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Graphical abstract
The agglomeration of Carbon Nanotubes was reduced via electrostatic atomization and a Schottky junction was formed easily.
Mono-distributed Single-walled Carbon Nanotube Channel in Field Effect Transistors (FETs) using Electrostatic Atomization Deposition

D.W.H. Fam & A.I.Y. Tok*

School of Materials Science and Engineering, Nanyang Technological University, Block N4.1, 50 Nanyang Avenue, Singapore 639798, Tel: (65) 6790 4142, Fax: (65) 6790 9081

Abstract

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Keywords: Carbon nanotubes, electrostatic atomization, monodispersed
1. Introduction

Field effect transistors (FETs) have found their uses in many applications in the microelectronics industry [1]. FETs typically consist of a gate, where the bias would be applied, a source and a drain electrode. Across the source and drain electrode is the channel which typically comprise of a semi-conductive material. There are many materials used as the semi-conductive channel [2] and Single-walled Carbon Nanotubes (SWCNTs) are one of them [3]. SWCNTs are essentially rolled graphene sheets which are of 0.4-3nm in diameter. They consist of sp2 hybridized carbon atoms and have three out of the four outer shell electrons participate in bonding with neighbouring carbon atoms while the fourth carbon is in a p-orbital perpendicular to the hexagonal lattice [4]. CNTs are used to fabricate field effect transistors due to their excellent electron mobility [5] which is very suitable for applications in high-speed transistors, memory devices and also chemical or biological sensors. There are essentially two different methods of fabrication of these CNT devices namely, via CNT growth and drop cast. Growing CNTs on the surface of a substrate involves the use of a catalyst [6-10] via a chemical vapor deposition (CVD) method [7, 11, 12] or by an arc discharge method [1, 13]. Although this method of deposition yields good transistor devices, the surface chemistries of the CNTs cannot be modified to suit different purposes; functionalization and decoration of the tubes could not be done easily in situ should the CNT devices be fabricated by tube growth. Functionalization and decoration of CNTs is done for a variety of sensing applications [4, 13-18] as well as to modify their electronic properties [19]. Another common method of fabrication of these CNT devices would be via drop-cast [20]. However this method of deposition results in much agglomeration and hence a consistent device characteristic will not be achievable. Hence a suitable method had to be found to both allow for easy manipulation of CNT surface chemistry and creating consistent transistor devices. Electrospraying has been explored as a method of
depositing double-walled carbon nanotubes and it yielded low-density bundles and even isolated double-walled carbon nanotubes [21]. Electrostatic atomization (EA) is a form of deposition in which a jet of liquid is exposed to an electric field which leads to a dispersion of the particles arising from either liquid polarization or free charge repulsion. This jet of liquid will then break into droplets when it is released at a controlled flow rate through a stainless steel needle [22]. The EA schematic is as seen in Figure 1. The solution is pushed into the capillary tube and into the needle at a constant flow rate whereby it experiences an electric field set up due to the potential difference between the needle tip and the ground electrode. The field at the tip then overcomes the surface tension of the liquid which results in a jet forming from the breakup of the liquid surface. This jet consists of extremely small liquid droplets which would be accelerated towards the stage, which is below the ground electrode hence depositing the liquid droplets onto the substrate on the stage. EA has been widely applied since its initial use on paints [23]. EA has also been applied to hydrocarbons [24, 25], ceramics [26] and a variety of other materials [27] to obtain self-assembled nanostructures [28]. However, one of the most poignant uses of EA was to create a mono-distributed thin film [29, 30]. Hence, this paper shows a novel method of preparing a transistor with a mono-distributed network of CNT via electrostatic atomization.

2. Materials

Single-walled carbon nanotubes (SWNTs) were bought from Carbon Solutions, Inc. and were used as bought. The SWNTs are then suspended in ethanol due to its low surface tension so that a stable cone-jet mode can be reached when it is atomized. SWCNTs, because of their nanoscale dimensions, they typically agglomerate in polar solvents like water. Hence surfactants would normally be used to suspend the nanotubes in the solvents and in this work; poly (4-vinyl pyridine) (P4VP) bought from Sigma Aldrich was used as the surfactant.
3. Methods

Sonication was applied to separate the nanotube bundles. After which, centrifugation was done to separate the free nanotubes from the agglomerated ones. S1 is a solution of 99.99wt% absolute ethanol and 0.01wt% P3 SWNTs (functionalized with carboxylic acid (-COOH) groups). S1 was made to sonicate for 20mins and centrifuged at 14000rpm for 75mins. The suspension characteristics like its conductivity, surface tension, viscosity and dielectric constant were then measured with a SCHOTT conductivity meter, Contraves low shear rheometer, contact angle measuring equipment and the Alpha TDR 5000 meter respectively. The extracted supernatant solution was then drop-cast or electrosprayed onto the device (Figure 2) channel as the semiconductor layer using a pipette. The stable cone jet mode for EA was achieved at 0.07ml/hr and the process was done for 3mins. Field emission scanning electron micrographs were then taken of the channel to compare its dispersity. The transfer characteristic, namely the drain current ($I_D$) against drain voltage ($V_D$) with different gate voltages ($V_G$) was then measured using a Keithley 4200 parametric analyzer. $I_D$ was swept from -5V to 5V and $V_G$ was stepped from -5V to 5V.

4. Results and Discussion

4.1 Fluid properties of test solutions

The properties of the suspension of SWNTs in ethanol solution, namely its conductivity, surface tension and viscosity has to be within ($10^{-3}$ – $10^{-7}$ S/m), (10 – 100 dy/cm) and $10^{-3}$ Pa.s respectively. The conductivity was measured to be 0.06µS/m, the surface tension 29.2dy/cm, viscosity 1.1 x $10^{-3}$ Pa.s and the dielectric constant 23.04.

4.2 Domains of the cone jet range

The cone jet mode takes place when the meniscus begins to merge in a conical shape. Upon its onset, the cone would take an elongated shape and the cone gets more defined as the voltage increases slowly while maintaining an optimum flow rate.
However, if the applied voltage is too high, the electric potential increases and would in turn result in multi-jet modes. If the applied voltage is too low, it would decrease in electric potential and result in dripping modes. At a very low or high flow rate, the stable cone jet mode would not be established easily. There are three phases in the cone jet range, namely cone jet hysteresis, cone jet initiation and cone jet top limit. Hysteresis takes place by decreasing the voltage while maintaining the cone jet mode. Cone jet initiation refers to the initial occurrence when the cone jet mode is stabilized. It was found that for the suspension, a stable cone jet mode could be reached with the spray parameters of 0.07 ml/hr at 3.61kV.

4.3 CNT device fabricated by drop-cast method.

The device channel fabricated by drop cast shows much agglomeration as seen in Figure 3. This is due to the low surface-area to volume ratio of the drop hence evaporation of the drop is slow which gives time for agglomeration of the nanoparticles. Furthermore, devices prepared by drop-cast method more often than not yields metallic junctions rather than Schottky ones as seen in Figure 4. This is due to the large volume of solution that is usually present in a single drop. This will result in the metallic tubes conducting most of the charges instead of the semiconducting tubes. In addition, there is no way of controlling exactly the amount of solution being dropped onto the channel. Hence the devices are usually not replicable. Devices fabricated by drop cast usually have CNTs all over rather than having them localized in the channel itself. This is because the drops are usually large and its diameter spans larger than the channel width.

4.4 CNT device fabricated by electrostatic atomization

The devices that were fabricated via electrostatic atomization could be reproduced with much consistency. When the SWNTs in the ethanol solution was sprayed and dispersed
onto the substrate, evaporation occurs almost instantaneously and leaves the SWNTs on the substrate in its un-agglomerated state.

4.4.1 CNT Device fabricated using S1

S1 is a suspension of CNTs functionalized with –COOH groups in ethanol. The CNTs which were functionalized are now polar and can suspend in ethanol without any aid from surfactants. FESEM images were taken of the device channel and also the junction between the channel and the electrode. From Figure 5, it can be seen that the tubes were more evenly distributed in the channel compared to if they were drop-cast. This was because of the large surface area to volume ratio of the droplets and the fast evaporation of ethanol, leaving very little time for the CNTs to agglomerate. The graphs of the drain current against the drain voltage for various gate voltages ($I_D$ vs $V_D$) were also obtained using a Keithley 4200 parametric analyzer and are seen in Figure 6. As can be seen from Figure 6, the device fabricated by electrostatic atomization shows gate control; changing the gate voltage will give the device a different set of $I_D$ against $V_D$ curves. This is because of the low number of tubes being deposited by electrostatic atomization. In the sample of SWNTs, up to one-third of the tubes are metallic while the rest are semiconducting. Hence if there are too many SWNTs in the channel, chances are that conduction would be via the metallic pathway instead of the semiconducting hence yielding a metallic junction. Hence, a low density of tubes is preferred for a good semiconducting performance [31] which is possible via electrostatic atomization.

5. Conclusions

A novel method of depositing single-walled carbon nanotubes via electrostatic atomization so as to fabricate a transistor junction was explored in this paper. Characterization with the FESEM shows that the carbon nanotube layer deposited via electrostatic atomization was more uniform and mono-distributed as compared to the layer deposited by the conventional method of drop-cast which had no drop volume
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Figure 1. Schematic of the Electrostatic Atomization setup which shows the needle under DC voltage bias and the computer connected to the microscopic camera recording the shape of the jet.

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