“*Carbon Nanotube Applications… Matching Materials, Process, and Purpose*”

Extended Abstract prepared by:
Robert Praino
Chasm Technologies, Inc
480 Neponset Street
Canton, MA 02021
781-821-0443
bpraino@chasmtek.com

Carbon Nanotube (CNT) Applications ? Matching Materials, Process, and Purpose

Introduction:

Carbon nanotubes (CNT’s) are the topic of much research and are actively being regarded as having the potential to revolutionize many industries requiring unique opto-electronic and mechanical performance enhancements. Chasm Technologies has been named as the Applications Development Center for SouthWest NanoTechnologies (SWeNT), a leading producer of single wall carbon nanotubes (CNTs) as well as other types of CNTs. This collaboration has enabled the presentation of work at Chasm Technologies. This paper will describe a portfolio of combinations of CNT materials, processes, and product structures which are aimed at satisfying the requirements of a variety of final product uses. Results of such work will be presented as a framework for linking fluid properties, application techniques, and product requirements to achieve an appropriate integration of specific demands. The product range of interest will include transparent conductive coatings, patterned coatings, and non-isotropic coatings which show promise for use in flat panel displays, photovoltaics, solid state lighting, and conductive composite fabrics.

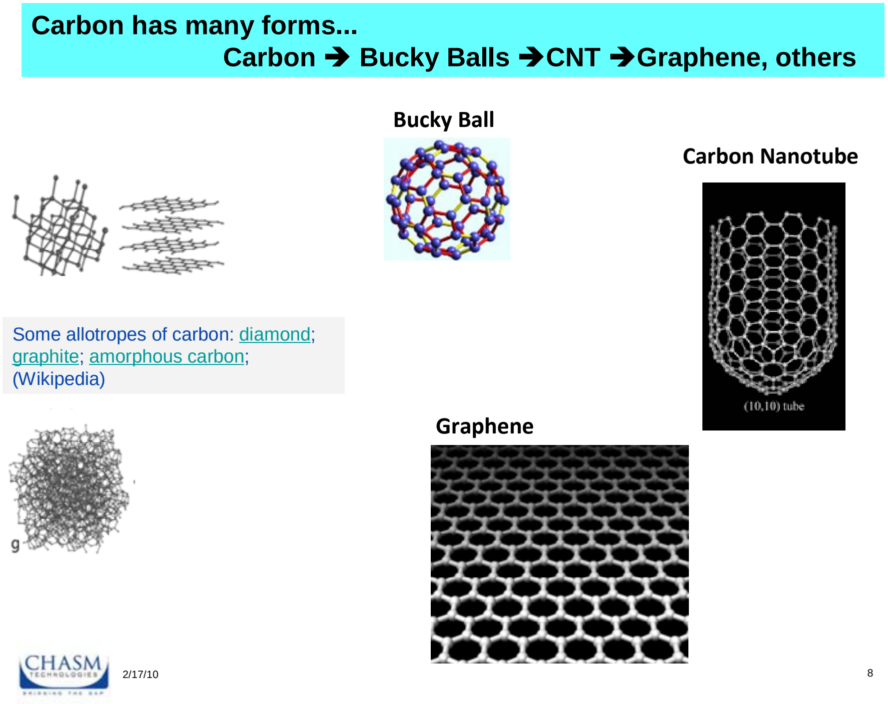
This paper is complementary to a presentation, “Carbon Nanotube Applications? Matching, Materials, Process, and Purpose”, made at the 2010 AIMCAL Fall Technical Conference in Myrtle Beach, SC, October 17-20, 2010.

CNT’s and the Uproar

Carbon nanotubes have been described as “a next transistor” relative to technology potential and the impact on peoples’ lives. In spite of the excitement, CNTs have made modest inroads into broad based applications beyond inclusion in polymer composites. Part of the limitation may be founded in the fact that all CNTs are not equivalent. There exists a range of materials starting with “multiwall CNTs” (MWCNTs), used in certain “less demanding” applications such as structural and antistatic materials; extending to high purity single wall CNTs (SWCNTs) aimed at high performance opto-electrical devices (i.e. high transparency as a coating and very high electrical conductivity to compete with indium tin oxide coatings).

This paper explores several current applications which are moving forward as products and attempts to describe a critical link between successful implementation and a diligent consideration of material property sets and methods of use of such material sets.

An important factor in nurturing the growth of CNT adoption is the need to understand how the definition of a carbon nanotube fits into other categories of carbon based materials. Towards this end, the following graphic displays that a range of carbon forms can exist.



Carbon has many forms...
Carbon ➔ Bucky Balls ➔CNT ➔Graphene, others

Bucky Ball

Carbon Nanotube

(10,10) tube

Some allotropes of carbon: diamond; graphite; amorphous carbon; (Wikipedia)

g

Graphene

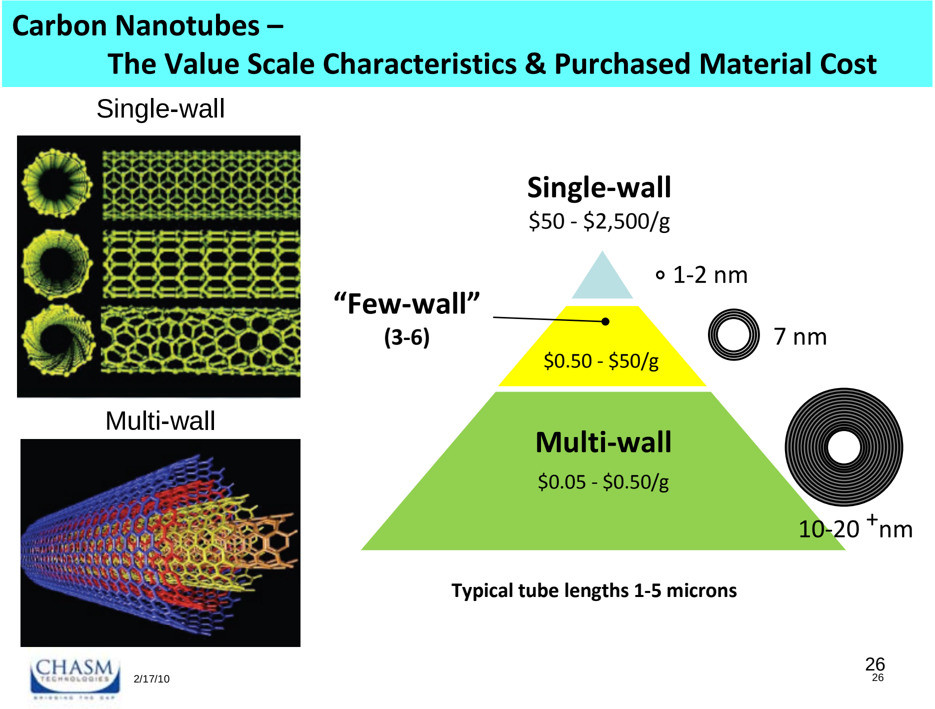
2/17/10

8

Applications generally take advantage of the properties of CNTs and aim to enhance optical, electronic or mechanical performance over products not utilizing the CNT attributes. Such product applications include transparent conductive uniform coatings, as well as patterned structures, antistatic coatings and composites, and specialized structural products. As mentioned in the introduction, the implementation of the applications can include flat panel displays, photovoltaics, solid state lighting, and conductive composite fabrics.

Although the promise of integrating CNTs, and particularly single wall CNTs, into various products has been enticing, ubiquitous presence has not yet been realized and an understanding of “why” is necessary for further industry growth. Understanding the methods of manufacture of CNTs, the cost, and the volume potential of certain processes will help to shed light on the adoption story. Noteworthy is the fact that CNTs have followed the path of many “new, revolutionary materials” (eg. Nylon, Teflon, Kevlar, OLEDs); it has taken decades before significant commercial adoption is realized.

The diagram below provides a “high level” view of the value scale for various CNT forms:



Carbon Nanotubes –
The Value Scale Characteristics & Purchased Material Cost

Single-wall

Multi-wall

Single-wall
$50 - $2,500/g

∘ 1-2 nm

“Few-wall”
(3-6)

$0.50 - $50/g

7 nm

Multi-wall
$0.05 - $0.50/g

10-20 ⁺nm

Typical tube lengths 1-5 microns

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26
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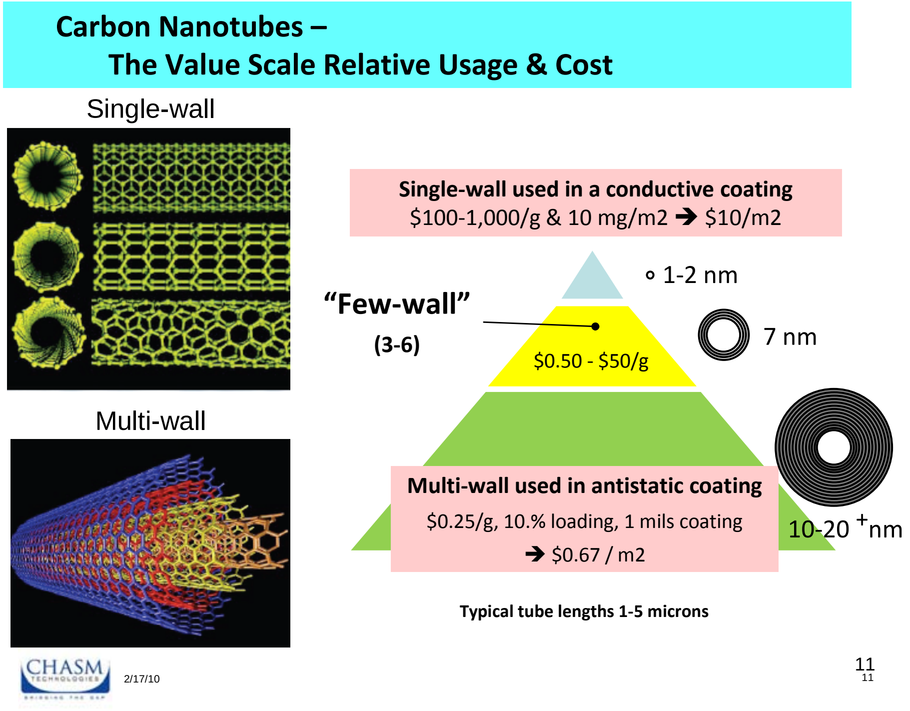
However, a closer look at the applications and materials used shows that although SWCNTs have a significantly higher selling price, the “usage factor” brings such costs more in line with expectations and demonstrates that SWCNTs can compete with other technologies (eg. ITO for highly conductive transparent layers).



Carbon Nanotubes –
The Value Scale Relative Usage & Cost

Single-wall

Multi-wall

Single-wall used in a conductive coating
$100-1,000/g & 10 mg/m2 ➔ $10/m2

∘ 1-2 nm

“Few-wall”
(3-6)

$0.50 - $50/g

7 nm

Multi-wall used in antistatic coating
$0.25/g, 10.% loading, 1 mils coating
➔ $0.67 / m2

10-20 ⁺nm

Typical tube lengths 1-5 microns

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11
11

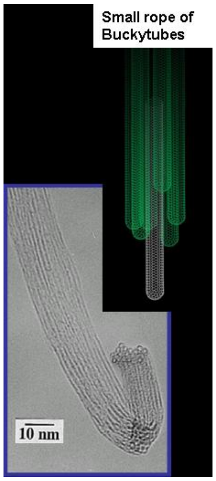
In the case of MWCNTs, the production of "tons per year" is common. The processes are already scaled to large volume, resulting in a cost/value proposition that has been accepted. However, for the "high end" applications, several roadblocks relative to both cost and more importantly availability have presented major challenges. High performance has been demonstrated from several process sources. However, the scale-up potential of some processes is not likely. This is summarized in Table 1 below:

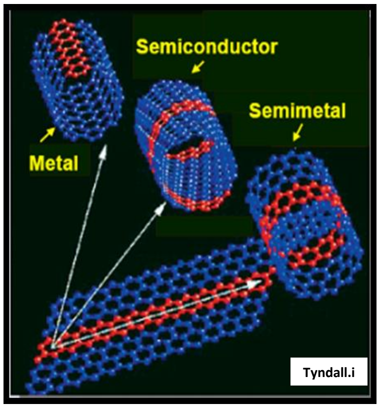
TABLE 1

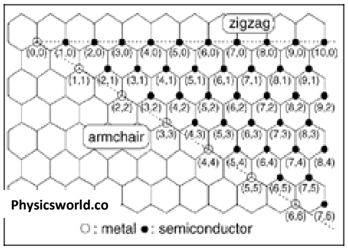
Process Approach	**Laser**	**ARC**	**C CVD**	**C CVD**
General Processing Description	High temperature ablation graphite target; gas phase combination of carbon fragments into CNTs	Graphite electrodes DC or AC arc to vaporize graphite and form into CNTs	Catalytic chemical vapor deposition: fixed bed & HiPco (hi P CO): carbon sources CO; alkanes; alkenes; etc.	Fluidized bed catalytic reactor carbon sources CO; alkanes; alkenes; etc.
Catalyst Requirements	SW CNT require use of a metal catalyst	Hollow anode with catalyst and powdered graphite	Catalyst on fixed bed; in furnace	CoMoCAT catalyst on silica support
Batch size	Very small batch process	Batch process : scaling through added reactors; utilization and short cycle time	Batch process: scaling through added reactors; utilization and short cycle time	Batch process; scaleable reactor
Purification Strategy	Standard purification strategies	Standard purification strategies	Standard purification strategies used (air oxidation, acid treatment for metals or oxidizing reflux)	Standard purification strategies used (air oxidation, acid or oxidizing treatment for metals)
Volume Potential -	mg to g; research	~ 10kg / year	~ 10kg / year	~ 1 kg at a time long cycle time up to tons / year

Over the past several years, laser and arc processes have transitioned to focus primarily in research areas to demonstrate the bounds of performance. This has been influenced in a large way by the recognition that high volume production with these processes will not offer significant economies of scale. Fixed bed CVD processes have shown the ability to make larger quantities, again, with limited scaling, other than multiplying of reactors or bold utilization strategies. In this case, these CVD tubes generally have a higher defect rate (ie. disruption of the CNT structure of the tube shell) than either laser or ARC. In addition, laser, ARC, and fixed bed CVD CNTs produce several forms of carbon, as well as a significant level of polydispersity of the SWCNT chiralities. On the other hand, the fluidized CVD process appears to offer a beneficial combination of product quality, material specificity, and volume potential to serve various demanding markets. The fluidized bed CVD tubes are of high purity, but as a result form tight rope structures. De-bundling of these ropes is THE challenge to overcome (for formulation into coating fluids and printable inks).

Acknowledging that SWCNTs are the most likely to fulfill the high end applications, understanding the control parameters associated with performance becomes useful. It turns out that chirality and size is a driver and the ability to influence chirality (and the degree of metallic vs semi-conducting CNTs) can play a role in product application. If one accepts the fact that SWCNTs hold the promise of superior opto-electronic performance, being able to deliver SWCNTs in a form compatible with both process and product applications becomes a critical target. The aforementioned ability to “de-bundle” the SWCNT ropes is necessary, with ropes shown below. The CNTs must also be of the appropriate chirality to realize the expected benefit. As such, products can only be designed if the processes and materials can be modified to meet the end-use requirements. This means that fluid properties and coating/processing technologies must behave compatibly to assure successful product implementation.







Assuming that the CNTs being used are optimized for a particular application, the CNT powder (which is the product of the various synthesis techniques) must be converted into a usable form for coating. A range of processes are being used to accomplish this, but all must include the general steps of dispersion (to allow manipulation of the tubes easily and avoid airborne CNTs), debundling (which generally requires a relatively high energy process such as Sonication), purification (to remove unwanted species from the original powder), and final formulation compatible for the application technique of interest. Both the formulation characteristics and the application options generally in use are shown in Table 2 and Table 3 below.

Utilizing a variety of application techniques, the general fluid formulation options and characteristics are summarized in Table 2.

TABLE 2 - Ink Characteristics & Post-processing

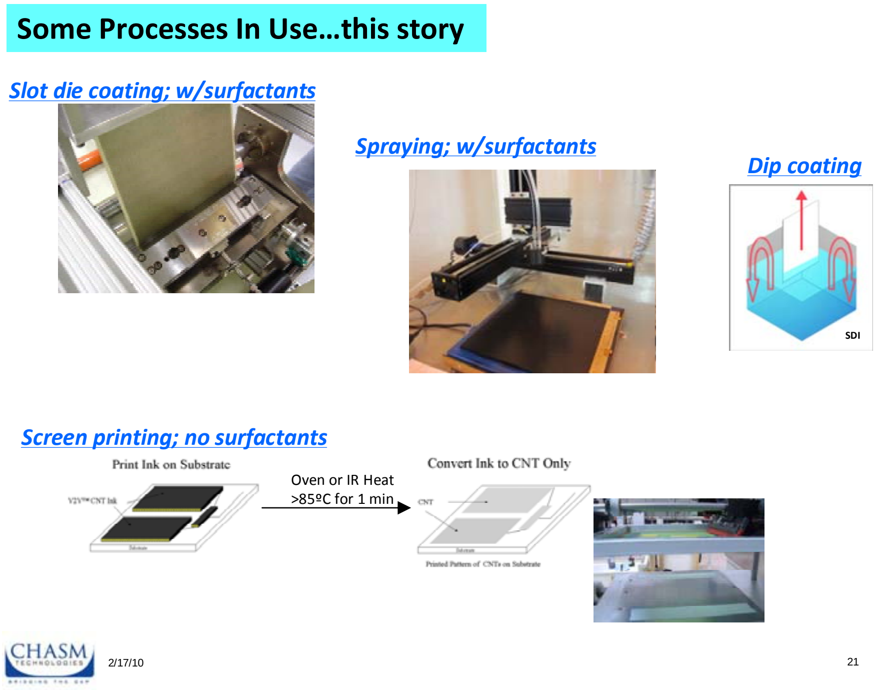
CNT Form	CNT wt% solids	Solvent system	Typical Viscosity, cp	Dispersing & coating aids	Product or process need
Pure powder	100%				Secondary process to separate bundles
Spray fluids	0.001 to 0.03	Aqueous or organic	1 to 50	w/ & w/o Surfactants	Secondary process to remove surfactants
Coating fluids	0.01 to 0.1	Aqueous or organic	1 to 50	w/ & w/o Surfactants	Secondary process to remove surfactants
Screen print inks	0.05-0.2	Aqueous or organic	1000-50000	w/ & w/o Surfactants	Secondary or none
Dispersions	Up to 0.15	Aqueous or organic	1 to 1000	Dispersants/ surfactants.	Binder materials
CNT Pastes/Gel	4+	Aqueous or organic	1000 to 500,000	Surfactants	Binder materials that are part of the coating or fugative

General application processes using selected fluid formulations (from the above table) are shown in Table 3.

Table 3 - Application Methods

Process Family	Application Technology	Fluid viscosity, cp	Wet film, microns	General Process Speed Characteristics	Other Considerations
Printing					
	Screen	1000-50,000	10-30	Fast	Resolution limit?
	Flexo	50-500	1	Fast	Resolution limit?
	Gravure	10-200	2	Fast	Resolution limit?
	Ink jet	3-10	1	Slow to Mod	Nozzles?
	Aerosol jet	3-10	1	Slow to Mod?	New
Coating					
	Slot die	1-20	10	Fast	"Thin" films
	Spray	1-20	<1	Slow	Typcially wafer fab
	Spin	1-20	< 4	Slow	Typciall wafer fab; EHS?
	Dip	10-50	4-20	Slow to Mod	Uniformity ctrl
	Rod	1-20	4-12	Moderate to Fast	Uniformity ctrl
	Knife/roll	10-50	4-20	Slow to Mod	Uniformity ctrl
Compounding	SWCNTs NA DUE TO DISPERSION DIFFICULTY				

As mentioned above, in all cases, the primary goal is the creation of a fluid having highly dispersed SWCNTs. With process materials and operating attributes defined, and a capability for high volume production emerging, a specific challenge limiting broad adoption begins to unravel. As proof of this, use of scalable processes and materials is beginning to emerge, resulting in the incorporation of CNT structures into products of interest. These are highlighted in the graphic below.



Some Processes In Use…this story

Slot die coating; w/surfactants

Spraying; w/surfactants

Dip coating

Screen printing; no surfactants

Print Ink on Substrate

Oven or IR Heat
>85ºC for 1 min

Convert Ink to CNT Only

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21

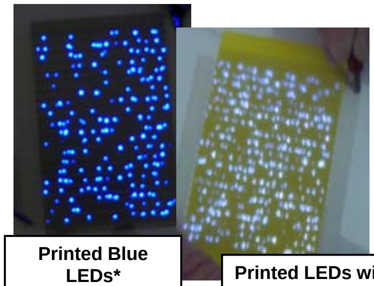
It is expected, that as more understanding is gained on how to manipulate CNTs (and especially SWCNTs) into additional usable processing forms (both materials and processes), that the growth of adoption of CNTs into many products will be inevitable.

Smart Fabrics*

Structural Sensors for FRP Composites!

Affordable, easy & safe to use.

* Patents pending



Printed Blue LEDs*

Printed LEDs with Phosphor Shift to White*

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Chasm Team

David Arthur, John Ferguson, Rick Heroux, Bill Hurley, Denise Radkowski

SouthWest NanoTechnologies (SWeNT) Team

Ricardo Prada, Yongqiang Tan, Dr Daniel Resasco (OU)