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Efficient Transfer of a VA-SWNT Film by a Flip-Over Technique

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Single-walled carbon nanotubes are currently the focus of intensive interdisciplinary study due to their remarkable physical and chemical properties and their prospects for various scientific and practical applications ranging from electronic to biological devices.[1]

Recently, vertically aligned SWNT film (VA-SWNT film) growth has been reported by a number of groups.[2−6] Since the variety of substrates suitable for the growth of a VA-SWNT film is relatively low, the ability to transfer films to new surfaces greatly increases the usefulness of these films.

Previous work on the transfer of VA-CNT films has been reported.[5,7,8] This work has demonstrated transfers based upon a variety of mechanisms and has been shown to achieve complete film transfer to a variety of substrates. Transfer of VA-SWNT films has been performed using aqueous treatments to debond a film from the growth surface and deposit it onto another surface.[5,7] Such physical treatments will not create a high degree of contact between the film and the deposited layer; such contact is vital to most applications for these films. Other transfer methods have been successful in transferring VA-MWNT films to metal surfaces while maintaining contact between the film and the substrate.[8] However, this method has been demonstrated only for VA-MWNT films in which the ends have been open.

The technique herein reported has significant advantages over these previously reported methods in range of usefulness and ease of implementation. The exposed surface created by a flip-over technique consists of the bottom of the as grown VA-SWNT film; this consists of vertical, well-aligned bundles of uniform density. Also, the transfer of the film onto conductive surfaces allows the integration of VA-SWNT film into electronic devices such as field emission devices, supercapacitors, and fuel cells.[9−11]

VA-SWNT films were grown according to the report of Hata et al.'s.[3] For the catalyst preparation, 10 nm of Al_2O_3 was deposited using an e-beam evaporator onto the Si-substrate with 3.5 μm silicon oxide layer, and additionally 1 nm Fe was deposited as a catalyst. The growth conditions were ethylene/H_2/Ar = 100 sccm:400 sccm:600 sccm at 750 °C at 1 atm total pressure for 10 min. The first few experiments were tried with and without water. No vertically aligned film was grown. Later, we found that the pretreatment of deposited catalysts is imperative. Oxidation at 500 °C in the air for 10 min, followed by reduction at 750 °C in 40% of H_2 balanced with Ar at 1 atm total pressure for 5 min, or alternatively, oxygen plasma treatment for 1−2 min without reduction is found to be a treatment that allows us to grow a VA-SWNT film.

The diameter of the tubes varies from 1 to 7 nm in TEM images (One of the TEM images is shown in Figure 1B). The average height of the film was about 30 μm in the absence of water, and a maximum height (80 μm) was achieved with 10 ppm of water as measured by a water sensor (Super-dew, SHAW) which measures the dew point of water at the exhaust. To grow a VA-SWNT film, water was not critical, but helpful when the right amount of water was used.

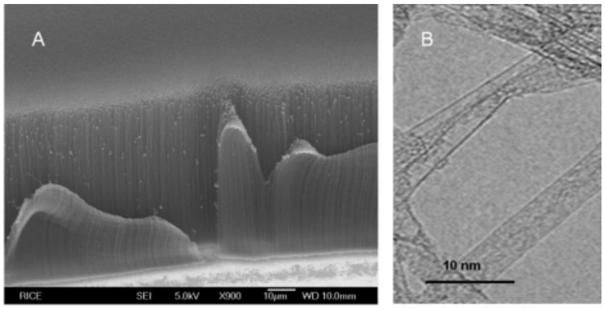

Figure 1. (A) SEM image of a VA-SWNT-film. (B) TEM image of the tubes in a VA-SWNT film.

Raman data (Supporting Information) were collected with a Raman microscope (Renishaw Micro-Raman System 1000) using three different excitation lasers (514, 633, 780 nm), the polarization was exactly matched to the direction of bundles to enhance signal. Sharp RBMs were observed, and diameters from the RBM data vary from 0.9 to 1.35 nm; however, the Raman data we have collected with three lasers cannot detect large diameter tubes over 1.5 nm because Raman spectra of SWNT is resonantly enhanced.[12]

To use a VA-SWNT film for field emission devices or electrodes for a super capacitor or a fuel cell, the first problem was that the top surface of VA-SWNT film is covered by a mat of entangled bundles (Figure 2, A and B). This morphology is common to the growth of VA-SWNT films. However, bundles at the bottom of the as-grown film are aligned normal to the optically flat Si wafer substrate; therefore, a transfer method which exposes the bottom of the as-grown film for application is extremely useful.

As shown in Figure 2C, ceramic cement (Omega CC High Temperature cement) was mixed with liquid binder and spread uniformly on a silicon wafer. A VA-SWNT film was applied to cement mixtures and cured for 24 h at room temperature or 4 h at 65 °C. After curing, a VA-SWNT film was detached by a mechanical force applied between two substrates. Thus, an optically flat surface of exposed carbon nanotube bundle tips is created which is mechanically strong and resilient against high-temperature exposures.

As illustrated in Figure 2, D and E, the VA-SWNT film has been flipped over, exposing an optically flat surface and very well-aligned, clean bundles. The entire film transferred over due to the high tensile strength of the nanotubes. Gold particles can be

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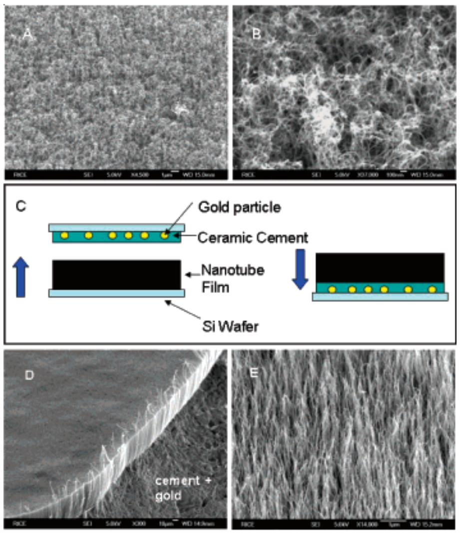

Figure 2. (A,B) Low- and high-magnification SEM images taken from the top of the film showing entangled bundles. (C) Schematic drawing of the flip-over technique using cement with gold particles. (D,E) Low- and high-magnification SEM images taken from the bottom of the as grown film, exposing flat surface with clean and well-aligned bundles.

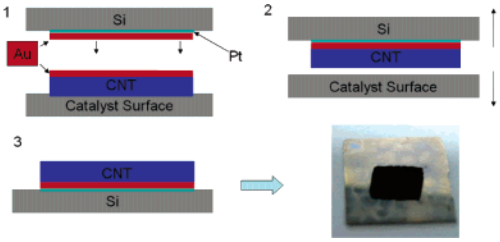

Figure 3. Schematic drawing of the flip-over technique with deposited gold, and a picture showing that the entire grown film has been transferred to the conductive surface.

embedded in cement to confer conductivity through the transfer base as indicated by an elimination of charging observed under SEM.

An alternative flip-over technique has also been developed to transfer a film to a conductive surface (Figure 3). A 70-nm-thick gold layer was deposited by a sputter coater or an e-beam evaporator onto both a Si wafer coated in a thin Pt layer and onto a VA-SWNT film. The gold-coated VA-SWNT film was pressed against the gold-coated Si wafer and baked in Ar at 800 °C for 5 min to fuse the two gold films. High pressure ($\sim$55 lb/cm^2) tends to produce a bending of the nanotubes in the carpet which is retained with a wavy morphology. Such bending also creates a shearing force between the nanotube and the substrates at the points of contact. The transfer substrate is thought to have a higher resistance to shear force so that the nanotube is preferentially debonded from the growth substrate. After baking, the Si wafer and growth substrate were pried apart; the flipped-over film was removed from the growth surface and transferred intact to the transfer substrate. Through this means, we were able to flip over the entire surface of the as-grown film (Figure 3) to the conductive surface reproducibly without disrupting the morphology of the as-grown film.

This method creates a better mechanical connection than previous methods (indicated by increased resistance to destruction by sonication) and mechanically stabilizes the structure of the film. Upon wetting and drying, the as-grown carpet shows significant morphological change, and the flipped-over surface shows only minor effects from this treatment. This type of flip-over treatment has proven to be robust for a variety of uses. By sputtering a metallic layer onto plastic sheets and other flexible materials, transfer of the carpet has been achieved to wide variety of substrates. However, no thermal annealing step was performed. The two metal film surfaces were pressed together and pulled apart. It is conjectured that this bonding does not require a thermal annealing step because the applied pressure is locally greater due to substrate flexing.

It has been observed that extended heat treatment of transferred films can cause the gold to bead and, when it does, it carries the embedded VA-SWNT film with it, drawing the VA-SWNT films into denser “islands” instead of a uniform film. It is therefore supposed that this method can be readily adapted to patterning of these transferred carpets by prepatterning a layer of material under the gold with various regions of different wetting characteristics for the molten gold.

In summary, the flip-over technique has been developed for transfer of a VA-SWNT film onto various surfaces. Specially, transfer of the film on electrically conducting surface with an exposed flat end with very well-aligned bundles will open the possibility of application of VA-SWNT films into various electronic devices.

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Supporting Information Available: Raman data, diameter analysis by the RBM, XPS, and TEM data, and cement penetration data. This material is provided free of charge via the Internet at http://pubs.acs.org.

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