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ACCELERATED INSERTION OF MATERIALS-ELECTRONICS (AIM-E) Delivery Order 0011: Production of Electronic Type-Specific Buckytubes for Next Generation Defense Electronics

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1.3 Technical Information

1.3.1 Introduction

The Jordan V alley Innovation C enter at M issouri S tate U niversity (JVIC-MSU) along w ith Unidym, Inc. and Brewer Science, Inc. (BSI) worked to develop and scale up a supply of buckytubes having specific electrical properties. The "Production of Electronic Type-Specific Buckytubes for Next-Generation E lectronics" co vered t hree main tasks w hich i ncluded t he pr oduction of t he r aw s ingle walled c arbon n anotubes (SWNTs), the r efinement of the r aw S WNT m aterial to yield a high purity electronic t ype s eparated f orm of t he o riginal material, and finally m aterials el ectronic p roperties characterization and device application. The first task was performed by Unidym, Inc., the second task was performed by BSI, and the last task was performed by JVIC-MSU. The following is a summary of the task performed by each project partner and the conclusions that resulted.

1.3.2 Subcontractor: Unidym Task Summary

1.3.2.1 Buckytube Synthesis, Quality and Diameter Control

Unidym Inc.'s por tion of t he project w as t o s upply r egular H iPCO " as-produced" S WNT Buckytubes. Referred to as "R" grade SWNTs, during the initial screening of these materials 2 lots were provided to B SI, which were determined to have important protocols for further refinement. Initially, Unidym investigated various QC tools to study these "R" grade lots, such that they can relate the QC variables f or s ynthesis c onditions. A T hermal G ravimetric A nalysis (TGA) conducted s howed differences in purity levels between the 2 lots that were initially investigated. These initial TGA results show differences in both the catalyst level and the peak burn-off temperature as shown in figure 1.



Figure 1: TGA graph of the 2 lots of HiPCO "R" Grade SWNTs

During the period of performance of this project, a number of batches (12) were provided to BSI for further r efinement. Unidym w as also developing an alternative m ethod of SWNT production,

specifically, an MGPx process with emphasis on diameter and chirality control. Initial results were encouraging, with SWNTs being produced with diameters comparable to HiPCO material (figure 2). As the project progressed, different batches of the two buckytube synthesis techniques were produced for further analysis and refinement.



Figure 2: TEM image showing cross-sectional image of "rope"/"bundle" of SWNTs synthesized via the MGPx process

Along with the standard "R" grade material, another grade of HiPCO material referred to as "P" grade was also provided to BSI. "P" grade HiPCO is a purified form of the HiPCO "R" grade material that Unidym can provide. Although this material is not at the level of purification that BSI can produce, it was believed that it would make the BSI process more efficient since less rigorous acid treatment would be necessary. In addition, the special "P" grade HiPCO material contained tubes shorter than the norm, which would improve dispersibility and thereby facilitate type separation.

Synthesis e xperiments us ing the MGPx p rocess w as conducted i n w hich one -wall na notube synthesis w as attempted us ing t hree di fferent t ypes of c atalyst. The di ameter di stributions of t hese nanotube samples were measured using cross-sectional TEM (transmission electron microscope) images (figure 3). The m edian di ameter of t he one -wall na notubes s ynthesized us ing t he M GPx process i s approximately 1 nm , w hich i s c omparable t o t hat of H iPCO SWNTs. F igure 4 shows c umulative distribution functions comparing the diameters of HiPCO and three different batches of MGPx one-wall

nanotubes, C H3A-0234, C H3A-0235 a nd C H3A-0236, s ynthesized us ing di fferent c atalyst formulations. CH3A-0234 and CH3A-0235 were approximately 75% one-wall nanotubes and 25% two-wall na notubes while C H3A-0236 was more than 95% one-wall na notubes with the remainder being two-wall na notubes. T herefore, b y c hanging t he c atalyst f ormulation, the pr oportion of one -wall nanotubes to two-wall nanotubes can be controlled.



Figure 3: TEM i mage showing cross-sectional i mage of "rope"/"bundle" Buckytubes synthesized via MGPx process; the majority of which are one-wall nanotubes. Median diameter of MGPx tubes in this particular sample was approximately 1 nm.



Figure 4: C umulative d istribution f unctions c omparing di ameters o f MGPx a nd H iPCO one -wall nanotubes. Median diameters of MGPx and HiPCO tubes were 1.1 and 1 nm, respectively.

A number of d ifferent g rowth p arameters f or "R" g rade H iPCO m aterial w as al so p roduced. Three different materials, HPR180.1, HPR183.2 and HPR183.3 were produced and provided to BSI. For ease of handling, the tubes were delivered in four (4) 0.5 g aliquots for each material. These tubes were synthesized a t t emperatures t hat de viated f rom t hat us ed t o s ynthesize s tandard H iPCO tubes; their synthesis temperatures are summarized in Table 1.

	Synthesis Temperature	Catalyst
HPR180.1	770 C	Fe + Co*
HPR183.2	1029 C	Fe + Co*
HPR183.3	944 C	Fe + Co*

Table 1: HiPco material synthesis at different temperature

*Amount of Co detected in final product was negligible (less than 0.05 at. % by EDS)

It was h ypothesized that tube synthesis at temperatures lower than standard would result in a higher proportion of defects on the buckytube walls, thus facilitating functionalization and, therefore, dispersibility and stability in water. The high temperature synthesis material was provided for contrast. Comparison of T EM micrographs of H PR180.1 a nd H PR183.2 (figure 5) showed no s ignificant differences i n t he m aterials w ere ev ident at m edium m agnifications (100K). However, T EM micrographs of HPR180.1 and HPR183.2 (figure 6) at high magnification (250K) appeared to indicate that t he h igh t emperature m aterial w as s lightly "cleaner", i.e. contained l ess n on-tubular c arbon, particularly on the tube walls, than the low temperature material.



Figure 5: TEM micrographs of HPR180.1 (left) and HPR183.2 (right). Scale bar = 20 nm. At 100K magnification, differences, if any, between the two materials are not evident. In both materials, fringe lines in the nanotube ropes are clear enough to be visible at medium magnifications. The dark particles are metal catalyst particles.



Figure 6 : TEM m icrographs of H PR180.1 (left) and H PR183.2 (right). S cale bar = 10 nm. A t magnifications hi gher t han 100K, f ringe l ines i n T EM m icrographs of H PR183.2 appear to be marginally cleaner than those in HPR180.1, possibly indicative of less non-tubular carbon coating tubes and ropes.

1.3.2.2 Alternative Diazonium Salt Type-Separation Method

In addition to providing HiPCO SWNTs to BSI, Unidym had been active in carrying out its own semiconductor enrichment work. Standard HiPCO tubes were reacted with a diazonium salt solution in an attempt to s ynthesize s emiconductor SWNTs (s-SWNTs). U pon r eaction with the di azonium s alt solution, dr amatic c hanges oc cur in the R aman profiles of the SWNT solutions. F igure 7 shows the Raman profile for a SWNT solution after it has been reacted with a 1000 microliter aliquot of diazonium salt solution.



Figure 7: Raman profiles for SWNT solution reacted with 1000 microliters of diazonium salt solution, centered around the RBMs. The top profile was measured using a 633 nm laser. The bottom profile was measured using a 785 nm laser.

Under a 633 nm l aser, t he obs ervable R BM's c an or iginate f rom e ither s emiconducting or metallic SWNTs assuming a d iameter r ange t ypical of H iPCO tubes. U nder a 785 nm l aser, t he observable SWNTs with diameters typical of HiPCO tubes are semiconductors. Thus, the elimination of the RBMs observable under a 633 nm laser and the persistence of the RMB's observable under the 785

nm l aser ap pear t o give s ome ev idence of s emiconductor en richment af ter t he r eaction of HiPCO SWNTs with a diazonium salt solution.

Further evidence of s emiconductor e nrichment i s pr ovided by measuring t he c hange i n t he electronic transport properties of the HiPCO nanotubes upon doping. Assuming a statistical average of the distribution of the possible chiralities given a nanotube diameter, one would expect 33% of the tubes to be metallic and the r emaining 67% to be s emiconducting. The addition of c harge carriers to the metallic tubes would have a n egligible effect on t heir r esistance while the effect on s emiconducting tubes would be dramatic.

Films were made of different "inks", each reacted with different levels of diazonium salts. The solutions were filtered through anodisc 20 nm pore size filters and washed with 200 mL of DI water. Once the films were dry, leads were painted onto them using silver paint/epoxy. The resistance of the films was measured with a Keithley 2400 and measured in-situ while they were p-doped with NO₂ gas. Figure 8 shows the ratio of the initial film resistance to film resistance a fter NO₂ doping versus the concentration of the diazonium salt solution added to the SWNTs.



Figure 8 : The r atio o f i nitial r esistance t o r esistance af ter N O_2 doping ve rsus t he di azonium s alt concentration of the initial "inks". The rise in the resistances ratio upon addition of diazonium salts to the H iPco tubes in solution supports the conclusion that the reaction of diazonium s alts and SWNTs results in semiconductor enrichment.

A correlation is seen as the effect of NO_2 doping increases with an increase in the amount of diazonium s alts a dded t o t he S WNTs i ncreases. For ch aracterization of t he d iazonium s alt t reated material, a SWNT based transistor was fabricated and then characterized. Figure 9 shows the on/off ratio

vs. the density of the carbon nanotubes. The typical on/off ratio for a nanotube network transistor is around 1000, which is much too small. One obvious route to improve the on/off ratio is to "kill" the metallic nanotubes chemically or electronically; typical avenues of achieving this goal are via diazonium functionalization or electrical breakdown.



Figure 9: Dependence o f on/ off a nd on -current o n t he n anotube d ensity before an d af ter el ectrical breakdown.

The transistor device that was made is depicted in the schematic shown in figure 10. The channel width i s 1000 μ m a nd t he c hannel l ength varies f rom 5 μ m t o 500 μ m. T he t ransistors' t ransfer characteristics a re m easured with one K eithley 2400 for a pplying V_{sd} and m easuring I_{sd} and a nother voltage source to apply the gate voltage. The applied V_{sd} = 100 mV and the gate voltages sweeps with a step of 0.5 V.



Figure 10: Transistor s tructure w ith C VD-grown S WNT ne twork on a SiO₂ as ch annel an d P d as source/drain contacts.

Figure 11 shows a typical transfer curve of a nanotube network transistor with a 500 μ m channel length. The mobility is calculated with equation 1 and is found to be 5 c m/V s. Note that the device shows a 1 arge h ysteresis, which m ay be due to t rapped water m olecules or charge b uild-up at the SiO₂/nanotube interface

$$\mu = \frac{l}{w} \frac{\mathrm{d}I_{\mathrm{sd}}}{\mathrm{d}V_g} \frac{d}{k\epsilon_0} \frac{1}{V_{\mathrm{sd}}} \tag{1}$$



Figure 11: A typical transfer curve of CVD-nanotube network transistors on silicon substrates.

1.3.3 Subcontractor: Brewer Science, Inc. Task Summary

1.3.3.1 Buckytube Refinement and Purification

For BSI's portion of the project, the work involved further processing of the as-produced HiPCO "R" grade SWNTs provided by Unidym to remove metallic catalysts and carbonaceous contaminants. The second task was to take the as-produced SWNTs and d isperse them in either a surfactant based aqueous solution or functionalizing (purifying) via acid-treatment to produce a surfactant-free aqueous solution for the purpose of metallic and semiconducting na notube separation using di electrophoresis. Initial studies in to type-separation included development of a simple inter-digit mic ro-array electrode system, which was connected to an AC signal generator. By providing an AC signal between conducting electrodes it was demonstrated as shown in the scanning electron microscopy (SEM) image in figure 12, that the metallic S WNTs (m-SWNTs) align themselves per pendicular t o the l ength of the pa rallel electrodes. These i nitial studies were conducted on electrodes that were 1 50µm ap art and therefore alignment of the tubes was not significant, therefore electrode geometry optimization was necessary, which will be discussed in more detail in the next section.



Figure 12: SEM image of Au electrodes with m-SWNTs aligned along the electrode.

Raman phot ospectroscopy was u sed t o ch aracterize/compare the S WNT s olution predielectrophoresis (Pre-DEP), post-dielectrophoresis (Post-DEP), as well as the SWNTs extracted by the electrode. It was found that relatively higher m-SWNT content was deposited between the electrodes as opposed to that of the pre-separated solution. Relatively higher s-SWNT content was found in the Post-DEP solution as c ompared t o t hat of the Pre-DEP solution. A lthough t hese pr eliminary r esults were positive and encouraging, further refinement was required to optimize the entire process.

1.3.3.1.1 SWNT raw materials processing

The materials r eceived from U nidym of di fferent g rades and ba tches were pr ocessed us ing different chemical treatments. Raman analyses were conducted on these materials and compared to those obtained from the SWNTs solutions derived from these raw materials. It was found that the dispersion characteristics of each material were different and consequently, the purification process needed to be tailored a ccordingly. It was c oncluded that the e in consistency of the r aw material h ad a d etrimental impact on t he e ffectiveness of a s et pur ification process t o pr oduce c onsistently pe rforming S WNT solution products.

Various SWNT m aterials were p rovided b y U nidym, which were produced under different conditions, specifically using different growing temperatures and reactor set-ups. In addition, the HiPCO materials came in three different forms: a s-produced fluffy, mud (wet cake), and granular (sand). The wet cake contained more than 98% water, and the granular SWNT materials were freeze-dried after the as-produced SWNT material had gone through certain treatment steps. The as-received HiPCO materials were dispersed into liquid form with appropriate media, such as water or organic solvents. For purifying the as-received materials, an aqueous media is required.

A total of 12 batches of HiPCO materials, with different growing parameters, was obtained and The t hree fo rms o f a s-received HiPCO r aw m aterials possessed different ha ndling processed. characteristics. The granular (sand) and mud (wet cake) were easier to handle than the fluffy powder materials. The fluffy material was very difficult to handle due to its feather-light characteristics. The as-received HiPCO materials were handled inside a glove box for weighing and converting into liquid form with a ppropriate media, s uch a s w ater o r or ganic s olvents, t o pr event pe rsonnel f rom being exposed to SWNTs. The liquid form solutions were then processed accordingly. For purifying the asreceived m aterials, a queous m edia w as us ed. The as -received H iPCO m aterials w ere ch aracterized using a tomic force m icroscopy (AFM) to de termine na notube length and t hermogravimetric analysis (TGA) to detect r esidual s ubstances (mostly m etal impurities) in the materials and to determine the decomposition onset temperature. S ome were characterized using UV-VIS photospectrometer. The SWNT mean length ranged from 469 to 1420 nm and median length ranged from 352 to 1315 nm. The HiPCO materials, due to different growing parameters, had a very wide range, specifically, 8% to 48%, of residual (metal) content. It was observed that the highest residual content material aggregated around the magnetic stirring bar at the very beginning of the purification process. These analytical results are summarized in Table 2.

SWNT Batch	Received Amount	Information	Form	Length (AFM) (nm)	TGA	UV- Vis	Dispersion characteristics (with BSI process)	Approximate Stability of purified/ dispersed product
R0558	Purchased 8/3/07	HiPCO tubes, standard process	Fluffy powder	Median: 495 Mean: 742	Residual: 29% T _{onset} ~340 °C		Easily dispersed. Final product: OD>3 possible	Stable f or >6 months
R0559	Purchased 8/3/07	HiPCO tubes, standard process	Fluffy powder	Median: 1164 Mean: 831	Residual: 22% T _{onset} unknown		Moderate dispersibility. Final product: OD>3 possible	Stable f or s everal months
R0546	Purchased 1/4/08	HiPCO tubes, standard process	Fluffy powder	Median: 352 Mean: 597	Residual: 25% T _{onset} unknown		Moderate dispersibility. Final product: OD~3 possible	Stable f or s everal months
RR183.5	Received 8/8/08	HiPCO tubes, standard process	Fluffy powder	Median: 579 Mean: 1003	Residual: 26.5% T _{onset} ~400 °C	\checkmark	Difficult to disperse. Final product: OD~1.9 possible	Stable f or s everal days
ATP035	Received 9/9/08	Purified (post processed) HiPCO tubes	Fine sand free- flowing powder	Median: 1315 Mean: 1416	Residual: 11.3 % T _{onset} ~400 °C	V	Difficult to disperse. OD 2.7 obtained.	OD=2.7 S table f or 1 day. OD= 1.89 stable for ~ 1 week
R0238	10/08/08	HiPCO tubes, treatment with E tOH post synthesis	Sand	Median: 379 Mean: 469	Residual: 48% T _{onset} ~350 °C	\checkmark	Extremely difficult to disperse. OD~2.2 obtained	Uncentrifuged sample stable for 2 days (OD=2.2). Centrifuged sample stable for > 2 weeks (OD=1.49)
P0356	11/13/08	Purified HiPCO tubes	Fine sand free- flowing powder	Median: 531 Mean: 677	Residual: 8% T _{onset} ~340 °C	\checkmark	Not pos sible t o disperse un der standard conditions	NA
TST178-1	12/26/08	MGPx process (rich in SWCNT's, made w ith low c ost metal cat.)	Mud		Residual: 21.7% T _{onset} ~420 °C		Abandoned - process may not be r eproducible at this time	NA
HPR179.2	12/26/08	"In ki nd" tubes m ade with ne w HiPCO reactor	Fluff		Residual: 21.7% T _{onset} ~300 °C		Not pos sible t o disperse effectively under s tandard conditions	NA
SWCNT Batch	Received Amount	Information	Form	Length (AFM) (nm)	TGA	UV- Vis	Dispersion characteristics (with BSI process)	Approximate Stability of purified/ dispersed product

HPR180.1	1/4/09	Synthesized at 770 °C	Fluff	Residual: 19% T _{onset} ~400 °C	Difficult to disperse	Difficult to disperse, unstable
HPR183.2	1/4/09	Synthesized at 1029 °C	Fluff	Residual: 33% T _{onset} ~380 °C	Extremely difficult to disperse. OD~0.4 obtained	Stable for 1 day
HPR183.3	1/4/09	Synthesized at 944 °C	Fluff	Residual: 21% T _{onset} ~380 °C	In progress	

Table 2: Basic information and characterizations of all batches of HiPCO raw materials and purified SWCNT solutions characteristics.

1.3.3.1.2 Purification of HiPCO raw materials

The purification process for SWNTs mainly involved a series of chemical treatments (typically an acid reflux process and BSI's proprietary chemical treatment processes), pH adjustment, sonication, filtration, and centrifugation steps. E ach step involved extensive and precise processing control. The steps were also inter-related and required close attention to improve processing of the materials. A representative purification process flow is shown in Figure 13.



Figure 13: A representative schematic SWNT purification process.

The HiPCO SWNT is first weighed and dispersed into deionized water, and then sonicated to exfoliate the bundled SWNTs prior to any further processing. The solution is acidified to a certain pH or concentration using various acids such as nitric acid, sulfuric acid, and hydrochloric acid. The main purpose of this acid reflux step is to digest the metallic nanoparticulates and carbonaceous impurities as well as break down the SWNT tips to digest the metal nanoparticulates encapsulated inside them.

The refluxed solution was then subjected to proprietary chemical treatments and then subjected to filtration to r emove d igested me tal (from me tal n anoparticulates) a nd o xidized c arbonaceous impurities. Subsequently, a specially designed filtration system is deployed for removing the digested metal a nd c arbonaceous impurities from the S WNT s olution. This system a lso provided a m eans t o concentrate the nanotube solution, if necessary. The permeate and retentate are characterized for their optical d ensities (ODs) u sing a U V-VIS s pectrometer. T his t echnique is used to d etermine if the carbonaceous impurities have be en removed from the solution, as well to determine the relative CNT concentration. Overall, it was found that the as-produced fluffy HiPCO material was easier to disperse and purify.

1.3.3.1.3 Characterization of purified SWNT solutions

The purified SWNT solutions were characterized using Raman spectroscopy for the appearance of SWNTs with different diameters and electronic characteristics (metallic or semiconducting), as well as to detect the presence of carbonaceous impurities and/or defect levels. Scanning electron microscopy (SEM) and Atomic Force M icroscopy (AFM) were u sed t o c haracterize t he de posited S WNTs f or coating quality, carbonaceous impurity, and SWNT length.

Raman spectroscopy equipped with a 632.8-nm wavelength laser was used to characterize the purified SWNT materials for the appearance of G (1540 cm⁻¹ to 1600 cm⁻¹), D (about 1330 cm⁻¹), and RBM (radial breathing mode, about 100 cm⁻¹ to 400 cm⁻¹) bands, as shown in figure 14. A small volume of S WNT s olution is filtered on a \sim 2-inch-diameter filter d isk and d ried. This filter d isk was then characterized u sing the Raman spectroscopy. A typical doublet tangential mode (G⁺ and G⁻ bands), which indicates the existence of S WNTs, is clearly observed. The observation of the disorder-induced mode (D b and) i ndicates ei ther the p resence of d efects on n anotube s urfaces and t ube e nds or the presence of c arbonaceous impurities. It also can be caused by the carboxylic functional groups on the nanotubes after the acid-reflux purification process. The presence of the RBM bands is a characteristic unique to CNTs which is not observed in other carbonaceous materials.

The e lectrical c haracteristics of the SWNTs, t hat is, me tallic a nd s emiconducting, c an be identified according to the K ataura plot in figure 15. Also, as shown in figure 15, the R aman shift at about 194 c m⁻¹ is identified as m-SWNTs, while the s-SWNTs contributed to the R aman shift at about 258 c m⁻¹. The pe ak at about 218 c m⁻¹ is also identified as m-SWNTs however; it is debatable as to whether or not the peak is caused by bundled SWNTs of m- & s-SWNTs. When different wavelengths of laser light are used in the Raman spectrometer, they will resonate with different diameters, therefore, different chiralities of SWNTs.



Figure 14: A representative Raman spectrum obtained from the purified SWNTs on a filter disk. The radial br eathing m ode (RBM; 100 c m^{-1} to 400 c m-1), di sorder-carbon (D; a bout 1330 c m^{-1}), a nd tangential (G; about 1540 cm⁻¹ to 1600cm⁻¹) modes are labeled.



Figure 15: SWNT radial breathing mode (RBM) Raman shifts within the range of 120 cm⁻¹ to 380 cm⁻¹ in Figure 2.

SEM and A FM were used to complement R aman spectroscopy for characterizing the purified SWNT material. In figure 16(A), S EM characterization indicates a very dense S WNT fabric coated onto a silicon wafer s urface with 1 ittle or no carbonaceous i mpurities (mostly a morphous c arbon). Amorphous carbon blurs the nanotube images seen in the SEM micrographs. In addition, no not iceable particulate, which c ould a lso r esult from t he s pin-coating p rocess, w as obs erved a cross t he S WNT fabric. A FM data shows the SWNT lengths ranging from a few tenths of a micron to greater than 2.5 μ m; see figure 16(B). It was evident that the majority, if not all, of the carbonaceous impurities (mostly amorphous carbon) were removed, as indicated by SEM and AFM characterization, after the purification process.



Figure 16: (A) SEM and (B) AFM micrographs of spin-coated SWNTs on silicon wafer substrates.

1.3.3.2 Buckytube Type-Separation via Dielectrophoresis

Dielectrophoresis was used to separate metallic and semiconducting SWNTs in aqueous media. Both as-produced and purified SWNT solutions were used to demonstrate the feasibility of using this separation technique. This work was carried out using a small cell (steady solution) dielectrophoresis setup for the initial proof-of-concept. A s-produced SWNT material was dispersed into a queous media and another SWNT solution was prepared through the purification process. Both solutions were used for metallic and semiconducting nanotube separation using dielectrophoresis. Simple small inter-digit array electrodes, a bout 1 c m x 1 c m, were fabricated on a silicon ox ide wafer for initial proof-of-concept purposes. The el ectrodes w ere f abricated w ith C r/Au co ating o n t he silicon o xide w afer w ith photolithography, wet chemical etching, and resist stripping processes. The wafer was diced to produce an i ndividual e lectrode. The i ndividual e lectrode w as c onnected w ith a n A C s ignal generator and approximately 400μ L of S WNT aqueous was placed on t he electrode, and an AC signal was applied. SWNTs were found on t he electrode a fter the dielectrophoresis process as was shown in the initial results in figure 17.

Raman photospectroscopy was used to characterize the SWNT solution Pre-DEP and Post-DEP, as well as the SWNTs extracted by and adhered between the electrodes. The HiPCO SWNTs were dispersed into deionized water using one of two methods; surfactant or purification to study both pre and post purification solutions after the dielectrophoresis process was carried out. The SWNT solution that was extracted and SWNT material that adhered to the electrodes was also characterized using a Raman spectroscopy, as s hown in figure 17. It also s hows the R aman spectra for the p re-purified S WNT solution, which clearly reveals that the relative p eak in tensity and are a ratios for m-SWNTs and s-SWNTs have changed drastically for those S WNTs extracted from the electrode as opposed to those from the a s-produced S WNT s olution. The de crease i n s -SWNTs on t he e lectrode i s evident, a s indicated b y the d ecrease i n the relative in tensity of the s -SWNT pe aks (256, 258, a nd 284 cm⁻¹) compared to those obtained from the as-produced SWNT solution, while the m-SWNT peak (197 cm⁻¹) remains constant.

The s ame s tudy w as d one on t he acid-treated (purified) S WNT a queous s olution and a subsequent R aman study was carried out as shown in figure 18. The Pre-DEP and Post-DEP SWNT solutions have very similar R aman spectrum profiles. This is due to the relative larger amount of the solution us ed f or dielectrophoresis. H owever, the S WNTs on the electrode p ossess a v ery d ifferent Raman spectrum profile, as clearly seen in Figure 18. The s-SWNT peak intensity at 257 cm^{-1} and 284 cm⁻¹ is reduced greatly while the m- SWNT peak intensity at ~196 cm⁻¹ remains constant. This indicates that the SWNTs on the electrode are predominantly m-SWNTs after dielectrophoresis.



Figure 17: Raman spectra (633-nm laser) of the as-produced SWNT solution and the SWNTs adhered onto the electrode Post-DEP.



Figure 1 8: Raman s pectra (633 n m l aser) of t he P re-DEP and P ost-DEP S WNTs and the SWNTs adhered to the electrode after dielectrophoresis.

A continuous flow dielectrophoresis cell and electrode as shown in figure 19 was designed and fabricated as p art of t he S WNT s eparation s cale-up e ffort. T he c ell w ould be us ed t o t ype-separate carbon SWNT solution in larger quantities. The m-SWNTs can be extracted from the electrode and re-dispersed into the appropriate solvent.



Figure 19: A continuous flow dielectrophoresis cell configuration with inter-digitated electrode array at bottom.

It was demonstrated that h igh-purity, surfactant-free SWNT aqueous solutions was developed using only 1 or 2 types of HiPCO S WNT material, and the process can be controlled and scaled up. From a mass production s tandpoint, bot h process controllability and r aw materials consistency are required. A bench-scale dielectrophoresis process for s eparating m-SWNTs and s-SWNTs has been proven and developed, but still requires refinement.

1.3.4.1 Identification of Electrical Properties of SWNTs

JVIC's t ask on t his project w as t o provide o verall m anagement a long w ith f acilitation of materials electronic properties characterization as well as device application. J VIC al so produced the electrode systems via photolithography that BSI required to perform the dielectrophoresis studies. It had been d etermined t hat ap art f rom t he b asic r oom t emperature 4 -point IV and t emperature d ependent resistance measurements to electrically characterize the refined SWNT material, developing a number of device applications would allow for further electrical characterization.

In indentifying the electrical properties of the type-separated SWNT's, initial room temperature IV and t emperature d ependent r esistance m easurements w ere conducted on t he Pre-DEP H iPCO SWNTs. T his a llowed for a baseline m easurement to be conducted p rior to type-separation w hich would e stablish a protocol f or c omparison w ith the Post-DEP S WNTs. Hi PCO S WNT's we re s pin coated onto two oxide wafers; one was coated with 2 coats and the other was coated with 5 coats. The wafers were characterized for b oth room temperature IV as well as temperature d ependant r esistance measurements.

For t est pur poses 3 r egions on t he wafer (near edge 1, middle, & near edge 2) of a 100m m diameter wafer were cut out and measured for room temperature IV as well as temperature dependent resistance characterization. The dies where chosen along the diameter of the wafer as shown in figure 20. Since the SWNT solution was spin coated and the coating application is a radial effect, this would allow for a quick check to see the uniformity of the coat along the length (diameter) of the wafer. The IV plots for the 2 coat wafer for the three regions are shown in figure 21; the slope of the linear equation is the resistance of the SWNT material being measured. The same is shown for the 5 coat wafer in figure 22. It is evident that there is some slight non-uniformity along the diameter of the wafer but this method is sufficient as a quick check to determine the order of magnitude of the coated SWNT material when the electrical property comparisons of Pre-DEP and Post-DEP coated wafers are being made.



Figure 20: Die laser scoring scheme of 100 mm wafers; dark regions represent the 3 regions tested.



1(A)





I (A)

Figure 22: Room temperature IV characterization of 5-coat wafer (slope = resistance).

Table 3 shows the electrical values for both the 2 and 5 coat wafers; the extrapolated resistance (R) values along with the calculated sheet resistance (R_s) and Conductance (G) values. The resistance was determined from the slope of the linear fit of the IV curve for each sample measured. The sheet resistance was then calculated using the following equation:

(1) Rs = R W/L (Ω/\Box) where, L = 2.00 mm & W = 12.00 mm

And the conductance (G) is calculated using the following equation: (2) $G = 1/R (\Omega^{-1})$

It can be seen from the table that the order of magnitude for the most part is primarily in the $10^4 \Omega$ range for both the 2-coat and 5-coat samples. This was the basis for the next step which was to conduct a temperature dependent resistance characterization.

Coat	Region	R (Ω)	R (Ω/□)	G (Ω ⁻¹)
2	Edge 1	2.076E+03	1.246E+04	4.817E-04
2	Middle	5.182E+04	3.109E+05	1.930E-05
2	Edge 2	1.516E+04	9.096E+04	6.596E-05
5	Edge 1	5.696E+02	3.418E+03	1.756E-03
5	Middle	1.010E+04	6.060E+04	9.901E-05
5	Edge 2	1.516E+04	9.096E+04	6.596E-05

Table 3: Resistance, Sheet Resistance and Conductance values for the two (2 coat & 5 coat) wafers for the three respective regions.

The temperature dependent resistance characterization was conducted on the two middle region samples of both the 2-coat and 5-coat wafers. This study was conducted to first verify that the SWNT material coated onto the wafers is dominated by semiconducting SWNTs versus metallic SWNTs. This will be another check to make comparisons between the Pre-DEP and Post-DEP SWNT material. Figure 23 shows a temperature vs resistance curve for the 2-coat and 5 coat samples. It is evident from both curves that the SWNT material at the Pre-DEP stage is mostly semiconducting for both coats.



Figure 23: Resistance vs Temperature for the 2-coat & 5-coat (middle region samples).

One of t he i ssues w ith t he s pin-coating me thod is th at f ilm c oat u niformity is n ot a lways consistent. A S onoTek Ultrasonic D eposition s ystem w as pur chased t o r emedy t his i ssue s uch t hat fabrics c ould be s prayed uni formly. T he s ystem a llowed f or t wo a dvantages over t he s pin c oating method of deposition. This first advantage was that it would produce a more uniform film over a given area. T he s econd a dvantage i s l ess m aterial c onsumption over s pin c oating s ince t he s pray coated material could be done on smaller substrates and only on the area of interest. Figure 24 below shows an AFM i mage o f a f abric t hat w as s pray c oated us ing t he ul trasonic deposition s ystem. N ote t he consistency of the fabric film which can be controlled and produced without voids. This is important in making the electrical measurements of the systems once comparisons are being made to characterize the Pre-DEP and Post-DEP SWNT material.



Figure 2 4: A FM ima ge o f S WNT ma terial s pray coated o nto a g lass substrate us ing t he S onoTek Ultrasonic Spray Coating System.

1.3.4.2 Design and Developmental Work of CNT-TFTs

Developing proof-of-concept devices was the next step in demonstrating the applications of typeseparated material. One such device is a carbon nanotube thin film transistor (CNT-TFT), which could be f abricated us ing s tandard m icrolithography techniques. Figure 25 b elow s hows a r epresentative schematic diagram of the CNT-TFT device that was under development. The proof-of-concept device was to allow for characterizing/comparing of the Pre-DEP and Post-DEP S WNT material in a d evice form.



Figure 25: Schematic Diagram of Proposed CNT-TFT Device.

The S EM i mage i n f igure 26a s hows t he s ource a nd d rain e lectrode scheme w ith v arying dimensional separation which is where the CNT fabric under test would be patterned. The Au contacts are 125 μ m s quare w ith a minimum separation of 15 μ m up t o 100 μ m b etween ad jacent co ntacts. Figure 26b shows an example of a patterned polymer material which currently serves as a place holder to pattern the SWNT material of interest. The separation locations are designated as numeric rows and alphabetic columns. The separation between contacts along with the designation locations are provided in table 4.



Figure 26: a) S EM i mage of S ource/Drain e lectrodes configured i n an a rray form w ith va rying separation between Au contacts; b) SEM image showing patterned material where CNT fabric is placed to complete the CNT-TFT device.

	А	в	С	D	ш	F	G	н	Ι
1	15 x 125	15 x 100	15 x 75	15 x 60	15 x 45	15 x 30	15 x 25	15 x 20	15 x 15
2	20 x 125	20 x 100	20 x 75	20 x 60	20 x 45	20 x 30	20 x 25	20 x 20	20 x 15
3	25 x 125	25 x 100	25 x 75	25 x 60	25 x 45	25 x 30	25 x 25	25 x 20	25 x 15
4	30 x 125	30 x 100	30 x 75	30 x 60	30 x 45	30 x 30	30 x 25	30 x 20	30 x 15
5	45 x 125	45 x 100	45 x 75	45 x 60	45 x 45	45 x 30	45 x 25	45 x 20	45 x 15
6	60 x 125	60 x 100	60 x 75	60 x 60	60 x 45	60 x 30	60 x 25	60 x 20	60 x 15
7	75 x 125	75 x 100	75 x 75	75 x 60	75 x 45	75 x 30	75 x 25	75 x 20	75 x 15
8	100 x 125	100 x 100	100 x 75	100 x 60	100 x 45	100 x 30	100 x 25	100 x 20	100 x 15

Table 4: Dimensional (row height x column width) designation. All dimensions are in microns.

In lig ht o f c haracterizing t hese C NT-TFT de vices a s w ell a s c onducting t he ba sic r oom temperature IV and t emperature d ependent r esistance m easurements, a K eithley 4 200 s emiconductor characterization s ystem (SCS) was pur chased. This s ystem would also allow us to obtain parametric data o f t he C NT-TFTs onc e t hey w ere de veloped. T he s ystem w as c hosen for t hese s pecific measurements b ecause i t conforms t o a nd s upports t he ne w IEEE S tandard P 1650TM-2005: I EEE Standard Test Methods for Measurement of Electrical Properties of Carbon Nanotubes. Initial work with this system included set up, which included interfacing with an existing 4-wire probe station, an existing temperature variable cryostat and familiarization with the systems GUI.

During the course of development of the CNT patterned fabrics it was determined that some of the et ching s teps d uring t he l ithography p rocesses act ually af fected t he el ectrical p roperties of t he SWNT fabric. There was some difficulty in getting the CNT fabrics patterned. This was a critical step that we unfortunately were not able to overcome in terms of the SWNT fabric's el ectrical properties consistency after the lithography patterning process.

1.3.4.3 Modification of Project Tasks

The 5th quarter's work for this project involved the restructuring of project tasks. The original project tasks were divided among the three groups working in collaboration on this project; Unidym, Inc (buckytube m aterial p rovider), Brewer S cience, Inc (buckytube p urification and t ype s eparation developer), and JVIC-MSU (buckytube application and characterization). During the 4th quarter of this project, Unidym went through an internal restructuring and closed its materials development division. In light of this restructuring other commercial buckytube material vendors had to be investigated.

At this point BSI had completed its task to develop a dielectrophoresis process to separate the SWNTs after their established purification process which produces stable surfactant-free purified SWNT dispersions. However, the process still required refinement and scale-up to produce large volumes of material. At this point JVIC continued the work independently to refine the process to allow for scale up and test the materials using standard characterization techniques as well as testing of a pplication test devices.

1.3.4.4 Alternative Buckytube Supply Vendors

With U nidym g oing t hrough a c orporate r estructuring w hich i nvolved t he c losure of i ts buckytube m aterials di vision, ot her buc kytube supply ve ndors h ad t o be i nvestigated. A nu mber vendors were investigated which included S outhwest Nanotechnologies, Inc, S wan Chemcial, Inc, and Nanolab, Inc. The initial work involved an investigation of each of the company's material data sheets to determine the purity levels as well as chirality in formation of their as-produced S WNT material. O ut the va rious c ompanies t hat w ere i nvestigated, t hree w ere de termined t o pr ovide t he hi ghest q uality material. T he t hree v endors t hat w ere ch osen f or t heir m aterials ev aluation i ncluded S outhwest Nanotechnologies, Inc, Swan Chemcial, Inc, and Nanolabs, Inc.

1.3.4.4.1 Qualification of Buckytube Supply Vendors

Raman spectroscopy was performed on the different SWNT materials that were purchased for comparison of quality and di ameter di stribution of t ubes c omprising the materials. T hese materials include Southwest Nanotechnologies SWeNT CG100, SWeNT CG200X, NanoLabs D1.5L-1-5-S CVD, and T homas S wan P R0925. T hese materials were compared t o t he Unidym H iPCO material t o determine w hich v endor's materials most closely compared for e ase of di spersibility, di ameter distribution a nd quality/purity (figure 27). C onditions for the sample preparation a re as follows; 10 grams of SWNT material was placed in 100 ml of 0.5% wt. sodium dodecyl benzene sulfonate (SDBS) solution, the solution was then horn sonicated for 30 minutes at 72% amplitude using a ¹/₂" probe. 10 ml of solution was used to prepare a vacuum filtration disc. Raman was then performed on the filter disc using lasers of 532 nm (2.33 eV), 633 nm (1.96 eV), and 785 nm (1.59 eV) wavelengths.

The D band known as the defect band gives insight as to the amount of defects in the sample, a higher intensity is indicative of m ore defects. The degree of broadness in the peaks indicates either defects in the SWNTs for narrower peaks or the level of amorphous carbon present for broader peaks. From the shape of the D m ode of the S WNT s amples m easured, it would seem that there is more amorphous carbon present than tube defects. The quality or purity of the sample is determined by the D/G r atio of the R aman s pectra, which is shown in t able 5 be low. It is a pparent that the S WeNT CG200X has the highest quality of tubes with a D/G ratio of 0.024, while the NanoLabs D1.5L-1-5-S has the lowest quality with a D/G ratio of 0.050. The purity for the NanoLabs and HiPCO materials closely matches that of their data sheets with a purity >95% and ~97% purity, respectively.

Sample	D	G	D/G
SWeNT CG100	41428.3	1247750	0.033
SWeNT CG200x	41435.2	1755750	0.024
NanoLabs D1.5L-1-5-S	105598	2101880	0.050
Thomas Swan PR0925	106320	2197210	0.048
Unidym HiPCO	75637.5	1923760	0.039

Table 5: D/G Ratios for the various materials tested.



Figure 27: Raman of the D mode and G mode using 633 nm laser.

The shape of the G mode gives insight into whether the species of SWNTs are semiconducting or metallic. The presence of the G⁻ peak of the G mode suggests that the SWeNT materials, CG100 and CG200X, both contain amounts of metallic SWNTS (m-SWNTs). The other samples' lack of a G⁻ peak suggests ov erwhelming semiconducting S WNT (s-SWNT) populations. The radial br eathing m ode (RBM), between 100 c m⁻¹ and 400 cm⁻¹, gives the tube populations diameter distribution, e lectronic properties and a ggregation states. Another feature of note is the existence of a bundling peak in the RBM due the effects of overlapping energies of tubes.

The di ameter di stribution of t he s amples s tudied w as be tween 0.6 nm to 1.7 nm, with t he NanoLabs material having the largest distribution of 0.6 nm to 1.7 nm and both S WeNT C G100 and CG200X having the smallest distribution of 0.6 nm to 1.3 nm. The Thomas Swan materials compared similarly to the Unidym HiPCO material with both having a diameter distribution of 0.7 nm to 1.7 nm. It was d etermined that the S WeNT C G200X material s eemed to b e b etter in q uality th an the other materials that were investigated, and best compared to the HiPCO material.

Sonication conditions were studied once it was determined that the SWeNT CG200X was the material of c hoice t o d etermine t he be st c onditions f or di spersion with t he l east amount of tube destruction. Both an amplitude and time study were conducted for this purpose. The graphs in figure 28 below show the R aman results of this study, where it was determined that a 50% amplitude for a 30 minute sonication period had the least amount of tube destruction.



Figure 18: Sonication amplitude and time showing relative amounts of tubes in solution for S WeNT CG200X.

The sonication time solutions were then centrifuged to see how well the SWNTs dispersed in the solution. Absorbance was measured for the pre and post centrifuged solutions to see a change in material removed from the solution. From figure 29, it shows that the 60 minute sonication sample had a higher concentration of S WNTs r emaining i n t he s olution be cause of t he s mall a mount of c hange i n absorbance. This would indicate that a 60 minute sonication time will yield the best dispersion, however the R aman data suggests that the 30 minute sonication time had the least amount of tube destruction. Even if there is more material in solution a fter a 60 m inute sonication, the tubes w ould have more defects. Therefore the best sonication conditions for the SWeNT CG200X will be at 50% amplitude for 30 minute sonication time.



Figure 29: Absorbance of pre and post centrifuge solutions with different sonication times.

1.3.4.5 Continuous-Flow Type-Separation System

Work into refining the setup for a continuous flow system was continued where it was shown that refining the electrode geometry yielded better results as shown in figure 30, which shows both an AFM a nd S EM i mage of t he m -SWNTs t hat h ave al igned b etween t he el ectrodes d ue t o dielectrophoresis.



Figure 30: AFM (left) and SEM (right) images of m-SWNTs aligned between electrodes.

A continuous flow dielectrophoresis system was designed to accommodate a number of different electrode geometries onto a fluidic chamber system that would allow for greater separation. This would be done by creating a multiple electrode scheme that is connected in a parallel configuration similar to capacitors in parallel. Each electrode system (1cm x 1cm) chip can then be housed in a fluidic chamber with chambers that run in series but the electrodes being electrically connected in parallel. This would allow f or a s ingle A C s ignal s ource to p rovide th e s ame amplitude o ver mu ltiple e lectrodes simultaneously. The setup design is illustrated in figure 31 below.



Figure 31: Continuous-Flow electrode setup for scale up of dielectrophoresis process.

1.3.4.5.1 Dielectrophoresis Electrode Design

The parallel electrode geometry that was designed would allow for more surface area for SWNT type-separation. It was also determined that out of all the electrode geometry patterns two designs; radial and inter-digitated yielded the highest separation of metallic SWNTs from solution. The microelectrode design is shown in figure 32 below, where there are 8 electrode cells per configuration and one being radial and the other being inter-digitated.



Figure 32: Top image is a full patterned electrode design with radial on the left and inter-digitated on the right with a zoomed optical microscope close-up of each electrodes configuration below.

These electrode schemes were dimensionally designed such that they could be house in an offthe-shelf fluidic cell chamber system. The fluidic cell chamber system was modified such that it would allow for a continuous flow rather than a static chamber for each cell. Figure 33 below shows an image of the continuous flow setup that was developed. The manipulator probes applied the AC signal to the electrodes along with measurement of the signal.



Figure 33: Top image is the continuous flow dielectrophoresis system setup and bottom image is a closeup of the system fluidic chamber system.

The system mode of operation is illustrated below in the figure 34. The solution is fed into the inlet using either a syringe pump or a peristaltic pump at rates of microliters or nanoliters per hour. As the A C s ignal i s a pplied t o t he e lectrodes, t he s olution that r uns t hrough e ach w ell c hamber i n a continuous or r e-circulating fashion i s processed for t ype s eparation t o cr eate a s emiconducting r ich solution where the metallic S WNTs are immobilized onto the metal electrodes. This setup produces milliliters of volume and still requires further refinement to scale up to produce liter level volumes of material.



Figure 34: Top-view image of system design and flow scheme mode of operation.

The system showed significant improvement over previous design systems where a large amount of metallic SWNTs were evident on the electrodes as shown in figure 35. As can be seen with in this case the r adial configuration shows a large amount of metallic SWNT a lignment between the metal electrodes. T his level of s eparation w as also o bserved with the inter-digitated electrode g eometry. Figure 36 shows an SEM image of the m-SWNTs having aligned between the Au electrodes.



Figure 35: C onfocal Laser S canning image of Post-DEP where metallic SWNTs are aligned between the Au electrodes of a radial geometry configuration.



Figure 36: Scanning Electron Microscope image of Post-DEP with metallic-SWNTs aligned between the Au electrodes.

To make the system more efficient the electrodes were easily cleaned using a P lasma Etching process such that they could be re-claimed and used again. The continuous flow system was designed such that the electrode could be cut to size and be inter-changed with the fluidic well chamber system such that the multiple electrodes c ould be f abricated and used one after the other. To increase the volume of production, a higher number of electrode cells on a single setup needs to be designed such that a larger area is available for type-separation and scale up.

Electrical characterization was conducted on the Pre-DEP solution and the Post-DEP solution to conduct a quick check to determine the degree of type-separation using electrical test methods. It was determined t hat t he q uickest ch eck would be t o conduct a t emperature d ependent r esistance measurement to see the Δ R/R change as a function of decreasing temperature down to cryogenic temperatures. Figure 107 shows that data plotted of a batch of S outhwest N anotechnologies C G200x material that was characterized both Pre and Post-DEP. As can be seen the Δ R/R change is higher for the P ost-DEP m aterial v ersus the P re-DEP m aterial with c hange of 29.41%. T his i ndicates t hat t he quantity of s emiconducting S WNTs i n t he b atch of m aterial r un t hrough t he continuous f low dielectrophoresis s etup was higher t han compared t o be fore i t w as run t hrough t he s ystem. Further studies a re s till r equired to o ptimize th is s eparation me thod in in crease o verall s eparation yield percentage per run.



Figure 107. Resistance vs Temperature curve normalized to R @ 300K for each sample run to compare resistance change between Pre-DEP and Post-DEP

1.4 Conclusion

In conclusion, it has been demonstrated that a supply of SWNT material can be separated based on electronic-type via the dielectrophoresis method. A bench scale dielectrophoresis system has yielded milliliter amounts of type-separated material, specifically semiconductor enriched SWNTs. At this point the levels of enrichment are still low and need further refinement to meet the levels required for high level integration into next generation electronics. The restructuring of Unidym materials development division required a modification of tasks for the project where the majority of the effort was focused on the dielectrophoresis setup. As most of the effort during the last portion of the project being focused on the dielectrophoresis system, this resulted in the device application portion of this project to not be fully completed.

The base CNT-TFT device platform was designed and implemented with the patterning of the SWNT fabric which remained pending. Out of the 12 batches that were obtained from Unidym only a couple of the batches seemed to work with BSI's purification process. The inconsistency of the raw asproduced material was a limiting factor in BSI's effort to produce a high purity surfactant free stable solution o f S WNT ma terial for m ost of t he m aterials pr ovided. B SI's in itial d esigns f or th e dielectrophoresis s etup w ere opt imized t o yield hi gher s eparation, but t here i s s till r oom f or improvement and scale-up.

It has been determined that a number of different SWNT manufacturers can be utilized for the type-separation process. One the main concerns, Post-DEP are whether or not the materials can then be purified using BSI's proprietary process. For large volume production, the purification process that is implemented r equires the batch of material (Post-DEP) to be consistent from batch to batch. It was determined that the S outhwest N anotechnologies S WeNT CG200X grade of material seemed to most closely resemble the properties of the H iPCO SWNTs. A nother a lternative w ould be to purify the SWNT material first and then c onduction type-separation. It was noticed that purifying the S WNT material first did not yield separation in some cases compared to S WNT solution being dispersed in surfactant based s olution. It is h ypothesized that this may be due to the functional groups (COOH) rendering the metallic tubes inert and therefore not adhering to the electrodes during dielectrophoresis; this however needs to be further investigated.