IC-COMPATIBLE DEPOSITION OF VERTICALLY-ALIGNED CNT FORESTS FOR MICRO-SUPERCAPACITORS

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Abstract: An IC-compatible process has been demonstrated to obtain vertically-aligned carbon nanotube (VACNT) forests on a stainless steel (SS) substrate using high-voltage electrophoretic deposition (HVEPD). Multi-walled carbon nanotubes (MWCNTs) were deposited onto an SS electrode from an aqueous dispersion with Mg(NO₃)₂ salt, which simultaneously forms a holding layer. In order to obtain desirable results, different HVEPD parameters were investigated and compared, such as the concentrations of MWCNTs and salt, deposition time and voltage. The electrical resistance between the VACNT forest and the SS substrate was studied to confirm the good contact between them. The prospect of using such VACNT forests as electrodes in micro-supercapacitors was explored and evaluated by cyclic voltammetry measurement. The result shows that the capacitance of the VACNT forest is 93 µF/cm² while the laying-down carbon nanotubes by traditional electrophoretic deposition (EPD) is only 1.24 µF/cm².

Keywords: Vertically-Aligned Carbon nanotubes, High-Voltage Electrophoretic deposition, supercapacitors.

INTRODUCTION
The advent of carbon nanotubes (CNTs) has brought forth new possibilities in the field of electronics and microelectromechanical systems (MEMS). The excellent electrical properties possessed by CNTs have made them attractive electrode materials for powerMEMS devices. Due to their anisotropic electrical conductivity, CNTs vertically-aligned on the substrate usually exhibit enhanced electrical properties. Traditionally, these VACNT forests are prepared by catalytic-chemical vapor deposition (CVD) method under a process temperature of 700-1000°C. Since such a high temperature is incompatible with the manufacturing process of integrated circuits (IC) and MEMS [1], its on-chip integration capability and application in powerMEMS are seriously limited. Attempts have been carried out to align CNTs vertically using chemical techniques [2], magnetic fields [3], filtration through hydrophilic membrane [4], and electrophoretic deposition (EPD) in nanopores [5]. However, most of the methods have faced problems like bundle formation and/or lack of good alignment. There are still significant challenges to achieve well-separated, dense array of VACNTs with room-temperature post-growth deposition methods.

EPD is a simple, room-temperature deposition process, which uses an electric field to move charged particles in a suspension and deposit them as thin films [6]. While high voltage is shown to achieve such alignment, bundles instead of separated CNTs were obtained [7]. It has also been suggested that CNTs align themselves along the electric field direction during the EPD process, but usually do not maintain the vertical orientation after removal of the field [7].

In this work, we demonstrate HVEPD to align individual MWCNTs while simultaneously forming a holding layer to preserve the vertical orientation. The goal is to find the appropriate concentrations of metallic salt and MWCNTs as well as suitable voltage and time of deposition such that a holding layer can be simultaneously deposited during the HVEPD process due to the disassociation of the metallic salt into ions. At the same time, the concentration of MWCNTs is appropriately lowered so that bundle formation can be avoided. The HVEPD-deposited VACNT forest is also employed as the electrodes of a micro-supercapacitor [8] to demonstrate its potential applications.

EXPERIMENTAL PROCEDURE
In this study, vertically-aligned MWCNTs were obtained using a single-step process of HVEPD with the formation of a holding layer, which is schematically shown in Fig. 1.

Fig. 1: Schematic of HVEPD process for VACNT.
A stable dispersion of MWCNTs in distilled water was prepared by sonication for 30 minutes. Mg(NO₃)₂ salt was then added to this dispersion which was sonicated again for 15 minutes. The salt will render positive charge to the dispersed MWCNTs and facilitate their deposition on the cathode under suitable voltage. Stainless steel electrodes with an exposed area of 2.54 x 2.54 cm² were used in the electrod depo sitio n cell with an electrode gap of 7 mm. Care was taken that the electrodes were parallel to each other. The DC voltage was then applied for specific times to deposit VACNT forests on the cathode. VACNT forests were obtained when a voltage of 150 V was applied for 1 min, with the concentrations for MWCNTs and Mg salt set at 0.125 mg/ml and 0.075 mg/ml respectively, which were maintained for the control experiments. A set of control experiments for different times of deposition, voltages and concentrations of Mg salt were performed and investigated to understand the deposition phenomena better. After deposition, the samples were dried under room temperature in a desiccator for 24 hrs.

**RESULTS AND DISCUSSIONS**

A key technology to hold the HVEPD-deposited VACNTs in the desired position/orientation is the simultaneous deposition of a holding layer. Usually, Mg(NO₃)₂ salt is added to the dispersion to render charges to the MWCNTs because the latter can adsorb Mg⁺ ions to form an electric double layer around their surface so that they can be moved when a voltage is applied. However, this additive can also form a holding layer due to the reaction between the Mg⁺ ions and the OH⁻ ions at the cathode. The simultaneous formation of a holding layer during the EPD process and its composition was determined by using the electron dispersive spectrum (EDS) of a JEOL, JSM-6400 SEM. Fig. 3 shows the EDS spectrum of such layer formed during the deposition of MWCNTs. The atomic percentage of magnesium and oxygen are in a 1:1 ratio which confirmed the formation of an MgO holding layer.

Fig. 2: Setup to test the electrochemical properties of the obtained VACNT forest for its application in micro-supercapacitor.

The MWNTs were purchased from MER Corporation with a diameter of 140 ± 30 nm and a length of 7 ± 2 μm. The sonication was carried out by a probe sonicator in pulse mode (30 sec. live and 10 sec. dead time). Scanning electron microscope (SEM) images were taken with a Hitachi S-4700 FESEM at 5 kV.

The contact resistance of the deposited films was also measured to ascertain that the MWCNTs were in contact with the steel substrate. A micro-supercapacitor, as shown in Fig. 2, is assembled by employing the VACNT samples as electrodes. Cyclic voltammetry was carried out for a two-electrode device with a 50 μm spacer in a 2M KCl aqueous solution as the electrolyte.

**Fig. 2: Setup to test the electrochemical properties of the obtained VACNT forest for its application in micro-supercapacitor.**

The dispersions formed with the salt being stable for a few days until settling-down of the CNTs was observed. The positive charges due to the absorption of Mg⁺ ions cause cathodic deposition of the CNTs with the simultaneous deposition of Mg(OH)₂ which on drying, forms a strong MgO holding layer. Alignment of the CNTs though, is only achieved at high voltages.

SEM images in Fig. 4 show the comparison between HVEPD (a-c), traditional EPD at 25 V for 2 mins (d-f) and a film formed by evaporating a drop of the dispersion placed on the SS substrate (g-i). Under high voltage of HVEPD, the VACNT forests show well-separated individual MWCNTs with fairly uniform, vertical orientation which has seldom been achieved by other post-growth techniques in earlier works. By contrast, the control experiments (d-i) did not yield any vertically aligned nanotubes, but instead displayed a film of laying-down CNTs.

![EDS spectrum of holding layer determining its composition to be MgO.](image-url)
We thus ruled out the possibility that such VACNT forest can be formed in random deposition.

**Effect of concentration of CNTs and salt**

The effect of concentration of both CNTs and salt in the dispersion was investigated during this work. The use of highly-concentrated CNTs caused over-deposition, bundle formation and reduction in the possibility of alignment even under high voltages. During the EPD process, the speed in which the CNTs reach the electrode surface and their flux play important roles. With a higher concentration, more number of nanotubes may be accelerated towards the surface, with layers of CNTs pushing the layers before them. This may result in forming a film of randomly oriented nanotubes which are not vertically aligned. It was observed that reducing the concentration of nanotubes can lead to good separation and moderate density.

If the concentration of the salt is too high, a very thick MgO layer will be formed to bury the CNTs. On the other hand, if the concentration of the salt is too low, it cannot form a uniform MgO layer with enough thickness to hold the CNTs in their aligned position.

**Effect of voltage and time of deposition**

During the trial experiments, it was observed that only high voltage can align the CNTs along the direction of electrical field. At lower voltages there was no alignment of CNTs observed. It was previously reported that CNTs can align themselves beyond a threshold value of electric field (> 200 V/cm) [7], below which no alignment had been found. Higher voltages caused too many nanotubes to deposit on the surface and initiate the formation of bundles instead of well-separated CNTs. However, bundle formation can be effectively oppressed by reducing the time of deposition and concentration of CNTs.

It will require further theoretical analysis and experimental confirmation to find out the exact time required for the nanotubes to get aligned and reach the surface as well as the conditions for the formation of a sufficient holding layer. However, it is indeed experimentally observed that neither very short nor very long deposition time can yield desirable VACNT forests with individual CNTs. In the sample after very short deposition time the CNTs didn’t show significant amount of vertical CNTs, which can be attributed to the fact that they didn’t get enough time to align themselves along the electrical field before reaching the SS substrate. On the other hand, much longer deposition times caused over-deposition to form additional layers of CNTs on top of existing nanotubes. More detailed investigation on the above-mentioned parameters is expected to reveal the optimum conditions under which the VACNTs can be obtained.

**Electrical and Electrochemical testing**

In order to employ the VACNT forests as the electrodes of powerMEMS devices, the electrical conductivity between the VACNTs and the SS substrate is very important because contact resistance will negatively affect the performance of the device. Fig. 5 shows negligible electrical resistance till the distance between the VACNT forest and the testing electrode is smaller than several µm, which confirms the good electrical contact on the interface. Compared with the control samples, the VACNTs stay in contact with the substrate for much longer distance, which further confirmed the vertical alignment of MWCNTs.
over the whole sample surfaces. In order to further characterize the alignment of VACNT forests and explore their applications, a micro-supercapacitor was prepared with two VACNT-planted SS plates as the electrodes, as schematically shown in Fig. 2. The CV curves for the device are measured and shown in Fig. 6. The specific capacitances of the VACNT forests electrodes and the control samples are calculated from these curves, by using the relation $C = I/ ((dV/dt) \times A)$, where $I$ is the current, $dV/dt$ is the voltage scanning rate, and $A$ is the effective area.

The specific capacitance for the device with VACNTs was found to be 93 µF/cm², in contrast with the value 1.24 µF/cm² found for the device with laying down MWCNTs and MgO holding layer deposited by traditional EPD.

CONCLUSIONS

HVEPD has been developed as a single-step, post-growth deposition method to form VACNT forests with well-separated, moderately-dense MWCNTs. The technique proposed herein is simple, economic, uniform and effective. Low contact resistance and high electrochemical capacitance were obtained, suggesting promising potential to use the obtained substrates for micro-supercapacitors and other powerMEMS devices.

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REFERENCES


