## A Novel Technique for Purification and Segregation Of HiPCO CNT'S Using INKJET Technology

Dr. Tulin Mangir, Juan Chaves, Mukul Khairatkar, Sindy Chaves.

California State University Long Beach Long Beach, California, 90840-8303 temangir@csulb.edu, jchaves@csulb.edu, mkhairat@csulb.edu, schaves@csulb.edu

#### ABSTRACT

In paper we describe a technique to purify and segregate carbon nano tubes (CNTs) from the iron impurities to use the CNTs for thin films. After extensive research into a proper and repeatable cleaning process we developed a new method of using bacteria to remove impurities from CNTs. This gives us the ability to manipulate the CNT. We also developed an apparatus based on inkjet technology that deposit the bacteria containing CNT on conductive surfaces such as silicon, plastic, or any other conductive surface. In this way we create a simple way to manipulate the CNTs for the creation of organic LED, Thin Films, or even electronic devices such as transistors using a simple process. Our methods specifically apply to CNTs obtained by the HiPCO process. However, we assume the method can be extended to other cases. We expect this approach will lead to finding novel conductors, structures and thin films for future nano-engineered devices that could be investigated further for use in nano-scale electronics, implants and bio-materials.

*Keywords:* HiPCO CNT, Inkjet, bacteria, purification, segregation.

## **1 INTRODUTION**

Today, the race to find materials with stronger and faster carrier mobility and smaller thickness for the fabrication of thin films that will yield smaller geometries and flexible electronic devices led to the experimentation with CNTs.

CNTs have attracted a lot of interest because their unique physical properties and because they show a lot of potential for their use in microelectronic and nanoelectronic applications. Hence, by developing an industrial process, they can be use in areas such as display technology, as thin film transistors in liquid crystal displays or Organic Light Emitting Diodes (OLED), as well as thin films for the manufacturing of CMOS devices and Field Effect Transistors (FETs). One of the physical properties of CNTs that made them very attractive to the manufacturing of FET is their carrier transport property. It is been estimated that the carrier mobility of a single CNT will be in the range of 1000 cm<sup>2</sup>/Vs [1]. Although, the carrier mobility of CNT seems to be a great advantage in the manufacturing of thin films, in reality it gets compromise somehow by the introduction of carbonaceous impurities as well as metal impurities due to the manufacturing process of CNTs. As an example a FET made out of a single CNT can carry limited currents generally in the range of nA or  $\mu$ A, but by using CNT thin film mesh the range can be significantly increase[1]. Hence, for CNT to be compatible with today's device fabrication at low cost and high throughput it needed to be in more aqueous stage e.g., a liquid material or solution, since the process of CNT growth requires high temperatures of 900 °C.

In our research we utilize SWCNTs (Single Walled Carbon Nano Tubes) obtain by the HiPco (High-pressure CO dissociation) process. One of the major drawbacks using this type of material was the amount of iron impurities contain in the CNTs, due to the use of iron as a catalyst in the process. Hence, a pioneering cleaning method was developed in order to obtain pristine SWCNT that could be use for the creation of high quality thin films, and the creation of the liquid material required to the manufacturing process of thin films.

## **2 EXPERIMENTAL**

The main purpose of our research was to create thin films for use in electronic applications. Consequently, we needed a simple way to purify the SWCNT from the iron contaminants induce thru the HiPco process at the time of their growth. After experimenting with several methods already being researched to clean the same type of material from their impurities, we concluded that these methods caused structural damage of the SWCNT which will also led to a change in the electrical properties. Hence, after trying different methods we created a more passive process for the purification that will prevent damage in the SWCNT structure, but at the same time eliminating over 90% of the contaminants such carbonaceous and iron impurities, leaving a pristine material to be use in the creation of thin films. For such reason we devise the use of a biological agent for the purification process. After, research several ways of processing the SWCNT dust and exposing it to a

variety of biological agents, we found that by using bacteria we achieve the cleaning task without affecting the condition and/or structure of the CNTs; thus eliminating most of the mineral contaminants in the process\*. The biological properties of the bacteria and the ubiquitousness of it, was so appealing for their use in this cleaning process.

(a)

(b)



Figure 1: (a) Optical image of CNT dust when bacteria are just applied; (b) Optical Image of CNT dust after 4h once the bacteria start the cleaning process. The red area is the Iron oxide from the Iron being pulled out from the inside of the CNTs.

After several attempts to formulate a procedure to expose the CNT dust to biological cleaning agents, we finally create a working protocol to generate a high yield of material with pristine SWCNT for the use in the manufacturing process of thin films\*.

Thru this biological cleaning process, the purified SWCNTs have been found to have higher surface areas retaining also their physical characteristics of conductivity, compare to the acid treatments or microwave treatments which were demonstrated to have good results in the elimination of metallic catalytic impurities but with a rise in structural and electrical changes in the end material [2]. Also this biological cleaning process was demonstrated to be superior and more cost effective that the gas oxidation process, in which the material has to be exposed to Argon or Oxygen gas flow for several hours, annealed and then clean by HCl acid exposing the material to structural damage [3-4]. In the biological process, the SWCNT were exposed to the right amount of biological agents with the right amount of CNT dust and then water rinse to eliminate the untreated material, making the cleaning process cost effective by eliminating the use of expensive acids or gases thru the process. Consequently, the process achieves high yields of the clean material reducing the cost and reducing the waste of the CNT dust during the process.

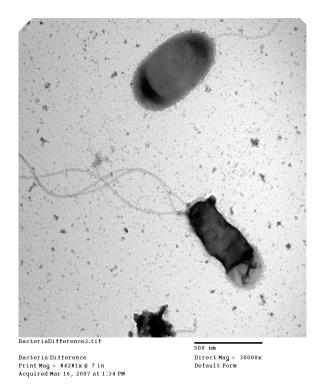


Figure 2: Bacteria Difference one without CNT and one with SWCNT inside.

In the biological cleaning process one of the bacterium main nutrients is Iron which is needed for the production of nitrogen. Using this to our advantage the bacterium is grow in a starving environment (lack of Iron nutrients) and then is released in an environment containing only the raw CNT. Once the bacteria colony reaches the raw material the absorption process starts. During this process each bacterium works as a "biological cleaning machine" absorbing the raw CNT to extract the Iron from the SWCNT. In figure 2 a TEM micrograph shows the difference between a normal bacterium and one after "ingesting" the raw CNT material. After the CNT are absorbed the bacterium breaks down the carbonaceous cocoons were the iron is enclosed leaving only clean SWCNT.

This absorption process is very significant in our research since it accomplishes two tasks at once. First, the cleaning of the material and segregation of individual SWCNT form their tangled bundles was achieved. Second each bacterium performs as a SWCNT "container or vessel", were the clean pristine material is enclosed after the cleaning process. Hence, allowing an easy manipulation of a SWCNT thin film mesh without disturbing the structural characteristics of the thin film as well as the conductivity properties of it. Figure 3 shows an SEM micrograph of the SWCNT mesh contained inside of an individual bacterium.

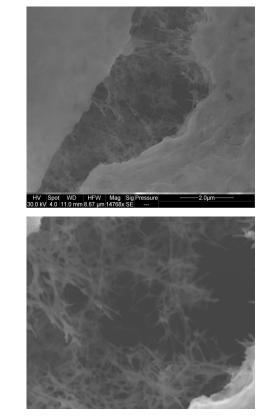


Figure 3: (a) SEM micrograph of the SWCNT thin film inside the bacterium; (b) a closer image of the SWCNT mesh thin film inside the bacterium.

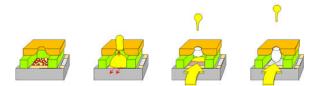
Once the absorption and cleaning process is done the bacteria gets selected and clean from any leftover raw material by a rinse process. After the rinse process is complete the bacteria vessels are ready to be deposited into the surface to create the thin film.

#### 2.1 Inkjet Dispersion of the SWCNT

The next step is the segregation of the individual SWCNT and the separation from the bacterium. This is achieved by using Inkjet technology developed by Hewett Packard [4]. A special ink was created with the bacteria containing the SWCNT thin film mesh inside\*. The ink was developed with a specific ratio that with yield a consistent number of bacteria population with SWCNT in them for every 50 ml of solution, making a very dense bacteria ink.

An inkjet cartridge was modifying to host the special ink and a printer apparatus was developed to use the special cartridge, for the process of deposited the SWCNT mesh virtually in any surface\*.

The principle of inkjet technology provides the last step of converting the material back from the wet environment to a dry environment. Hence, the method allows the use of the clean SWCNT in the manufacturing process of electronic devices\*.



# Figure 4: Inkjet process to release droplets of ink in a surface [4].

By using the thermal inkjet technology the solution is superheated to about 1,000,000 °C/second, the solution were the bacteria is contain is ejected without boiling but disintegrating the bacteria in the process virtually depositing the mesh of SWCNT in the surface. Each droplet released is about 150pl making this process very accurate to deposit the material virtually in any space or surface. Once the material is deposit in the surface the surface exposed to a quick heat treatment to eliminate any residual of the biological agent.

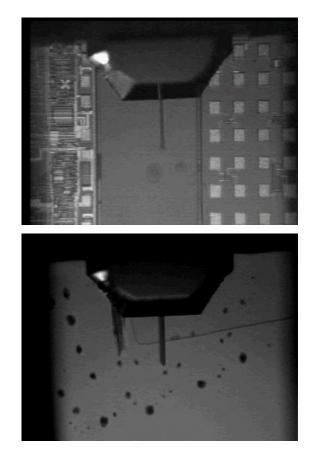


Figure 5: Pictures of the special ink droplet taking by the onboard camera of the AFM

(a)

(b)

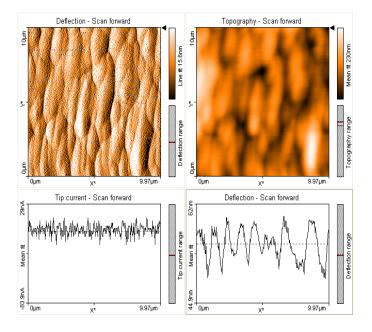


Figure 6: AFM image of the SWCNT mesh after deposited thru the inkjet nozzle on a silicon surface.

#### **3 DISCUSSIONS AND CONCLUSION**

Our results has shown that our biological cleaning and segregation process of HiPco SWCNT is less invasive, less damaging and more cost effective than processes that involved the use of HCl, Oxygen or Argon gas, as well processes that uses microwaves to clean the impurities in the raw material. Also, with the use of inkjet technology in conjunction with our biological cleaning process allow us to achieve the segregation of individual clean SWCNT and the manipulation of the thin film mesh form by them. Hence, with the creation of the cleaning protocol, the creation of the special bacteria ink, and the creation of the ink depositing apparatus we achieve an industrial process in the manufacturing of thin films for electronic applications. Further discussions of the major topics of this work and most of our data results are going to be presented at the conference.

#### REFERENCES

 Xuliang Han, Daniel C. Janzen, Jarrod Vaillancour, and Xuejun Lu. 2006. A flexible thin-film transistor with high field-effect mobility by using carbon nanotubes. Nanotechnology Materials and Devices Conference, 2006. NMDC 2006. IEEE 1 (2007-11-27) : 296-297.

- [2] Ester Vázquez, Vasilios Georgakilas, and Maurizio Prato. 2002. Microwave-assisted purification of HIPCO carbon nanotubes. *Chemical Communications*, no. 20: 2308-2309.
- [3] Chiang, I. W., B. E. Brinson, A. Y. Huang, P. A. Willis, M. J. Bronikowski, J. L. Margrave, R. E. Smalley, and R. H. Hauge. 2001. Purification and Characterization of Single-Wall Carbon Nanotubes (SWNTs) Obtained from the Gas-Phase Decomposition of CO (HiPco Process). *Journal of Physical Chemistry B* 105, no. 35: 8297-8301.
- [4] KIM Yeji, MINAMI Nobutsugu, ZHU Weihong, KAZAOUI Said, AZUMI Reiko, and MATSUMOTO Mutsuyoshi. 2003. Langmuir-Blodgett films of single-wall carbon nanotubes: Layer-by-layer deposition and in-plane orientation of tubes. Japanese journal of applied physics 42, no. 12 (December 10, 2003) : 7629-7634.
- [5] Rob Beeson.Thermal Inkjet: Meeting the Applications Challenge.
- \* This new approach is under a patent pending process, reason why some details were omitted from this paper.

Special Thanks to the Army Research Office for their support in this investigation thru their Grant "Assessing the Integrity and Integration Issues of Nano- Sensors/Nanostructures-Equipment".