Ps and Pm can increase simultaneously, whereas when total yield rate is high enough, the decrease of Ps means the increase of Pm, namely a restriction relationship between the Ps and Pm. Therefore, it can be deduced that both the 40% upper limits of Ps and the restriction relationship between the Ps and Pm result in that the change ability of all three types of electrodes Pm enhances with the increase of the interaction energy between the metal and SWCNTs as discussed in last paragraph.

There are other two types of abnormal phenomena in our Figure 5 (b) and Figure 6 (b). One is that the Ps of Pt-Ti and Pt-Hf at 1 MHz is smaller than at 5 MHz and 10 MHz, but the conditions of the P and Pm are opposite. The other is that the Ps of Pt-Al at 1 MHz keeps the same trend with the Pm and P, contrary to that of Pt-Ti and Pt-Hf. Both of the phenomena can be explained by the comprehensive consideration of all factors proposed previously, including the pinning effect at 1 MHz, the 40% upper limit of Ps and the restriction relationship between the Ps and Pm under the different interaction energies between SWCNTs and Al, Hf, Ti, when total yield rate is high enough. Therefore, the former phenomena can be explained by the relative large interaction energies of Hf and Ti with SWCNT, the Pm is enhanced so much by the pinning effect that the Ps decreases although the total assembly yield is increasing. Then, the latter phenomena is caused by the reason that the interaction energy between Al and SWCNT is so weak that the pinning effect helps the Ps increase as well as the Pm, so all three kinds of yield of Pt-Al is enhanced at 1 MHz.

5. Conclusion
In conclusion, the SWCNTs were self-assembled on three different metal electrodes of Pt-Ti, Pt-Hf and Pt-Al by the AC DEP technique and experiments show that the total, multi-bundles and single-bundle assembly yields all display the same order with that of the interaction energy of Ti>Hf>Al at different assembly conditions. This demonstrated that the interaction energy between the SWCNTs and electrode metal materials is one of the crucial factors in the DEP assembly of SWCNTs as playing a role in preventing the arrived SWCNTs from getting off the electrodes again when the suspension is blow-off, as expected. Therefore, the weaker the interaction energy of the electrode metal with SWCNT is, the higher voltage and longer time are required to obtain higher SWCNTs assembly yield. As for Ps, its upper limit should be paid attention as well if the electrode is not narrow enough.

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