FINAL REPORT

***CONDUCTIVE COATINGS FOR SOLAR CELLS USING
CARBON NANOTUBES***

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1. Introduction to Project

US Department of Energy (DOE) awarded a grant for Eikos Inc. to investigate the feasibility of developing and utilizing Transparent Conducting Coatings (TCCs) based on carbon nanotubes (CNT) for solar cell applications. Conventional solar cells today employ metal oxide based TCCs with both Electrical Resistivity (R) and Optical Transparency (T), commonly referred to as optoelectronic (RT) performance significantly higher than with those possible with CNT based TCCs available today. Transparent metal oxide based coatings are also inherently brittle requiring high temperature in vacuum processing and are thus expensive to manufacture. One such material is indium tin oxide (ITO). Global demand for indium has recently increased rapidly while supply has diminished causing substantial spikes in raw material cost and availability. In contrast, the raw material, carbon, needed for CNT fabrication is abundantly available. Transparent Conducting Coatings based on CNTs can overcome not only cost and availability constraints while also offering the ability to be applied by existing, low cost process technologies under ambient conditions. Processes thus can readily be designed both for rigid and flexible PV technology platforms based on mature spray or dip coatings for silicon based solar cells and continuous roll to roll coating processes for polymer solar applications.

This project was divided into four distinct focus areas. These are listed below with brief description:

- a. **Determination of TC Requirements for Solar Cells.** Eikos Inc. will collaborate with participant organizations including industry to create a requirements list for each solar cell type, wherein the transparent conductor (TC) specifications are listed and an assessment of technology insertion advantages and disadvantages are compared to existing TC coatings. Also, an evaluation of the potential uses of Invisicon® coatings in organic PV fabrication in both the TC layer and other potentially beneficial layers will be conducted. Other goal is to have a comprehensive market assessment of where the Invisicon® coating can be most useful across all PV technologies. Both technical and financial performance metrics may be defined based on this study and incorporated into an implementation plan for Eikos transparent conductive coating materials in photovoltaic cells. Most feasible PV cells that can incorporate CNT coatings will be fabricated and tested.
- b. **Optoelectronic Performance Improvements.** In this task several factors known to contribute to RT performance of the CNT based transparent conductors will be explored. More specifically, this section consists of research into four interdependent yet distinctive enough to be described in separate tasks. These areas are i) CNT Purification & Yield Improvement, ii) Morphology Evaluation and Control, iii) Study Dispersion Effectiveness, and iv) Metallic Type CNT

Enhancement. Additionally, as the mechanisms are better understood they will be immediately applied and exploited to increase RT performance towards the established goal of >90% transmission at 100 Ohms/sq. This was demonstrated through the fabrication of TCC, testing and insertion into PV cells.

- c. **Characterized of CNT Based Solar Cells.** During this task, transparent conductive coatings developed under this program were evaluated. Eikos Inc. fabricated and tested a wide variety of PV cells incorporating the CNT in the transparent conductive layer. By the end of the first year, a variety of photovoltaic cells were fabricated using the CNT coatings in various ways. The performance was evaluated and found suitable for present photovoltaic designs and other types of photovoltaics. Additionally, samples of CNT coatings were provided to and evaluated the leading organic PV cell producers to begin understanding their unique materials and processing requirements.
- d. **Investigated Application Methods.** Various methods for applying Invisicon® during PV cell fabrication were evaluated primarily for their performance, but also for utility as a method of inserting the coating into PV cell fabrication procedure. The Invisicon® coating technology is a versatile system that can be applied by various conventional application methods such as spray coating, transfer coating and direct application. However, each application method influences the optoelectronic performance of the coating and the performance is related to the dispersion quality, stability of the CNT in solution, drying conditions and binder material of choice.

1.1 Overview of Technology

Transparent and electrically conductive coatings and films have a variety of uses in the fast-growing field of opto-electronic applications. Transparent electrodes typically include semi-conductive metal oxides such as indium tin oxide, and conducting polymers such as poly(3,4-ethylenedioxythiophene), doped and stabilized with poly(styrenesulfonate) (PEDOT/PSS). In recent years, Eikos, Inc. has conceived and developed technologies to deliver novel alternatives using single-wall carbon nanotubes (SWNT). These technologies offer products having a broad range of conductivity, excellent transparency, neutral color tone, good adhesion, abrasion resistance as well as mechanical robustness. Additional benefits include ease of ambient processing and patterning capability.

Single-wall carbon nanotubes (SWNT) and related materials have been studied extensively during the last decade. Research funds continue to pour into nanomaterials research, development and characterization worldwide, with a broad range of target applications emerging. One area of significant interest is transparent conductors (TC), essential in many opto-electronic devices, including liquid crystal displays (LCD), organic light emitting diodes (OLED), touch screens, and photovoltaics (PV). Eikos, Inc. has developed carbon nanotube based materials technology known as Invisicon® that

could replace transparent conductors such as Indium Tin Oxide, a TC choice for over four decades in many applications [1].

Researchers at Eikos, Inc. have demonstrated that highly transparent conductive films can be formed when carbon nanotube dispersions are applied at thicknesses below 100 nm [2]. It has been further demonstrated that opto-electronic properties improve dramatically with increased CNT purity and degree of dispersion. Today, the highest quality Invisicon[®] CNT films result in 90-97% visible light transmittance and 200-500 ohm/sq sheet resistance – very close to the opto-electronic performance of sputtered ITO, making Invisicon[®] suitable for many flat panel display (FPD) applications. It is postulated that this new category of transparent conductors has remarkable potential for applications beyond FPDs, such as photovoltaics.

Eikos has developed a proprietary process that can convert commercially available CNT powders into high purity CNT dispersions. This process involves purifying CNTs in high yield, then dispersing them in a solvent of choice. The purification process is critical because certain purification techniques can cause CNTs to aggregate, shorten, or become damaged. Eikos has focused on making purified CNTs easy to disperse, which has aided in CNT ink production and application.

An advantage to the Invisicon[®] coatings over other TCCs is the ability to tailor the sheet resistance (R_s) over a large resistive range, from one order of magnitude up to as high as ten orders of magnitude, depending upon the target application. Invisicon[®] coating properties have been continuously improved over the recent years. It is anticipated that this performance range will soon reach performance requirements for various photovoltaic applications. CNT films display high transparency across the complete visible light spectrum, in comparison to ITO and the transparent conducting polymer, PEDOT, commonly found in organic electronic applications [2]. Invisicon CNT coatings exhibit high transparency (low absorbance) across the complete visible light spectrum, through infrared, for a broad range of surface resistance values. Whereas ITO limits the device photo-generated current, due to a rather strong free-carrier absorption of infrared (IR) photons, the spectrum for Invisicon[®] coatings is especially promising due to lower absorption at these wavelengths.

Mechanical durability of Invisicon[®] CNT coatings has been evaluated in tensile strain tests and cyclic loading behavior. In both cases, improved performance over ITO has been demonstrated [3]. Under tensile strain (0.1 mm/min) CNT coated PET was tested up to 18% strain. This resulted in a 15% change in surface resistance. As a comparison, ITO coated PET demonstrated catastrophic loss in conductivity under 2.5% strain. Given that CNT coated polymer substrates can be deformed well beyond the catastrophic failures of inherently brittle ITO, Invisicon[®] based transparent conductors are well suited for applications that require flexibility, mechanical durability, and light weight, including flexible and durable solar cells.

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- [2] D. Arthur, P. Glatkowski, P. Wallis and M. Trottier, “Flexible Transparent Circuits from Carbon Nanotubes”, *SID '04 Digest of Technical Papers*. p582 (2004).
- [3] Crawford, G.P., et al., *Applied Phys. Letters*. **76** (11), p1425 (2000).

1.2 Summary of Results and Accomplishments

During this program, Eikos created over 150 solar cells demonstrating exceptionally positive results for SWNT enabled solar cells. Eikos has passed the reliability and lifetime specification for one solar manufacturer and has successfully scaled application methods from 1”x3” microscope glass samples to 8.5”x11” size areas. In addition, Eikos demonstrated significant RT improvements, easily reaching 90%T at 100 $\Omega/\square$ and pushed the envelope to 70%T at 35 $\Omega/\square$. These optoelectronic values are useful for some types of solar cells, moving Eikos closer to commercial realization of CNT-enabled PVs.

Eikos’ worked with NREL and commercial businesses in replacing metal conducting oxides (ITO, Al:ZnO) with Invisicon[®] electrodes. These collaborations have been remarkably successful (Table 1). This research led to world’s-first device architectures in many cases.

The quality and novelty of this work is clearly evidenced by the publications that resulted from this project. Two Applied Physics Letters papers, one Physical Review B paper, and one Journal of Physical Chemistry C paper were all published. To date, one Applied Physics Letters paper on organic photovoltaics has been cited by other publications 14 times, an indication that the results are of significant interest and impact. Many aspects of this program have been presented at both the World Conference on Photovoltaic Energy Conversion (WCPEC) in Waikoloa, HI in May 2006 and the MRS Fall 2006 Conference in Boston, MA. In particular, research in OPV highlighting the replacement of both the ITO and ITO/PEDOT layers with single wall carbon nanotube transparent electrodes received award for ‘Most Novel Device and Material’ at the WCPEC. This work also was presented at the Organic Electronics Conference in Frankfurt, Germany in September 2006 and the PIRA Organic Photovoltaics Conference in May 2007.

Table 1 Efficiencies of solar cells with Invisicon[®] transparent electrodes.

Cell Type	Structure	Efficiency, %
OPV 1	SWNT/P3HT:PCMB/A1	1.43
OPV 2	SWNT/PEDOT:PSS/P3HT:PCMB/A1	2.61
CIGS 1	SWNT/Cds/CIGS/Mo	4.10
CIGS 2	SWNT/Parylene/SWNT/CdS/CIGS/Mo	8.22
CIGS 3	SWNT/i-ZnO/ CdS/ CIGS/Mo	12.60
CIGS 4	SWNT Contact/SWNT/i-ZnO/CdS/ CIGS/MO	12.98
CdTe 1	CTO/ZTOCdS/CdTe/CuTe/SWNT	12.4

The efficiency of SWNT enabled photovoltaics is approximately 80-90% of that of their ITO and ZnO counterparts. However, throughout this program the optoelectronic performance of Invisicon[®] coatings has been steadily increasing. During the program, Eikos hit a task stage goal by achieving 90% transparency at 100 ohm/sq. This was attained in part through increased purification and morphology control. NREL characterization of Eikos SWNT coatings has determined that they are the best known p-type conductor and exhibit excellent near-IR transmission that well exceeds that of metal oxide conductors. These factors demonstrate the promise of Invisicon[®] for organic PV and thermo-photovoltaics.

Solar cell reliability was established through lifetime and environmental testing. Eikos has developed a SWNT and binder coating that passes the heat, heat and humidity, and light exposure testing performed by a leading PV company. To ensure greater reliability, Eikos Invisicon[®] will be tested against the IEC international standard for photovoltaics.

Eikos has established that SWNT based Invisicon[®] films are an alternative to ITO and ZnO as transparent electrodes in solar cells. At its existing performance level, Invisicon[®] was utilized as an electrode in organic PV to achieve an efficiency of 2.6% for non-optimized devices with PEDOT and 1.4% for structures without PEDOT. These novel electrodes also enabled 2.9% efficient dye sensitized cells, 13.0% CIGS cells, and 12.4% CdTe tandem top cells. These efficiencies are expected to increase as the material's optoelectronic performance increases and the fundamental device physics are understood better. Lifetime testing has been passed for one solar cell variant, and the feasibility of various low cost application techniques has been demonstrated. Eikos Invisicon[®] coatings hold promise to enable efficient, reliable, and lower cost solar cells, helping the SETP meet its program goals.

2. TCC Requirements for Various PVs

A comprehensive survey based on literature and industry interviews was conducted to identify requirements pertaining to the use of transparent conductors in different solar cell structures. During this task technical and scientific publications were reviewed in order to collate detailed information on the different types of solar cell types and structures manufactured and investigated by the PV industry/community today. In addition, approximately 15 companies involved in PV manufacturing and technology research were contacted by phone and email in order to capture TCC requirements for specific solar applications. Such communications enabled Eikos to develop broader relationships with key players that further down the road would consider inserting Invisicon into their respective solar cell structures.

2.1. *PV Technology Survey*

Photovoltaic cell structures and designs could be broadly divided into three major technology tracks. Silicon based PVs clearly dominate, capturing about 93% of the PV cells manufactured today. Thin film technologies such as amorphous silicon, Cadmium Telluride and Copper Indium Gallium Diselenide (CIGS) combined have captured a 7% market share. 3rd generation PV designs such as organic solar cells are predominantly in a research phase, and will begin gaining market share once they enter mass production.

2.1.1. Crystalline Silicon Solar Cells

Insertion opportunities of Invisicon® for crystalline silicon cells exist in three areas.

1. Replace “contact”, made of metal in **Figure 1**, with a carbon nanotube transparent conductive coating. A binder for the nanotubes could also serve as a replacement for the anti-reflection film in this figure.
-see http://www.findarticles.com/p/articles/mi_qa3957/is_200506/ai_n13642859
or <http://www.mphasetech.com/NASATechBrief.pdf>
2. CNT stalks grown on the surface of the silicon to help collect more solar energy by trapping more photons
<http://www.azonano.com/news.asp?newsID=548>
3. Using doped semi conducting tubes as the p-type or n-type material in a similar n/p type, respectively, solar cell
<http://www.azonano.com/news.asp?newsID=548>

Figure 1

Of these opportunities, replacing or partially replacing the front surface metal contact is the most likely use of carbon nanotubes.

2.1.2. Thin Film Solar Cells

Insertion opportunities for thin film solar cells exist in the transparent conductive coating. In **Figures 2-4** below, these are the coatings indicated by “transparent conductor” or “ITO”.

Figure 2 Amorphous Silicon

Figure 3 Cadmium Telluride

Figure 4 Cadmium Indium Gallium DiSelenide

2.1.3. 3rd Generation Solar Cells

The next generation of solar cells provides more opportunities for carbon nanotube insertion. For one, they can be used as a transparent conductive coating, replacing the “Conducting Electrode” in **Figure 5**, ITO in **Figure 6**, and TCO in **Figure 7**. They can additionally be used as a charge collector throughout these designs, mixed in with the active layer to conduct charge back thru to the electrodes. Finally, they can also be used as the electron acceptor when exciton pairs are created.

Figure 5 Dye Sensitized

Figure 6 Small Molecule

Figure 7 Bulk Heterojunction

They can additionally be used as a charge collector throughout these designs, mixed in with the active layer to conduct charge back thru to the electrodes. Finally, they can also be used as the electron acceptor when exciton pairs are created.

2.2. TCC Requirements for PV-Cells

Eikos explored all photovoltaic categories to discover where carbon nanotubes could best be utilized as a transparent conductive coating. Table 2 summarizes the TCC needs of major solar cell manufactures in each of these categories, and Figure 1 plots these needs versus Eikos' carbon nanotube technology. As Figure 8 demonstrates, minimum transmittance and surface resistance requirements for transparent conductors are found between 10-100 Ohms/sq @80-95% transmittance. It is important to note that minimum TCC requirements identified for all PV applications, except Nanosolar, are beyond the performance capability of current Invisicon technology.

It can be seen in Figure 8 that the TCC in Organic Photovoltaics (OPV) and Copper Indium Gallium DiSelenide (CIGS) solar cells have requirements nearest in reach of carbon nanotube technology. Additionally, these solar types are typically targeted to be low-cost and also flexible, which are benefits of Invisicon® over ITO. Given the variety of application methods, including atmospheric printing methods, less expensive materials cost, and durability of CNT TCC, carbon nanotubes are best suited towards CIGS and 3rd generation solar cells.

Table 2 Minimum TCC Requirements for Different PV-Cell Structures

Tech Area	Tech Sub	Company	Min. Spec
Silicon 93% market share	Crystalline Silicon (c-Si) mono/poly	GE Energy	50 $\Omega/\square$ @ 94 %T
	Silicon Ribbon	Evergreen Solar	-
	mono and multi crystalline	BP Solar	10 $\Omega/\square$ @ 90 %T
Thin Film 7% market share	amorphous Silicon	Iowa Thin Film Technologies Inc	25 $\Omega/\square$ @ 95 %T
		Energy Photovoltaics	15 $\Omega/\square$ @ 95 %T
	Cadmium Telluride CdTe	First Solar	15 $\Omega/\square$ @ 90 %T
	Copper Indium Gallium Diselenide (CIGS)	Nanosolar	100 $\Omega/\square$ @ 90 %T
		Global Solar	25 $\Omega/\square$ @ 90 %T
3rd Generation		Shell Solar	15 $\Omega/\square$ @ 85 %T
		Energy Photovoltaics	10 $\Omega/\square$ @ 90 %T
		Daystar	20 $\Omega/\square$ @ 94 %T
		Miasole	20 $\Omega/\square$ @ 90 %T
	organic solar cells (OPV)	Global Photonic Energy	20 $\Omega/\square$ @ 90 %T
	dye sensitized solar cells (DSSC/Graetzel)	Konarka	28 $\Omega/\square$ @ 80 %T
		Konarka	28 $\Omega/\square$ @ 80 %T

Figure 8 Invisicon RT Performance

Add few comments on Invisicon coating technology improvements including DOE Program goals to achieve enhanced RT performance and new target applications specifying specific designs if possible

Eikos is currently pursuing collaborations with solar cell manufacturing leaders in device types that most benefit from the insertion of carbon nanotube transparent conductive coatings. Because of the nature of the technology, Eikos requires that collaborators have both a signed Non-Disclosure Agreement and a Materials Transfer Agreement in the case where Eikos' materials are put in their hands. Because flexible, low-cost, simple to manufacture cells are likely to benefit most from the insertion of carbon nanotubes, Eikos began relationships with several CIGS cell manufacturer, two amorphous silicon cell manufacturers, and two 3rd generation solar cell manufacturers.

3. CNT Performance Enhancement for 100 $\Omega/\square$ @90%T Target

Widespread utilization of carbon nanotubes as a replacement material for conventional conductors within solar applications requires improvement in electrical conductivity and optical transmittance. Various processes have been demonstrated to improve R/T performance. Higher quality raw material, coating parameter optimization, raw material and production improvements have all contributed in varying degrees to Invisicon® enhanced performance.

3.1. Purification & Yield Improvements

The carbon nanotube (CNT) purification process commonly includes an acid reflux step, followed by a number of extraction steps, to remove unwanted materials such as residual acid, metal catalysts, amorphous carbon, impurities, etc. The process continues until the desired ink purity or quality is obtained. Eikos furthers the ink quality and purity in a procedure designated as “AIF”; this is a focus of this report.

In most novel or emerging coating materials and applications, cost is a major factor in achieving widespread market acceptance. The cost of the purified carbon nanotube dispersion (ink) depends on the unpurified CNT soot (raw material) cost and the yield of purification process. Ink yield can be expressed by either volume or coating coverage. Ink yield characterized by volume is based on a fixed CNT concentration ink (absorbance, a.u. =1) produced from a gram of dry soot (liter/g). Alternatively, the area covered by one gram of dry soot (m^2/g) to produce a 500 $\Omega/\square$ coating is also a way to represent ink yield. These two representations do not always coincide. A higher purity (grade) ink may have lower yield in liter/gm, but may cover a larger area than a lower grade ink, since less of the higher grade ink is required to coat an identical surface area. This work focuses on the influence of certain purification process parameters on ink quality and yield, namely:

- 1) Ink concentration (absorbance)
- 2) Reflux time

3) Reflux chemistry.

3.1.1. Effect of Ink Absorbance on Ink Purity and Yield

The purified and concentrated CNT paste produced by Eikos' standard proprietary process can be diluted to the lower CNT concentrations required by different coating methods. Depending on the ink quality, further purification is carried out until the desired ink quality is obtained. Eikos has observed that as more purification steps are performed, a lower overall ink yield is produced. Therefore, it is necessary to optimize the number of purification steps to achieve yield and purity targets. The following sections will report results on recent studies conducted on exploiting extraction methods for improved ink purity and yield. Two "AIF steps" were applied to "Extraction-C" paste. Ink concentration, ink quality, and yield after two AIF steps are shown in Table 3.

Table 3: Effect of Concentration on Quality and Yield (2 AIF Steps).

Concentration for AIF1	Concentration for AIF2	Final %T	Final Yield, m ² /g soot	Final Yield ml/gm soot (1 a.u.)
6	6	97	5.13	473
6	9	96.7	6.85	670
6	12	96.7	8.83	864
9	6	96.5	6.49	661
9	9	96.2	8.63	936
9	12	96.3	9.31	989
12	6	96.3	6.07	644
12	9	95.9	7.73	894
12	12	95.8	9.23	1090

Statistical analysis shows a tendency of light transmittance improvement; after "2 AIF steps" improves with lower concentration of AIF1 and AIF 2 inks, (see Figure 9). The improvement may be associated with better dispersion achieved at lower concentration.

Figure 9: Effect of Ink Concentration on %T after 2 AIF steps.

The coating yield by area (m^2/g) improves with higher ink concentration after the second AIF step, as indicated in Figure 10. Additionally, the soot yield by volume (ml/g) improves with higher AIF1 and AIF2 ink concentration (see Figure 11). These improvements are somewhat offset by a decrease in light transmittance. The increase in yield may be associated with the lack of separation of highly conductive tubes. As a result, the %T is reduced, but since more inefficient nanotubes are still present, there is a perceived increase in yield.

Figure 10: Effect of Ink Concentration of Coating Yield (m2/g) after 2 AIF steps.

Figure 11: Effect of Ink Concentration on Ink Yield (ml/g) after 2 AIF Steps.

However, it can be observed that higher AIFlink concentration improved *volumetric yield* (ml/g), but did not influence transmittance (%T) or *yield by area* (m²/g).

Experimental data, supported by statistical analysis, imply that higher ink concentration during “AIF steps” increases yield but decreases its final transmittance (%T). This trend coincides with Eikos’ assumptions. It appears that “AIF process” favors carbon nanotubes that have fewer defects, fewer functionalizaion sites, and higher conductivity. Although higher ink concentration promotes flocculation, it improves yield while sacrificing selectivity of AIF process and ink quality.

3.1.2. Effect of Reflux Time on Ink Quality and Yield

As-produced nanotubes must be purified and processed to make them suitable for high performance transparent conductors in photovoltaics. In this section, the effect of reflux time on ink purity, including yield, is studied. Figure 12 depicts results from this study.

Figure 12: Reflux Time Versus Optical Transmittance and Ink Yield.

No appreciable change in ink quality and yield are derived from reflux times longer than 6 hours. A dramatic reduction in ink quality and increase in yield was observed with a 2 hour reflux time. As process time is a critical factor in any commercialization initiative, a reflux time between 2 and 6 hours needs to be further investigated. It is important to note that increased ink quality results in reduction in volumetric ink yield (l/g).

3.1.3. Effect of Reflux Chemistry on Ink Quality and Yield

Eikos evaluated the influence of reflux media on ink quality (purity) and yield. Acid solutions of different concentrations were made from H₂SO₄, HNO₃, and other common acids. Eikos[®] proprietary purification process was used to process the different reflux solutions and used as the control. The CNT paste produced from the acid mixture was further processed with “AIF” as described in the previous section. We found that oxidizing acids are required to obtain good optoelectronic performance. Unlike the earlier results demonstrated, increased optical transmittance (%T) does not necessarily imply

lower ink yield. In some cases, certain reflux solutions produced improved optical transmittance (%T) and coating yield when compared to the control solution.

3.1.4. High Purity CNT Materials via Reduction of Particles Using Centrifugation

Eikos has found a significant number of particles in the size range 200-1,000 nm in Invisicon[®] coatings. After extensive examination, we determined that the predominant particles were present in the ink and did not form during the nanotube network formation. Thus, we examined methods to remove the particles from the ink.

We found that filtration was not wholly effective at removing particles and degraded the performance of the nanotube ink. Further, significant amounts of CNT were lost in the filter. Variations on the method included pore size, filter thickness (membrane vs. depth filtration), and vacuum vs. cross-flow filtration. All variations had unacceptably deleterious effects on the CNT ink, and thus other methods were explored.

We postulated that high g force centrifugation could reduce the number of particles in the ink and thus in the coating. Centrifuge g forces vary based on the rotor diameter and rotor speed. Typical centrifuge parameters are listed in Table 4.

Table 4: Typical centrifuge speeds, g forces (RCF), and operation times.

Centrifuge	Speed RPM	Relative Centrifugal Force	Time (Minutes)
Eppendorf Centrifuge	10,000	9,000	15
Eppendorf Centrifuge	14,000	16,000	15
Centra GP8R	4,400	4,400	30
Centra GP8R	4,000	3,600	30
RC-6	22,000	27,000	30

From SEMs and optical microscopy, we can observe particles with a size range of *ca.* 100 nm – 1,000 nm. The particles also are observed in coatings at 50- 100 $\Omega/\square$ as haze. This haze decreases transparency by causing diffuse light scattering. Also, it has been observed that the transparency and resistance properties do not follow the theoretical curve of resistance and transparency at lower resistances and transparencies. This drop off effect may be due to the particles interfering with the carbon nanotube network formation and also due to the increase in haze from light scattering.

The first experiment performed was based on the concept that the particles are not as heavily functionalized and thus should fall out of solution during high speed centrifugation. Typically large-scale production inks are centrifuged at low RCF. The count for this procedure is usually between 100 and 300 particles per 250 square microns. For smaller batches of ink, a centrifuge with high RCF is used. The high g-force centrifuge was used for these following experiments.

The experiment was performed by making up a batch of ink that was made and centrifuged at the typical RCF. This ink was then sprayed to 96 %T at 500 $\Omega/\square$ and had 90 particles per 250 square microns. The same ink was then centrifuged at 16,000 RCF for 15 minutes and then sprayed to 96.4 %T at 500 $\Omega/\square$. The particle count for the sample went down to 3 particles per 250 square microns @ 94 %T. Of interest, the ink increased in transparency, and the particle count was the exceptionally low. This experiment was significant in the fact that, resistance and transparency were not adversely affected by the particle reduction procedure. The results can be seen in Table 5.

Table 5: Shows the particle reduction by using a higher speed centrifuge.

Sample (~96%T@500 $\Omega/\square$)	%T @ 500 $\Omega/\square$	Average particle @ 94 %T
Normal Sample Preparation 4400 RCF	96	90
Same sample Centrifuged @ 16,000 RCF	96.4	3

The next experiments were conducted to determine if the grade of ink is affected by higher g-force centrifugation. To track the reduction of particles, a moderate grade SWNT ink was made without centrifuging at low RCF. This ink was sprayed to get a baseline of how many particles were in the sonicated ink. This ink was then centrifuged and sprayed after each centrifugation. All inks, from 95%T to 40%T ink improved with repeated centrifugation. From these experiments, the number of particles was reduced from 150-200 particles to less than 10 particles at 94 %T per 250 square microns for all of the samples. This is a good indication that the particles are not attached to the SWNTs and that the particles are not responsible for loss of RT performance. By being able to separate the particles from the SWNT ink, the purity and particle number allows control of the product for different applications. In some applications, such as touch screens, the particles may be an important part of the product for surface conductivity. By having the particles in the coating, particles can protrude above the coating making surface contact easier. From these experiments the decision was made to use a larger centrifuge for scaling up this procedure of particle reduction. The larger centrifuge used was an RC-6 which can use 50 ml and 500 ml centrifuge tubes and up to g forces of 27,000 RCF.

Using the RC-6, the particle count was measured with varying g forces and time. The data is presented in figure below:

Figure 13: Particulate count versus centrifuge time and speed.

As can be seen from Figure 13, both higher centrifuge speeds and longer centrifuge times reduce particle counts. This observation lends credence to the theory that the particles have slightly lower effective density of stability in the nanotube ink. Also, it demonstrates that low particle ink can be produced on a larger scale.

It is clear that high speed centrifugation of nanotube ink has several advantages. It reduces the particle count in the coated film, which improves surface roughness, improves the RT performance of the ink, and reduces haze. Further, there are preliminary indications that particle removal could improve coating uniformity and R_s drift. One disadvantage is that absorbance of the ink is decreased upon high speed centrifugation. It is possible to improve ink absorbance by adding other substances to the ink, such as glycol.

3.2. Dispersion Effectiveness

Uniform dispersion of carbon nanotubes into any liquid medium is one of the most critical process steps directly influencing optoelectronic performance of Invisicon® coatings. Sonication disperses CNTs and breaks apart CNT flocculates and bundles by ultrasonic sound-waves. Because of its simplicity and broad applicability, sonication is one of the most commonly used CNT dispersion methods found in the scientific literature today.

Eikos placed efforts on developing broad understanding on key dispersion process variables that influence R/T performance of CNT coatings.

- Energy of sonicator horn
- Process time and amplitude for a given volume of ink
- Applicable dispersion equipment for scaled-up purposes

Experiments to disperse larger volumes of CNT tubes were conducted utilizing a commercial high pressure homogenizer process tool. Should this approach prove itself applicable, scale-up capabilities could be readily realized.

3.2.1. CNT Dispersion Process

Eikos studied the direct influence of sonication time and energy on optoelectronic properties of CNT coatings. A master batch of ink was prepared to use as a standard for all sonication experiments. The purpose of investigating influences of sonication time on CNT dispersion was twofold; to understand the effect of key sonication variables and the optimization of the sonication processes for optimum CNT dispersion, and thus performance. Sample volume, sonication time, and percent amplitude were selected as variables.

Sample with volumes between 10 mL and 1,000 mL were sonicated for various time intervals ranging from 0 to 6,000 seconds. Sonication amplitude was varied from 20 to 100 %. Because the ultrasonic horn generates heat, samples were kept in an ice bath to minimize temperature changes with time. Generally, short sonication times (~10 seconds) at medium power were considered optimum for 10 mL samples. Larger samples required mixing in addition to sonication to achieve uniformity and reproducibility.

Figure 14: Extended sonication time (10 mL, ice bath)

Extended sonication times caused significant loss in RT performance. We infer that this loss of performance is due to cutting of CNTs or other sidewall damage. Based on these results, it is recommended that sonication times be kept to a minimum, since CNTs disperse relatively quickly and do not require excessive sonication to maintain properties.

3.2.2. Dispersion by High Pressure Homogenizer

An evaluation was made to disperse CNT into a proprietary solvent blend via traditional high pressure dispersion techniques without ultrasound energy. Such homogenization methods could be well-suited for continuous inline operation, again supporting CNT ink process scale up and commercialization interests.

A CNT dispersion trial was conducted with a high pressure mixing device manufactured by Sonic Corporation. In this process, concentrated CNT fluid is forced by a positive displacement pump through a small orifice, and is accelerated to greater than 300 ft/sec speed. The fluid cavitates, as vortices of material are violently spun off in the opposite direction of the flow. The material then strikes a knife-like blade set in its path. Vortices of material are spun off simultaneously, forming a pulsating cavitation field around the blade. It is claimed that the quality of dispersion is determined solely by the pressure across the orifice, which in turn is determined by the selection of different pumps.

About 30 grams of concentrated CNT paste and 4 liters of proprietary solvent were first mixed in-situ with a metal agitator for 5 minutes to obtain a pre-mix of with absorbance 1.0. The pre-mix was then run through the system once. Samples were collected under different fluid pressure conditions. The pressure across the orifice was controlled by varying the fluid flow rate.

Thus collected samples were then fabricated to a 500 $\square/\square$ CNT coating, and % transmittance @550 nm were measured as demonstrated in **Table 6** and **Figure 15** below.

Table 6: % Transmittance versus Process Conditions

Dispersion Conditions		%T @500 $\Omega/\square$	
Pressure (Psi)	Flow rate (GPM)	Without Secondary sonication	With secondary sonication
500	NA	-	86.5
1000	1.02	-	87.9
2000	NA	88.7	88.4
3000	NA	87.8	85.1
4000	2.12	85.9	87.3

In an attempt to improve CNT dispersion, it was dispersed further by continuous treatment via high pressure homogenizer for 3, 4 and 5 minutes at 2000 ps, connecting the outlet tube back to the inlet tube, creating a closed loop system. Re-circulated samples demonstrated slightly improved dispersion, but degraded transmittance. During recirculation, the fluid temperature increased from 25 to 49 degrees C within 5 minutes. These temperature changes are considered unacceptable, so recirculation was not pursued further.

Figure 15: % Transmittance versus Process Pressure

From **Table 6** it can be seen that 2000 PSI fluid pressure gave the best CNT dispersion based on %transmittance. Reasons for this slightly spiked performance at this fluid pressure level are not understood. It, however, was noted that overall quality, consistency and R/T performance of CNT coatings fabricated from inks processed through high speed homogenizer dispersing methods were inferior in performance to that of ultrasound energy based technologies. It appears that this homogenizer, though operated under high shear forces, did not deagglomerate CNT bundles and agglomerates as large particulates were clearly visible in all collected samples.

3.3. *Metallic Type CNT Materials*

Alternative methods of nanotube purification and separation were investigated under this contract. Specifically, we explored literature reported methods to separate metallic CNTs from semiconducting CNTs. One area, porphyrin-based metallic and semiconducting CNT separation, was explored in great detail in close collaboration with Prof. Ya-Ping Sun of Clemson University. Eikos also experimented with amine selectivity concepts to separate metallic CNTs from semiconducting tube fractions.

3.3.1. **Metallic CNT Separation using Porphyrins**

Eikos explored several techniques of separating metallic single walled nanotubes from semiconducting single walled nanotubes. At the start of the project, there were several possible ways highlighted in the literature. Electrophoresis was used to isolate picograms of SWNTs in high yield, but the process did not produce enough materials to be useful for Eikos's application. Separation using selective non-covalent bonding and solubilization were demonstrated by several groups. Ya-Ping Sun of Clemson reported a

porphyrin-based method that solubilized semiconducting SWNTs, while leaving a residue of metallic SWNTs.

The technique developed by Dr. Sun of Clemson University for separating metallic from semi-conducting nanotubes appeared to show promise, so Eikos received samples of “separated” CNTs from Dr. Sun. The separation is performed by adding a porphyrin derivative that preferentially adheres to semi-conducting nanotubes. This approach also allows dispersion of semi-conducting nanotubes in solvents that are typically not conducive to CNT dispersion. Centrifugation should separate the semiconducting CNTs (liquid phase) from the metallic nanotubes (solids). Joint collaboration with Clemson University began in 2005 with emphasis on separation of single walled carbon nanotubes based on porphyrin selectivity and high temperature annealing of CNT coatings to remove impurities.

Samples from Clemson U. included non-annealed metallic (mCNT) and semi-conducting (semiCNT) CNT samples that were pulled out at various intermediate steps in the separation process, as well as samples further purified by Eikos proprietary methods. This investigative work was divided into two separate parts. The first part of the evaluation was composed of evaluating metal and semiconducting tubes per Eikos standard procedures, results of which are tabulated in Table 7 below. The second part of the evaluation focused on attempting to isolate the specific process step in the Clemson process is responsible or preventing further dispersion of enriched CNT to solvent media. A benchmark of 500 Ω /sq surface resistance was possible with both samples, the optical transmittance (%T) was poor. Acid reflux appeared to remove residue impurities still present in separated materials (72-63-1 & 72-63-2).

Table 7: Rs of Metallic and Semi-Conducting CNT Fractions

Sample	Ref #	3M Reflux Time (hrs)	Rs ($\square$ /sq)	%T	Comments
Enriched mCNT (72-63-1)	72-64-1	NA	7900	65.1	Stability =2
Enriched mCNT (72-63-1)	72-95-1	NA	7825	72.35	Stability = 3.5
Enriched mCNT (72-63-1)	72-63-3	18	500	33.75	Stability = 1
Enriched semiCNT (72-63- 2)	72-81-1	NA	499	42.4	Stability = 1
Enriched semiCNT (72-63- 2)	72-94-1	18 hrs	503.5	61.85	Stability = 1

As a comparison, consistent R/T performance of 95%T @500Ω/sq can be readily obtained through Eikos standard purification processes. Before metallic CNT coating can find any practical use, its R/T performance has to exceed this benchmark standard.

Surprisingly, the semi-conducting sample outperformed the metallic sample. Likely explanations for this include higher levels of organic contaminants or amorphous carbon present in the metallic sample. Another explanation could include that a portion of mCNT may have been destroyed during the process. It has also been suggested that pure metallic nanotubes may disperse poorly, thus hindering R/T performance.

Figure 16: SEM images of metallic CNT films (left) and typical CNT films (right).

It became apparent that the porphyrin process left residual contamination and agglomerated CNTs, requiring excessive energy to re-disperse. An experiment was set to identify which specific steps in Clemson process hindered dispersion. To identify this, intermediate samples were extracted from each respective process steps as outlined below:

- Sample 1: CNT raw material air oxidized at 350 oC
- Sample 2: Sample 1 + acid reflux
- Sample 3: Sample 2 + porphyrin addition
- Sample 4: metCNT prior porphyrin removal
- Sample 5: semiCNT prior porphyrin removal

Samples 1 to 5 were then evaluated in two separate ways. The first set of experiments consisted of dispersing all samples directly using Eikos standard carrier solvents to assess dispersion quality. The second and more comprehensive approach was to further purify and disperse received materials in order to measure R/T performance. These samples are found under “Refluxed” and “Refluxed & Extracted” subheadings.

Evaluating the samples as received indicated that the porphyrin addition plays a large part in the R/T performance loss of separated CNT. Samples 4 and 5 were unable to be evaluated as received due to lack of dispersion, which may also be due to the porphyrin additive employed in the actual separation process. Refluxing samples 4 and 5 in acid improved dispersion, and thus, may have removed part of the contamination and helped improve the sample morphology. It appears that if the tube separation process is to be successful, all residual contamination must be removed.

3.3.2. Metallic CNT Separation using Amines

It has been postulated that optoelectronic properties of carbon nanotubes can be further enhanced by metallic nanotubes. Several different separation techniques are cited in the literature. After a detailed literature survey, Eikos opted to duplicate Maeda et al, using small amines to separate HiPCO CNTs. This separation technique is based on a theory that certain amines preferentially bind to metallic carbon nanotubes. This coupling can then be exploited to extract metallic/amine complexes for solution. By further purification, pristine metallic tubes can be collected.

Experimental procedure employed followed the referenced authors work. Both semi-conducting and metallic CNT fractions were then evaluated using near infrared spectroscopy (Figure 17).

Figure 17: Vis-NIR spectra for HiPCO CNT raw-material (AP trace), first supernatant/metallic (OS1 trace), and first precipitate (OD1 trace).

The ratio of metal enrichment was calculated by taking the ratio of integrated areas of one of the semi-conducting (S_{22}) peaks to one of the metallic (M_{11}) peaks. The ratio, k , for each material fraction was found to be:

- AP: $I_{S22} / I_{M11} = k_{AP} = 2.94$
- OS1: $I_{S22} / I_{M11} = k_{OS1} = 2.25$
- OD1: $I_{S22} / I_{M11} = k_{OD1} = 4.1$

The differences in integrated areas give a semi-quantitative measure of the amount of enrichment, based on the assumption that the ratio of peak heights reflects the ratio of metallic and semi-conducting nanotubes in the sample. By assuming the raw material is composed of 33.3% metallic CNTs, the supernatant was found to be 39.5% metallic, and the precipitate was found to be 26.4% metallic CNTs. Repeating this procedure to further decrease the ratio of the S_{22} peak to the M_{11} peak resulted in a calculated value of 47% of the sample consisting of metallic CNTs. We found that such trends were not observable

for arc grown material; the ratios of the peaks were measured to be the same regardless of sample preparation.

Resulting material fractions were then dispersed to solvent media for the purpose of evaluating optoelectronic performance of the enriched fractions utilizing different dispersion conditions. The performance of each sample was measured from THF dispersions, as summarized in Table 8 below.

Table 8. RT performance of HiPCo and Arc CNT from attempted metallic and semiconducting nanotube separations. AP represent starting CNT, OS1 is the first supernatant, and OD1 is the first precipitate.

Sample	%T	Resistance, $\Omega/\square$	Dispersion Conditions
AP- HiPCO	26.2	3080	3.5 hour horn sonication, 8 hour centrifugation
AP- HiPCO	45.9	10,300	2 hour bath sonication, 4 hour centrifugation
OS1- HiPCO	75-88	>10M	3.5 hour horn sonication, 8 hour centrifugation
OS1- HiPCO	56.7	11,000	2 hour bath sonication, 4 hour centrifugation
OD1- HiPCO	32.7	9,350	2 hour bath sonication, 4 hour centrifugation
AP- Arc	24.6	18,600	3.5 hour horn sonication, 8 hour centrifugation
AP- Arc	15.9	~1M	2 hour bath sonication, 4 hour centrifugation
OS1- Arc	38.2	>10M	3.5 hour horn sonication, 8 hour centrifugation
OS1- Arc	~50	>10M	2 hour bath sonication, 4 hour centrifugation

From a functional perspective, again, all samples evaluated and corresponding data herein has no practical purpose. It however, can be observed that unpurified HiPCO CNT raw material demonstrated best dispersion into liquid media. Both separated fractions were difficult to disperse. This is reflected by high surface resistance and low optical transmittance.

The supernatant samples (OS1) representing metallic CNTs had barely measurable conductivity. In one case, a sample of marginal conductivity was obtained, but results could not be reproduced. Thus, it was concluded that the separation method employed based on vigorous sonication and centrifugation most likely damages the CNTs during the actual separation.

We found that such trends were not observable for arc grown material; the ratios of the peaks were measured to be the same regardless of sample preparation. Recent

publications also call into question the validity of using integrated intensity of near IR transitions to quantify separation of CNTs. Huang et al (J.Phys.Chem. B, 2006, 110, 4686) found that nanotubes in bundles have suppressed NIR semi-conducting transitions, compared to isolated nanotubes.

Observation of changes in NIR peak intensities may be due to isolation of different CNTs, different sample morphologies, or a combination of the two. The authors suggest that all work on separating semi-conducting and metallic nanotubes take into account the effect that they observe. Currently, no published or patented report on nanotube separation takes these observations into account, so additional research needs to be conducted to clarify the current literature base. Additionally, interpretation of Raman data of bundled and individual CNTs have been shown to be ambiguous, adding credence the idea that assessing nanotube separation may not be as straightforward as has been predicted.

3.4. High concentration CNT Inks

3.4.1. High Concentration CNT Inks with Glycol Additives

Recently, we observed that high speed centrifugation of CNT ink reduced particle counts in the coatings and improved the RT performance of the coating at low sheet resistances. However, high speed centrifugation has the disadvantage of reducing the concentration of the standard CNT ink, which decreases coating yield. Further, it has been found that standard inks subjected to high speed centrifugation cannot achieve an absorbance greater than 2. Here, we studied additives to standard CNT ink solvents to increase the absorbance of the ink and maintain the RT performance.

Inks consisting solely of glycol solvent can achieve much higher absorbances (~3-5), but glycol has a boiling point greater than 180 °C. The difficulty of evaporating the glycol makes coating more difficult, since the substrate remains wet for longer periods and significantly higher substrate temperatures are required to remove the solvent. Higher substrate temperatures affect substrate choices and can affect the CNT coating by causing R_s drift. A further issue with glycol inks is their viscosity, which can reduce the efficacy of particle removal during high speed centrifugation. Glycol blended with higher boiling point, lower viscosity solvents potentially could enable higher ink concentrations and ease of coating. Thus, we explored adding glycol in varying proportions to standard CNT ink solvents.

Experiment

An ink qualified at 92.3 %T @ 250 $\Omega/\square$ was used for these experiments. The paste to ink dilution ratio was previously measured to be 33 g of paste per 1 L of ink at an absorbance of 1.5. This dilution ratio was determined using a small quantity of paste and is generally found to differ when the ink production is scaled to a larger centrifuge. Target ink absorbances were chosen to be 1.5, 3, and 4.5, based on the qualified ink absorbance. The table below summarizes inks that were produced:

Table 9

Glycol Concentration	Target Absorbance	Sonication	Centrifugation
0%	1.5	60 sec, 70% ampl.	20,000 g, 2 hours
20%	3	60 sec, 70% ampl.	20,000 g, 2 hours
25%	3	60 sec, 70% ampl.	20,000 g, 2 hours
33%	1.5	60 sec, 70% ampl.	20,000 g, 2 hours
33%	3	60 sec, 70% ampl.	20,000 g, 2 hours
33%	4.5	60 sec, 70% ampl.	20,000 g, 2 hours

All inks were subjected to the same sonication time and energy, as well as centrifugation time and g-force. Inks sat for a day before spraying. Inks were manually spray coated using an airbrush onto a heated microscope glass slide. Samples with glycol were heated above 65 °C. Samples were sprayed to about 500 $\Omega/\square$.

Results

After centrifugation, the absorbance of the inks was measured using a spectrometer. The measured absorbance was found to be lower than the target absorbance by about 30%, with the high glycol, low absorbance ink showing the smallest loss of absorbance. Importantly, we were able to make inks with absorbance greater than 2 and almost as high as 3 after high speed centrifugation. The results are summarized below:

Table 10

Glycol Concentration	Target Absorbance	Measured Absorbance	Absorbance difference (%)
0%	1.5	1.055	30%
20%	3	1.895	37%
25%	3	1.834	39%
33%	1.5	1.120	25%
33%	3	2.060	31%
33%	4.5	2.805	38%

We also wanted to study the effects of glycol additives on the RT performance of the inks. Some additives have been found to significantly affect the ink RT performance. The control sample was found to spray as expected, though the coating was found to be 90.3 %T @ 250 $\Omega/\square$. This loss of performance is attributed to the ink sitting on the bench for a day. This deviation implies that the ink is undergoing some changes in its storage, which could be different with different ink compositions. The other samples are presented below in table 9:

Table 11

Glycol Concentration	Target Absorbance	Measured Absorbance	%T @ 250 $\Omega/\square$	Mottling
0%	1.5	1.055	90.3	N
20%	3	1.895	84	Y
25%	3	1.834	79	Y
33%	1.5	1.120	89	N
33%	3	2.060	87	Y
33%	4.5	2.805	90	N

Considering the high concentration of glycol, samples sprayed better than expected once substrate temperature was adjusted. Sample sheet resistance dropped slowly while the sample was being sprayed as glycol evaporated. Mottling was seen in some samples, which arises from incomplete drying of the CNT layer. Slower spraying or higher substrate temperatures should reduce mottling and improve RT performance. Also of note, the ink at absorbance 2.805 with 33% glycol performed similarly to the control ink, which indicates that glycol additives can result in high absorbance inks with similar performance to the standard inks.

3.5. Target Morphology Methods

3.5.1. Mechanical Pressure to Increase Conductivity

It is well understood that CNT film fabricated by various deposition techniques such as vacuum filtering, flow coating or spraying results to a porous network consisting of multiple voids surrounded by nanotubes ropes. Therefore, any method resulting in the film densification should improve rope-to-rope contacts, leading to conductivity enhancement. Thus, an external mechanical pressure applied to the formed network should provide the desirable CNT densification without reduction in the coating transmittance

An experiment was conducted to exert mechanical pressure on CNT networks of different thicknesses and sheet resistances employing a parallel plate heated press. As substrate surface roughness should be less than CNT network thickness, highly polished silicon wafers were employed in this experiment. CNT coatings with different sheet resistances (70 and 370 Ohm/sq) were spray-coated and sandwiched between silicon wafers and incrementally pressurized up to 1200 kg/cm² while R_s was recorded (Figure 18).

Figure 18: Sheet resistance dependence on applied pressure for 370 Ohm/sq (thin) and 70 Ohm/sq (thick) CNT networks.

It was observed that R_s of a relatively thick CNT network (70 Ohm/sq) exhibited practically unchanged R_s under applied pressure. Contrary, thin films (370 Ohm/sq) demonstrated a sharp R_s reduction of $\sim 20\%$ at low pressures followed by a gradual additional reduction as pressure exceeded 1000 Kg/cm^2 . As pressure was removed, R_s reversed back towards its starting level of performance.

Interestingly, CNT films sandwiched between two glass substrates did not show significant reduction in sheet resistance. Provided both substrates are glass, R_s change remained minimal suggesting that at least one surface needs to exhibit low surface roughness. CNT networks sandwiched between polyethylene terephthalate (PET) sheets did not lead to R_s improvement.

It is further noted that additional R_s boost can be realized when densification is utilized in conjunction with appropriate polymers. Previously, Eikos reported that certain compounds can reduce R_s by injecting additional carrier charges into carbon nanotubes that demonstrated a 20% decrease in sheet resistance. Under the pressure, Binder Alpha treated films exhibit an additional reduction of the resistance up to $\sim 50\%$ at 500 kg/cm^2 as shown in Table 12). It is suspected that the pressure improves the interfacial contact between CNTs and the doping agent leading to a more effective doping action.

Table 12: Influence of Mechanical Pressure on Sheet Resistance (500 kg/cm²)

Structure: top substrate/CNT/bottom substrate	Starting Rs, $\Omega/\square$	Rs Change, %
Glass/CNT/Glass (control)	395	3
Silicon/CNT/Silicon	370	20
Silicon/CNT/Glass	395	25
Silicon/CNT/Glass	370	35
Silicon/CNT/Glass	350	21
Silicon/CNT/Silicon	70	2
Silicon/CNT/Glass	65	4
Silicon/CNT/Glass	60	3
Silicon/CNT/PET	386	13
Glass/CNT/PET	386	6
PET/CNT/PET	390	2
Chemically Doped CNT Network		
Silicon/CNT-Binder Alpha/Glass	345	48
PET/CNT-Binder Alpha/PET	375	1

3.5.2. Colloidal Nanoparticle Deposition

It has been reported that deposition of metal species (Ag, Cu, Ni, etc) into carbon nanotubes via plating methods can impart enhanced electrical and other functional properties to its host. In the experiments following, Eikos attempted to precipitate colloidal metallic nanoparticles (gold, palladium, platinum) from salt solutions directly into formed CNT networks.

A fixed concentrated HAuCl_4 solution water/alcohol blend was prepared. Electrically conducting, optically transparent CNT network on glass substrate was fabricated to 500 Ohms/sq sheet resistance and soaked in aureate solution followed by drying per previously established process specifications. Sheet resistance (R_s) of thus treated CNT network was measured demonstrating up to 40% reduction in R_s . Electrical conductivity of CNT network was dependent on immersion time as was optical transmission (Figure 19).

Optical microscopy was employed to evaluate presence of gold deposits in CNT network that were soaked in gold aureate solution for 10 seconds and 5 minutes. These two films demonstrated different RT performance (Table 13).

Table 13: Influence of Soak Time on RT Performance

Soak Time	10 Seconds	5 Minutes
ΔT , %	-0.6	-6.6
ΔR_s , %	-26	-33

Figure 19: Change in transparency (green) and change in sheet resistance (blue) versus dip time for 0.75 mM HAuCl₄ solution in MeOH. Note that the change in %T axis varies from 0.5% to -4%, and the change in Rs axis varies from -15% to -40%.

With the goal of improved RT performance, shorter soak time was found more favorable. Both samples were examined under optical microscopy to analyze morphological differences (Figure 20).

Based on the optical microscopy images, it is evident that size of particles deposited onto the nanotube network increased with soak time. As seen in the shorter soak time resulted to particles that were close to 200nm in diameter, which was the resolution limit of the optical microscope. Longer soak time resulted in larger particles that were found to be approximately a micron in diameter. If concentration is invariant, then larger particles can arise from our CNT network having a greater electrochemical potential. Alternately, the presence of submicron contaminants could serve as nucleation sites.

Figure 20: 1,000x magnification images of CNT network soaked in HAuCl₄ solution (a) for 5 minutes and (b) for 10 seconds.

It appears that frequency of particles is high but varies over a large range. Though no quantitative particle counting has been undertaken, qualitative analysis shows the loss of transmission of the film is not due to deposition of new particles with time. Rather, the loss of transmission is more likely due to the original gold particles growing progressively larger with longer process times. Principally this growth pattern can continue until solid aggregates reach percolation threshold at which R_s would reduce dramatically due to the development of continuous connectivity between gold particles ultimately leading to polycrystalline film on CNT network.

Deposition of gold nanoparticles from aureate salt solution demonstrated a feasible approach to reducing sheet resistance of CNT network up to 40%. This improvement however, was realized with a loss in transmittance of $\sim 3.5\%$. Optical losses however can be controlled by process conditions. Comparable experiments with palliate salts resulted to minor reductions in R_s with substantial losses in transmittance rendering this approach unattractive. Finally, work with platinum colloids did not bring any change in the RT performance of the CNT networks suggesting that platinum failed to precipitate into carbon nanotube matrix.

3.5.3. Alignment of CNTs in a magnetic field

A recent paper study of buckypapers was undertaken at the Florida State University by Sheng Wang, which was published as a Master's Thesis. In it, the researcher reported on the alignment of nanotube buckypapers in high magnetic fields. Specifically, Sheng Wang correlated conductivity in the perpendicular and parallel directions with magnetic field.

Figure 21: (a) resistivity of buckypaper in the parallel direction versus magnetic field from 0 to 17.3 Tesla and (b) resistivity of buckypaper in the perpendicular direction versus magnetic field from 0 to 17.3 Tesla.

As can be seen from the figure, the resistivity in the parallel direction dropped 38% with an increase in magnetic field from 0 to 17.3 Tesla. The resistivity ($1.83 \times 10^{-3} \Omega\text{-cm}$) for a random FSU buckypaper is about 500 S/cm, or 1/10 of the value that Eikos typically achieves. The value for the aligned FSU buckypaper is about 1/6 of the value Eikos

typically sees. This change is smaller than one might expect, even though Wang assumes that the packing density of the buckypaper does not change upon alignment. It is expected that the aligned buckypapers will be more dense, and thus their volume conductivity will be higher with alignment. However, the optical cross-section will remain the same.

The change in resistivity in the perpendicular direction was found to be much more profound. The resistivity of buckypaper in the perpendicular direction was found to increase 296% upon alignment in a 17.3 Tesla magnetic field. This change is significant and indicates that very few nanotubes are contributing to the conductivity in the perpendicular direction. The observed electronic anisotropy is ~ 6.5 , which is a sign of good alignment. It seems counterintuitive that alignment disproportionately increases perpendicular resistivity while slightly decreasing parallel resistivity. However, if one views an SEM image of a nanotube network, the notion of perpendicular and parallel sticks does not describe the physical system. Rather, the nanotubes tend to stick to each other so that ends are not readily visible and that nanotube bundles converge and diverge smoothly and randomly. Thus, alignment appears to mostly remove conductive pathways in the perpendicular direction, while not significantly improving nanotube-nanotube contacts in the parallel direction.

3.6. Chemical Doping

Carbon nanotubes can be readily doped with various chemicals to impart complexation or other functional groups that facilitate the use of CNTs into other reactive media. Eikos exploited chemical doping to impart enhanced electrical conductivity on CNT films. Two concepts, oxidation [P. Avouris et al, Appl. Phys. Lett. 86(2005) 123108] and protonation [C. Engtrakul et al, J. Amer. Chem. Soc. 127(2005)17548] were studied. In both cases, CNT treatment by these compounds increased hole concentration due to electron withdrawing from the nanotubes. Holes are the main carriers in nanotubes at ambient conditions, thus additional hole injection due to doping should reduce the resistance of Invisicon® coating.

3.6.1. CNT Doping with Triethyloxonium Hexachloroantimonate

CNT films were first fabricated onto a glass slide by spray coating method. Thus prepared films demonstrated 95% transmittance @550 nm and a sheet resistance of $450\Omega/\square$. CNT coated substrates were then immersed into the solution of triethyloxonium hexachloroantimonate (OA) in methylene chloride for several minutes. The substrates were then removed, rinsed and let to dry under ambient conditions. Immediately after treatment, sheet resistance was measured 25-30% below its initial value. During subsequent days, Rs slowly increased leveling off the about 10% net reduction as shown in Figure 22 below.

Figure 22: Invisicon® Coating Doped by OA.

Absorbance spectra of the doped CNT film were then taken with near IR Spectroscopy. It can be readily observed that both S_{11} and S_{22} bands are reduced which is typical for CNT p-type doping action (**Figure 23**).

Figure 23: Absorption spectra of CNT film prior (red) and after (blue) OA treatment (spike at 850 nm is the artifact associated with switch of light source). Two spectra are normalized at 400 nm.

Thus, it can be concluded that OA doping can be used to reduce sheet resistance of CNT coatings. Additional experiments need to be conducted to optimize this enhancement method.

3.6.2. CNT Doping with Fluoro-Polymer

Here we report results from a doping experiment and subsequent increase in electrical conductive of the Invisicon[®] film by a fluorinated polymer. Binder Alpha solutions of different concentration were first prepared. CNT coated glass slides were then flow coated with each Binder Alpha solution and sheet resistance before and after coating were recorded (Table 14).

Table 14: Sheet Resistance (Rs) Dependence on Concentration.

% BA Flow Coating Solution	Starting Ohms/Square	After Flow Coating Ohms/Square	% Change After Flow Coating
0.000	389.5	370.5	-6.16
0.005	456.5	361.5	-12.2
0.050	482	401	-16.8
0.500	440	401	-17.8
5.000	463	365.5	-20

As can be seen from Table 14, BA coated over CNT films on glass showed substantial R_s improvements compared to the control, which was dipped in neat solvent.

To determine any electronic effects, the Vis-near IR spectrum of a SWNT sample on glass was measured. The first semi-conducting transition (S_{11}) of the SWNTs occurs at approximately 1700 nm. Any effects that can be attributed to doping would lead to a decrease in the S_{11} intensity.

Binder Alpha acts as an anti-reflective coating on glass, so it was coated onto a glass slide, and used to observe the optical effects from the binder. To determine doping effects, the BA and bare SWNT spectrum were added, and then compared to the spectrum of the same SWNT sample after coating with BA. In this experiment, a 5% solution of BA was applied using the mechanical dip coater at a very slow dip speed, to achieve the thinnest possible coating.

Figure 24: Vis-Near IR spectrum of a SWNT sample on glass before coating with Binder Alpha (Blue), Binder Alpha on glass (Green), SWNT sample after coating with Binder Alpha (Red), and Blue + Green (Pink).

As can be seen in Figure 24, BA increases transparency across the entire spectrum, from 400 nm to 2,500 nm. BA's AR properties will be discussed later. To separate doping effects from optical effects, the pink and red curves must be compared. The pink curve represents the addition of the BA and SWNT spectra; if BA and the SWNT film do not electronically or chemically interact, then the pink curve would result. Any qualitative differences may be attributable to electronic effects, such as doping. Indeed, we see that the S_{11} peak is totally suppressed, indicating that fluoro-polymer is acting as an effective dopant. As further confirmation, the sample went from 465 Ohms/sq to 379 Ohms/sq after dipping, a decrease of 18.5%. Note that the absorbance in the visible region is negative in portions of the visible spectrum, i.e. the 379 Ohm/square film is as transparent as an uncoated glass substrate. Since BA is a polymer, we infer that the stability of doping may be greater than for a volatile dopant, such as iodine.

Binder Alpha is a low index of refraction material, and coating glass with BA results in consistent increase in transparency. The quarter wavelength for maximum transparency can be tuned by controlling to the dip speed.

Figure 25: Vis-NIR curves showing Binder Alpha Transmission for various thickness coatings on glass. Dip speed 0 (Red), speed 2 (Green), speed 3 (Pink), speed 4 (Turquoise), Speed 6 (Brown), two coats at Speed 6 (Blue). BA concentration was 5%.

As can be seen from the interference fringes in Figure 25, it is easy to make coatings less than a few hundred nanometers thick. Binder Alpha also maintains high transparency into the near IR and suppresses SWNT peaks in the near IR, which makes it an interesting binder coat for highly transparent IR photovoltaic applications.

Binder Alpha has demonstrated a unique balance of opto-electronic properties attributed to doping. More comprehensive assessment of its R/T and mechanical performance under harsh environmental conditions are reported under Environmental Testing of Invisicon® Coatings.

3.7. Commercial CNT Materials

The optoelectronic performance of nanotube films and coatings is highly dependent on the nanotubes employed to make such films. Several physicochemical factors directly influence the electrical conductivity (sheet resistance) obtained from CNT networks for a constant film thickness (or absorbance). These include:

- Nanotube length
- Nanotube defect density
- Nanotube diameter
- Relative amount of metallic nanotubes
- Relative content of impurities
 - residual metal catalyst
 - amorphous carbon
 - graphitic particles
 - multiwalled nanotubes
- Level of sidewall functionalization
- Quality of CNT dispersion in solvents

These physicochemical factors result from different production and purification methods including nanotube dispersion. These processing methods frequently affect several physicochemical variables simultaneously, therefore how these components lead to a poorly performing transparent conductor (TC) versus a high performance TC, is difficult to assess. The CNT manufacturing variables include:

- Method on nanotube growth:
 - Laser
 - Arc discharge
 - Chemical Vapor Deposition (CVD)
 - High pressure carbon monoxide (HiPCO)
 - Flame
- Growth parameters
 - Carbon source
 - Temperature of growth
 - Catalyst
 - Addition of water or mild oxidizing agents
 - Growth time
- Purification method
- Functionalization method
- Use of dispersing agents (i.e. surfactants, polymers)

Throughout this research program, Eikos previously has explored purification, side-wall functionalization, doping techniques, effects of dispersion agents and application methods on the RT performance of CNT networks. It is evident that nanotubes produced through arc discharge method provide a path towards excellent RT performance. However, there may be performance, purity and cost advantages to using nanotubes made by other techniques. Thus, an attempt was made to test and rank, a variety of nanotubes

from universities and commercial suppliers. Table 15 lists commercial single walled carbon nanotubes sources identifying supplier, materials, production method, purity and prices as of December 2006.

A significant number of SWNT manufacturers are currently offering nanotube products for commercial purposes. Eikos has developed comprehensive expertise in using arc produced types to fabricate high purity transparent conductors. Though HiPCO produced carbon nanotubes sold by CNI are referenced in many scientific publications, TC performance derived from these materials by Eikos scientists has been inferior to that of arc materials. However, many new CNT suppliers have emerged, improved quality control, changes in production process with reduced prices making them more attractive as material suppliers.

Based on current conversion and yield factors of converting CNT soot into TC, prices from \$20 to \$60/gram are attractive from commercial perspective. In addition, CVD grown nanotubes are demonstrating promise as excellent control over growth parameters is feasible leading to longer, more pure, more graphitic nanotubes. The flow-through CVD method is also capable for continuous production in high volumes making CVD nanotubes the front-runner for producing low cost, high quality nanotubes on an industrially relevant scale.

Table 15: List of Commercial SWNT Suppliers

Manufacturer	Location	Material	Technique	Price/g	Purity
TimesNanoWeb	Chengdu, CN	SWNT	CVD	\$20	60%
CarboLex	Broomall, PA	SWNT	Arc	\$25	50%
Apex Nanomaterials	San Diego, CA	SWNT	Arc	\$28	50%
Cheap Tubes	Brattleboro, VT	SWNT	CVD	\$30	50%
MER	Tuscon, AZ	SWNT, DWNT	Arc	\$35	12%
Carbon Solutions	Riverside, CA	SWNT	Arc	\$50	40%
Guangzhou Heji Trading	China	SWNT	CVD	\$55	60%
NanoCarbLab	Moscow, RU	SWNT	Arc	\$60	40%
Helix Material Solutions	Richardson, TX	SWNT	CVD	\$61	50%
MicroTechNano	Indianapolis, IN	SWNT	CVD	\$100	90%
NanoLab	Newton, MA	SWNT	CVD	\$150	40%
Nanostructured & Amorphous Materials	Houston, TX	SWNT	CVD	\$150	50%
Nanothinx	Greece	SWNT	CVD	\$150	70%
BuckyUSA	Houston, TX	SWNT	not specified	\$250	NS
Nanocs	New York, NY	SWNT	Arc, CVD	\$250	NS
Nanocyl	Sambreville, BE	SWNT, DWNT	CVD	\$250	80%
Thomas Swan	United Kingdom	SWNT	CVD	\$270	90%
CNI	Houston, TX	SWNT, DWNT	HiPCO	\$375	65%
SES Research	Houston, TX	SWNT	CVD	\$425	92%
SouthWest Nanotech	Norman, OK	SWNT	CoMoCat	\$500	90%

3.7.1. Thermal Gravimetric Analysis (TGA)

TGA is the process of heating a sample and monitoring its weight change to determine composition and thermal stability of the material. In this study, TGA was used as a method to determine the amount of carbon and catalyst present in the sample. Amorphous carbon oxidizes at the lowest temperature, followed by single walled nanotubes, multiwalled nanotubes and, lastly, graphite. Metal catalysts oxidize somewhat continuously throughout the process, depending on how accessible the metal surface is to oxygen. The generic reactions of importance during TGA are:

where C represents solid carbon in the form of amorphous carbon, nanotubes, or graphite, and M represents the metal catalyst. Thus, weight loss in TGA is attributed to oxidation of carbon, whereas weight gain is attributed to oxidation of metal catalyst. Figure 26 represents a typical TGA for single walled carbon nanotubes.

The curve representing the weight of the sample versus temperature shows a relatively flat oxidation profile until about 350 °C, followed by a rapid weight loss until about 500 °C. The weight loss continues until about 750 °C, upon which the weight of the sample begins to increase. The first derivative of weight versus temperature yields more information about the rates of oxidation of materials. Specifically, the major weight loss between 350°C and 500°C consist of (at least) two different materials. The more easily oxidized material is typically assigned to amorphous carbon, whereas the more thermally stable material is typically assigned to single walled carbon nanotubes. This curve indicates that this sample contains a qualitatively higher weight percentage of amorphous carbon than single walled nanotubes. The first weight derivative also reveals that some graphitic particles are present in the sample. The remaining weight is that of the oxidized metal catalyst. If the catalyst is known, the amount of oxygen in the residual weight can be calculated and subtracted to reveal the amount of catalyst in the sample. However, nanotube manufacturers frequently do not reveal their catalyst composition, thus the catalyst weight is typically given as the residual weight remaining after a full TGA run.

Figure 26: Typical TGA of carbon nanotube materials with weight percent and derivative of weight percent versus temperature.

TGA was conducted on 2-10 mg of material, which was limited by the size of the sample pan and analyzed in air. Dry samples were heated at 2 °C/min from room temperature to 1,000°C, and then held at 1,000 °C for 500 minutes to fully oxidize any residual metal catalyst. Wet samples were dried at 100°C in air until dry, followed by the procedure for dry samples. This slow burn yields a thermodynamic oxidation process that is less dependent on sample size and morphology. We have found reproducibility of ± 5 °C of the maximum oxidation rate for a within one batch of nanotubes for sample weights from 0.8 mg to 5 mg.

Results from TGA analysis for various nanotube samples are shown in Table 16. The sample with the lowest thermal stability was produced by MER. Both Nanocyl SWNT and DWNT materials showed the most residual catalyst. The Carbolex material demonstrated the highest catalyst of any arc discharge sample. Material from NanoC was received as a purified and dry material, resulting in a low catalyst weight percent. The Thomas Swan material was received as a purified wet cake with about 5% solids thus resulting to a low catalyst weight percent.

Table 16: Summary of TGA data for various as-received CNT materials.

Sample	Residual Catalyst (%)	CNT weight (%)	Oxidation Temperature (Max. Rate)		
			a-C (°C)	CNT (°C)	Graphite (°C)
Carbolex	36.4	~30	356	403	651
Glerup	17.6	~70	-	463	614
Standard Material	16.0	~35	432	463	714
Nano-C	5.4	~35	445	463	-
Thomas Swan	4.7	>95	-	542	-
MER	13.2	~35	319	369	663
Nanocyl DWNTs	57.6	~40	448	590	-
Nanocyl SWNTs	92.6	~5	240	359	620

Carbon nanotubes from Thomas Swan exhibited highest thermal stability. This can be attributed to exceptional low weight percentage of catalyst and high degree of graphitization. As the presence of catalyst is known to decrease the oxidation temperature high purity samples tend to have higher oxidation temperatures. An exception to this rule was the Nanocyl DWNT material, which showed ~60% residual weight, but oxidized around 600 °C. Also, single wall carbon nanotubes from Marianne Glerup demonstrated TGA characteristics with a high oxidation temperature.

3.7.2. Process Based Analysis

Purification and dispersion processes can have a detrimental effect on the physicochemical properties of nanotubes. Oxidizing treatments, such as air anneals and nitric acid refluxes, are frequently used to remove amorphous carbon, since it oxidizes more easily than carbon nanotubes. However, oxidations that are too aggressive will lead to shortened or damaged nanotubes. Additionally, some processing steps can cause the nanotubes to tightly bundle, making them difficult to disperse. Sonication has become a common way to disperse nanotubes in a solvent, but it also can cut nanotubes and increase sidewall defects.

Further analysis was conducted with ten different types of nanotubes that were fabricated using CVD, arc discharge, and flame growth methods. Samples with high commercial

promise (low cost, good initial performance, manufactured in large quantities) were studied more thoroughly. All such materials were processed through with Eikos proprietary reflux and extraction procedures. Some samples were also dispersed in alcohols and sprayed as-received to determine performance prior to any purification treatment. Other samples were dispersed in water with surfactants and made into films using the filtration method. These various methods were used to assess the effects of the potentially damaging standard reflux and extraction procedures.

3.7.3. CNT Purifying by Acid Reflux

Eikos scientists have developed a procedure to purify and functionalize CNTs using an oxidizing reflux. This process serves several purposes:

- Dissolving metal catalyst
- Oxidizing amorphous carbon
- Opening graphitic shells
- Functionalizing CNT
- Debundling CNT
- Doping CNT

Several features of this process have been optimized to yield the highest performance for control nanotube material. Many of the effects of the reflux go beyond purification, and affect conductivity by doping, as well as possibly changing bundle morphology and nanotube defect levels. Some nanotube materials may be good conductors, but tend to damage easily, and thus the reflux process may need to be tuned for such materials. For example, a nanotube's propensity to be damaged can be measured by the temperature at which it oxidizes most rapidly. Using thermal gravimetric analysis (TGA), a nanotube's resistance to oxidation can be inferred. Thus, based on TGA data and other factors relating to the type of impurities in a sample, an attempt was made to vary reflux conditions for the purposes of deriving best possible RT performance from each tested material.

3.7.4. Performance, Analysis and Discussions

The results of different CNT processing and analysis methods detailed above are summarized in the Table 17. It should be noted that only one CNT material matched or exceeded the performance of Eikos' control sample. Materials from several suppliers trailed slightly behind in RT performance. These include materials from Thomas Swan, Michael Kiedar of University of Michigan, and the arc produced SWNT from Clemson University. Amongst these three, Thomas Swan is the only commercially available source.

Thomas Swan materials were found to be exceptionally pure and stable thermally. This material was exposed to standard as well as modified acid reflux conditions to improve CNT dispersion. However, the modified reflux sample performed poorly, compared to the standard reflux and wrapping in surfactant. Notably, the as-received material showed the best RT performance after surfactant wrapping, which is indicative of the material's high purity and good electronic quality.

Nanocyl SWNTs contain an exceptional amount of catalyst (92.6% by weight), and thus the raw material required some processing to remove that material prior to assessment of RT performance. The material performed reasonably well, ~65% @500 $\Omega/\square$. This performance was not matched by the standard reflux, indicating that more work is needed to determine appropriate reflux parameters.

CheapTubes, *Nano-C*, and *MER* all yielded samples with poor RT performance, which can be attributed to *MER*'s low thermal stability and to *Nano-C*'s short length (per manufacturer's data). The *CheapTubes* material was not analyzed beyond RT performance, but it is likely that the nanotubes were highly defective and thus did not withstand the reflux process.

The Carbolex material performed poorly for an arc discharge material, which typically yields RT values in the 80s-90s. This could be attributed to the material's high catalyst weight and lower thermal stability than the standard material. This material is priced competitively, but only has performance that is good enough for anti-static applications.

Four research groups also submitted CNT samples for Eikos evaluation. These include U. Michigan, Clemson U., U. of Oslo, Norway and Chinese Academy of Sciences. All materials performed well demonstrating optical transmittances from 80 to 95% at a sheet resistance of 500 $\Omega/\square$.

Table 17: Various CNT materials, processing, and resulting performance

Manufacturer	Material	Processing Method	%T@500 $\Omega/\square$	Substrate
Thomas Swan	CVD SWNT	Shear, sonication in alcohol	15	Glass
		Surfactant in H ₂ O	64.3 73.1	Filter PET
		Standard reflux, extractions	63.5 89.1	Glass Glass
Nanocyl	CVD SWNT	Shear, sonication in alcohol	0.5	Glass
		Standard reflux, extractions	57	Glass
Nanocyl	CVD DWNT	Shear, sonication in alcohol	1.6	Glass
		Standard reflux, extractions	35	Glass
Cheap Tubes	CVD SWNT	Standard reflux, extractions	5.9	Glass
Nano-C	Flame SWNT	Shear, sonication in alcohol	0	Glass
		Standard reflux, extractions	17.5	Glass
MER	Arc SWNT	Shear, sonication in alcohol	0	Glass
Control Material	Arc SWNT	Shear, sonication in alcohol	24.8	Glass
		Surfactant in H ₂ O	42.8	Filter
		Standard reflux, extractions	95+	Glass
Carbolex	Arc SWNT	Shear, sonication in alcohol	3.1	Glass
		Standard reflux, extractions	60.4 66	Glass Glass
U. Oslo	Arc SWNT	Standard reflux, extractions	95.9	Glass
U. Michigan	Arc SWNT	Standard reflux, extractions	91.1	Glass
Clemson Univ.	Arc SWNT	Standard reflux, extractions	94.1	Glass
IMR, Chinese Academy of Sciences	Arc SWNT	Standard reflux, extractions	81	Glass

Based on this comprehensive analysis, it is evident that the arc discharge nanotube materials perform well under well defined process conditions. It is thought that the nanotubes produced by arc discharge have significantly fewer defects, i.e. that they are perfectly graphitized attributed to the high temperature plasma processing. Additionally, we can attribute our observed performance advantage with arc nanotubes to resources spent optimizing Eikos processing procedure to remove difficult impurities, such as graphitic shells. It is believed that CVD based nanotubes will experience reduction in price and quality will improve in the coming years.

3.8. **CNT Transparent Conductors: 100 $\Omega/\square$ @90%T**

An R/T performance target was established as 100 $\Omega/\square$ sheet resistance with an optical transmittance of at least 90%. Prior to this contract, Invisicon[®] CNT based coatings had a demonstrated capability to achieve R/T performance of 86 %T at 100 $\Omega/\square$. During the contract, the number of available improvement techniques has expanded and are categorized in Table 18.

Table 18: Notable Process Improvements

Category	Improvement	Improvement Mechanism
<i>Soot Purification</i>	Reflux Chemistry	Contaminant Reduction
	AIF Purification	Contaminant Reduction
	Raw Material Purity	Contaminant Reduction
<i>Ink & Coating</i>	Ink Deposition Technique	Uniformity Increase
	Delivery Method	Dispersion Stability
	Ink Concentration	Haze Reduction
<i>Post Processing</i>	Doping of CNT Films	Rs Decrease
	Antireflective Binders	%T Increase

The process improvements identified above were employed in the experiment following. Certain improvements were held constant throughout the experiment due to previous optimization efforts, while others were treated as variables. Different purification, coating techniques and variables that were explored are tabulated in Table 19.

Table 19: Purification and Coating Experimental Parameters

Improvement	Set 1	Set 2	Set 3
Raw Material	Laser	Arc	Arc
Reflux Chemistry	Nitric	Sulfuric/Nitric	Sulfuric/Nitric
AIF	Yes	Yes	Yes
Ink %T @ 500 Ω /sq	96.0	96.1	96.5
Ink Absorbance	0.6	2	1.5
Process Parameter Optimization	Yes	Yes	Yes
Ultrasonic Delivery Method	Yes	Yes	Yes

Every test set consisted of a statistically significant number of microscope slides coated to 100 $\Omega/\square$ surface resistance with Invisicon[®]. These substrates were doped chemically and coated with various binders in an effort to improve conductivity and % transmission respectively. The dopant and binder matrix is shown in Table 20.

Table 20: Dopant and Binder Test Matrix

Sample Number	Dopant	Sol Gel	Binder Coat
1	None	None	None
2	None	None	Binder Alpha
6	None	None	Fluoropolymer
9	None	None	Teflon AF
12	None	None	Binder Alpha + Teflon AF
14	None	None	Binder Alpha+ Fluoropolymer
16	Sb*	None	Binder Alpha
17	Sb*	None	Teflon AF
18	None	Two step	Binder Alpha
19	None	One step	Binder Alpha

The R/T performance was measured at various points throughout each test. Data was taken immediately after CNT coating, after doping (if applicable), and after binder coat application. Resistance was measured using silver electrodes painted on each test sample. A Perkin Elmer Lambda 900 spectrophotometer was used for all transparency measurements.

3.8.1. Test Results

The results for the experiment described above are contained in Table 21. The best results were obtained with Test #3, with three slides exceeding the goal of 90%T at 100 $\Omega/\square$. Test #3 represents a culmination of Eikos' optimized technologies. Tests #1 and #2 failed largely due to lower ink quality and reflex chemistry (Set 1).

The initial R/T performance and the ink absorbance proved to be especially important. CNT materials produced by laser ablation method experienced significant instability leading to flocculation. Test 2 employed ink with the absorbance of 2 appeared to be too concentrated thus causing instability. The R/T data for the control slides demonstrated that the values normalized to 500 Ω /square were 1.2% and 1.1% off from original ink value for Tests 1 and 2 respectively.

This discrepancy is a sign of ink instability. The ink used for Test 3 was found significantly more stable. The R/T @500 Ω /□ was within 0.5% of the original specification. Before the application of the binder coat, the samples made from this ink exceeded our original record of 86% @100 Ω /□ by 0.7%.

Table 21: Results of R/T Performance Trial at 100 Ω /□

Dopant	Sol Gel	Binder	%T @ 100 Ω /sq		
			Test 1	Test 2	Test 3
None	None	None	82.5	81.7	85.9
None	None	Binder Alpha	87.3	85.9	88.4
None	None	Fluoropolymer	81.9	81.7	85.2
None	None	Teflon AF	82.1	82.4	85.4
None	None	Binder Alpha + Teflon AF	-	88.5	90.8
None	None	Binder Alpha + Fluoropolymer	85.6	86.8	90.9
Sb*	None	Binder Alpha	87.7	86.3	-
Sb*	None	Teflon AF	86.9	84.8	-
None	Two step	Binder Alpha	79.8	-	83.3
None	One step	Binder Alpha	76.5	-	79.2

* triethyloxonium hexachloroantimonate

Of the binder coats and dopant employed, most materials exhibited increased R/T performance. Without exception, high performance samples from each test set were binder coated with Binder Alpha (Eikos proprietary polymer) in some variation. The three samples that exceeded 90%T were coated with a combination of Binder Alpha and Teflon AF or a fluoropolymer. Respectable results were also obtained on samples coated solely with Binder Alpha or doped with antimonate prior to depositing Binder Alpha binder.

In addition to doping and binder coats, certain test coupons were also coated with sol gel formulations followed by a Binder Alpha. The sol gel coatings enhance environmental performance of Invisicon® and were thus included in the test matrix. This family of materials will play an important role in the overall performance scheme of Invisicon® materials.

3.8.2. Conclusions

Eikos was able to achieve two samples at greater than 90%T @100 $\Omega/\square$ using combination of optimized technologies. A high grade CNT ink with R/T performance of 96.5%T @500 $\Omega/\square$ minimum is required to achieve 90%T @100 $\Omega/\square$. Final boost is provided by choice binder coat. Highly stable ink composition is imperative for high RT performance especially at low sheet resistance levels regardless of initial ink grade. Binder coats that incorporate Binder Alpha appear to give the greatest transparency increase of CNT coated samples.

3.9. *Towards 10 $\Omega/\square$ @70%T Target*

The second optoelectronic performance goal for Invisicon® CNT coatings was set at 10 $\Omega/\square$ surface resistance with an optical transmittance of 70% (@550 nm). Eikos produced an RT curve of a high grade ink with low particles in order to determine how well inks sprayed down to low sheet resistances. The ink used was qualified to be 95.7%T at 500 $\Omega/\square$. As seen in Figure 27, the bare CNTs sprayed down to about 83.6%T at 100 $\Omega/\square$ and ~65%T at 50 $\Omega/\square$. **At the target of 70%T, the measured R_s was found to be 45 $\Omega/\square$.** This is considered to be much better than previously observed; in the past, high grade inks with high particle count were found to be ~80%T at 80 $\Omega/\square$, ~70%T at 70 $\Omega/\square$, ~60%T at 60 $\Omega/\square$, ~50%T at 50 $\Omega/\square$, and so on. This 10%T drop per 10 $\Omega/\square$ drop in R_s deviates from Beer-Lambert's & Ohm's Laws. However, reduced particle inks were found to give significantly better RT performance at lower sheet resistances.

To further improve the RT performance, Eikos used its proprietary binder α to increase transparency and reduce R_s . As can be seen from the arrows in Figure 27, the samples showed a consistent increase in transparency and a drop in sheet resistance after coating with binder α . Also evident, the RT curve of the CNT and binder intersects the previously achieved DOE goal of 90%T at 100 $\Omega/\square$ (note the star in Figure 27). **Further, the CNT coating with binder α at 70%T was measured to be 35 $\Omega/\square$.** This value represents the significant improvements made during the performance period.

Figure 27: Resistance versus transparency curve for CNT film (blue) and CNT film with binder (pink). Stars indicate that targets for the DOE contract. Arrows indicate the shift in %T and R_s .

4. Evaluation of CNT in PV Structures

Eikos worked with the National Renewable Energy Lab in Golden, CO to evaluate Invisicon in various PV architectures. Prior to creating devices, some basic characterization of the CNT coatings was undertaken. Once we understood electronic characteristics of the coatings, we fabricated several different classes of devices. Samples of Invisicon were fabricated under this contract. Invisicon coating characterization and solar cell fabrication was conducted under DOE contract DE-AC36-99G010337 and is presented below. NREL and Eikos fabricated organic, CIGS, and CdTe solar cells, of which the results are shown below.

4.1. CNT Characterization with NREL

During the contract period, NREL characterized Invisicon® coatings for their PV suitability. NREL further examined the electrical and optical properties of Invisicon® carbon nanotube films. Optical properties were examined using a variety of techniques, including transmission and reflection spectrometry, and variable angle spectroscopic ellipsometry (VASE). Additionally, NREL conducted tests on the electrical properties of CNT networks, including determining the majority carrier type and work function.

Fundamental to how a transparent conductive coating performs in photovoltaics is its resistance and transmittance properties. Eikos coated eight microscope slides with Invisicon® for evaluation of these properties. These slides were measured for their transmission in the visible and near infrared spectrum as seen below in Figure 28.

Figure 28: Optical Transmission of Various Resistive Invisicon® Coatings.

Optical transmission is comparable to many commonly used transparent conducting oxides. It is additionally promising for multi-junction devices and others that utilize the near infrared portion of the spectrum that the optical transmission increases through the near infrared, allowing more energy into the cell for photo-conversion. NREL measurements for optical transmission are shown in Figure 29.

Figure 29: Optical Transmission for Carbon Nanotubes versus Al-ZnO layers.

NREL further characterized Invisicon® coatings with X-ray Photoelectron Spectroscopy (XPS). XPS measurements reveal the work function of a material. NREL calculated a median work function for Invisicon® coatings at $\Phi = 4.8$ eV, see Figure 30. Proper work function matching between sandwiched materials allows for good electron conduction, and thus efficiency in a solar cell. The Invisicon® work function is very similar to indium tin oxide, a dominant transparent conductor in use in photovoltaics today. This implies a promising work function match for Invisicon® in solar devices.

Figure 30: Work function measurement using XPS for several CNT samples.

XPS of a 50 $\Omega/\square$ Invisicon® sample revealed mostly sp^2 carbon, as expected for carbon nanotubes. This is illustrated by the C1s peak. The glass microscope slide also “shined” through during the measurement, due to the porous nature of Invisicon® coatings. This glass (SiO_2) substrate gave XPS peaks for Si2p, Si2s, and O1s energies.

Invisicon® was characterized using spectroscopic ellipsometry to model of the optical properties of the CNT coating. Eikos spray applied suspended carbon nanotubes on quartz slides until the sheet resistance 50 $\Omega/\square$ to 100 $\Omega/\square$ was obtained. These slides were then analyzed at NREL to create an ellipsometry model. Atomic Force Microscopy (AFM) was used to determine the thickness of the Invisicon® layer. Figure 31 shows that the average thickness of the 50 $\Omega/\square$ layer is 39.8 nm, with an RMS roughness of 31.1 nm. At 100 $\Omega/\square$, this layer is 25.8 nm thick, with an RMS roughness of 12.0 nm.

Figure 31: AMF microscopy revealed a thickness of 39.8 nm for 50 ohm/sq coatings, and 25.8 nm for 100 ohm/sq coatings of Invisicon®.

Thickness data from AFM measurements were used in modeling ellipsometry data for Invisicon®. Specifically, the 50 $\Omega/\square$ layer, with thickness of 39.8 nm, was taken with an index grading of 30% at the substrate, followed by 86% at the substrate, to derive the model seen in Figure 32.

Figure 32: Completed ellipsometry model for Invisicon®, showing the index of refraction (n) and extinction coefficient (k), with corresponding permittivity (ϵ) values.

Ellipsometry modeling is significant for designing optoelectrical devices. It is important to match the index of refraction (n), of a layer with the layers surrounding it, so as to maximize transmittance and minimize reflectance. Proper index matching is often used in the form of anti-reflective coatings, which, when used in solar cells, increases the amount of solar radiation reaching the active layer and being converted to electricity. The Invisicon® ellipsometry model is within the range of $n=2.2-2.4$ over 1-3 eV (1240-413 nm), the useful wavelengths for most solar cells.

4.2. *Invisicon in Organic PV structures with NREL*

Eikos and NREL fabricated several viable organic excitonic solar cell structures where the conventional $\text{In}_2\text{O}_3:\text{Sn}$ (ITO) hole-collecting electrode was replaced by a thin single-walled carbon nanotube (SWNT) layer. The first structure included poly(3,4-ethylenedioxythiophene) (PEDOT) and gave a non-optimized device efficiency of 2.6%. The second did not use PEDOT as a hole selective contact and had an efficiency of 1.4%. The strong rectifying behavior of the device shows that nanotubes are selective for holes and are not efficient recombination sites. The excitonic solar cell, produced without ITO and PEDOT, brings one step closer the goal of a fully printable solar cell.

Organic photovoltaics (OPVs) are a promising alternative to Silicon and Thin Film solar cells. They are inexpensive and easily fabricated on large scale. A successful OPV approach to date has been to use ITO coated substrates functionalized with a layer of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) and an active layer consisting of a blend of conjugated polymer such as poly (3-hexylthiophene) (P3HT) with a C_{60} derivative such as 3'-phenyl-3'H cyclopropa[1,9][5,6]fullerene- C_{60} -Ih- 3'-butanoic acid methyl ester (PCBM). ITO is not ideal because it is expensive to fabricate and contains indium, an element whose availability is questionable. It is also optically, electronically and chemically problematic. PEDOT:PSS is possibly problematic since it is known to degrade under UV illumination, introduces water into the active layer of the device, and retains a degree of acidity.

A possible alternative to ITO and PEDOT:PSS are SWNT films. This material shows high conductivities combined with high optical transmission and is solution processable as opposed to ITO which has to be vapor deposited. SWNTs have already shown promise in light emitting diodes. The replacement of ITO and PEDOT:PSS with a SWCNT layer brings one step closer the promise of a fully printable solar cell. The only remaining vapor deposition step is the electron collecting contact or anode, which typically consists of either Al, Ca/Al, or LiF/Al.

Carbon nanotubes have previously been used in organic devices. Ago et al. demonstrated a solar cell using multi-walled nanotubes as the hole collector. This had very low short circuit current density (J_{sc}) and efficiency. Other devices have incorporated SWCNTs as electron recipients and transporters. These showed extremely low efficiencies of, typically around 0.01%. Recently, a device was demonstrated using SWCNTs as the cathode in the structure SWCNT/PEDOT:PSS/P3HT:PCBM/Ga-In. This cell, which still employs PEDOT:PSS as the hole-collecting layer had a power-conversion efficiency of 1%, illustrating clearly the promise of SWCNTs to replace ITO.

4.2.1. Experimental Results

Eikos and NREL created devices using the same P3HT:PCBM active layer, not just replacing the ITO but also the PEDOT:PSS layer with a thin film consisting of bundles of SWCNTs. The latter device, shown schematically in Figure 33, showed a non-optimized efficiency of 1.4%. We also report on a device of the structure

SWCNT/PEDOT:PSS/P3HT:PCBM/Al, which is similar to the device demonstrated before but with an efficiency of 2.4%.

Figure 33: Device structures employed in this study. a) Device A in which ITO is replaced by the SWCNT layer but PEDOT:PSS remains. b) Device B, in which both PEDOT:PSS and ITO are replaced by the SWCNT layer. In device B, the P3HT:PCBM is probably intermixed with the SWCNTs. c) top view of the device structure. 6 devices are created on a 1x1" glass slide. The black dots represent the points where contacts are made.

The SWCNT electrodes were fabricated at Eikos by coating microscope slides using arc-produced SWCNT. The nanotubes were purified by a process of acid reflux, washing and centrifugation to remove metal catalyst and non-tubular forms of carbon. As a consequence of the production process, the nanotubes consist of a mixture of about 1/3 metallic tubes and 2/3 semiconductor tubes.

Once purified, they were dispersed in water and alcohol to form an ink. No surfactant remains in the coating after application. The coating was essentially pure bundles of SWCNTs as evident from X-ray photoelectron spectroscopy (XPS). The layers coated on microscope glass used in this study typically had a sheet resistance of approximately 50 Ω/sq and a transmittance of 70% at 650 nm. These values compare well to the values reported for SWCNT substrates used in a previously reported organic solar cell (about 45% transmittance at 650 nm for a sheet resistance of 282 Ω/sq), likely owing to differences in production, purification, and deposition methods.

Figure 34: Atomic-force microscopy image of a 50 Ω /sq SWCNT layer on microscope slide glass.

As Figure 34 shows, Atomic-force microscopy (AFM) performed using a nanoscope IV AFM indicated that the substrates consisted of micron-long nanotube bundles lying parallel to the glass surface and having a random and braided in-plane orientation. Such a networked morphology is expected to decrease transparency, but to also increase conductivity. The SWCNT coated glass substrates were ultrasonically cleaned in acetone and isopropyl alcohol and in some cases; silver pads were deposited outside of the active area of the cells to provide efficient contacts. For device A, 30-nm layer of PEDOT:PSS (Baytron P VP AI 4083) was spun on at 4000 rpm. 0.1-1 μm films of P3HT:PCBM 1:1 (10mg/ml in chlorobenzene,) were drop cast or spin coated on top and allowed to slowly dry for 30 minutes in a argon-atmosphere glove box. The P3HT (4002 E) was obtained from Rieke metals. Aluminum top contacts (~ 100 nm) were then deposited onto the device by thermal or e-beam evaporation. Finally, the devices were annealed at 120°C for 30 minutes in the glove box. The fabrication procedure for device B was identical, but with the PEDOT:PSS layer eliminated. Several reference devices of structure A were produced on ITO for comparison. Two-terminal efficiency measurements, traceable to a primary standard, were made using NREL's XT-10 solar simulator with a silicon reference. The efficiency was measured using a specially designed cell holder that allows

the cell to remain in inert atmosphere. The light intensity was adjusted for the spectral mismatch between the P3HT:PCBM system and the silicon reference. The active area of the solar cells was approximately 0.1 cm^2 . The external quantum efficiency of the cells was measured using NREL's EQE user facility using a calibrated silicon reference.

Figure 35: Typical current-voltage plots for devices with the structures A (left pane) and B (right pane). The dashed lines indicate the curves measured in the dark. The continuous lines were measured under AM 1.5 equivalent conditions.

Figure 35 shows current versus voltage (J/V) plots in the dark and light, for a cell with structure A. The dark curve shows reasonable rectification for an applied bias of 1 Volt. Under illumination, the device gave $V_{oc}=0.5546$ Volt, $J_{sc}=9.656 \text{ mA cm}^{-2}$ and fill factor (FF) = 48.8%, resulting in an efficiency of 2.6%. This compares well with the efficiency of 3% for a reference device on ITO. The FF appears to be series resistance limited. Likely contributions to the series resistance include: relatively low conductivity of the SWCNT substrate, non-optimized P3HT:PCBM layer thickness leading to poor conductivity, and a high contact resistance in our test apparatus. In a similar device based on ITO, the series resistance is orders of magnitude lower.

The right pane of Figure 35 shows typical J/V curves from device B. In this device, both ITO and PEDOT:PSS were replaced by SWCNTs. Because the SWCNTs are readily wet by the chlorobenzene solvent used for the deposition of P3HT:PCBM and the SWCNT layer is highly porous, the P3HT:PCBM layer is expected to intercalate into the open-structured SWCNT film. In Figure 35a, the dark curve shows a high degree of rectification (we observed a maximum rectification factor of 107 at 0.75 Volts applied bias for a cell that is not shown here) and is limited by series resistance at high forward bias. These values indicate that the nanotubes are highly selective for hole injection into the P3HT:PCBM blend. This is consistent with XPS/UPS measurements that yielded an effective work function of about 4.8 eV for the mostly *p*-type semiconductor nanotubes, which is close to the valence band of the P3HT. The light curve in Figure 35b shows $V_{oc}=0.4441$ Volt, $J_{sc}=7.443 \text{ mA.cm}^{-2}$, $FF=43.1\%$ and an efficiency of 1.43%, which is a record for organic excitonic solar cell without both ITO and PEDOT:PSS. As was the

case for the PEDOT:PSS containing device, the light curve appears to be limited by a series resistance, most likely caused by the factors mentioned above.

4.2.2. Discussion

The series resistances estimated for the devices shown in Figure 35 were hundreds of Ohms. This is much larger than the value of $100\ \Omega$ expected from the geometry of the devices and the sheet resistance of the nanotubes. The limiting photocurrent of device B was lower than that of device A. This may be due to a different P3HT:PCBM layer thickness, caused by the inherent irreproducibility of the casting process, or to more recombination in device B than in device A. The devices that did not employ PEDOT:PSS show lower open-circuit voltages than those that do employ PEDOT:PSS. It is possible that this is related to a small amount of recombination occurring preferentially on the SWCNTs. Also, due to the inherent reproducibility of the casting process and the difference in interaction with the deposition solution between the SWCNT layer and PEDOT:PSS layers, these devices might not have had the same layer thicknesses leading to differences in efficiency. Lastly, it is possible that the PEDOT layer completely isolates the SWCNT layer from the top contact, decreasing shunting of the device by errant nanotubes penetrating the entire active layer. The efficiencies reported here are higher than those reported in the literature for a similar device employing PEDOT:PSS. The higher efficiencies are likely due to higher quality SWCNT layers, different active layer deposition and purity, and to the use of an evaporated back contact instead of a eutectic that readily forms interfacial oxides.

Figure 36: External Quantum efficiency of the SWCNT device in structure B (no PEDOT:PSS) at short circuit (continuous line) and at a reverse bias of 1 volt (dashed line). The inset shows the same data on a semi-logarithmic scale. The units on the right and top axes are the same as on the left and bottom ones respectively.

Figure 36 shows external quantum efficiency (EQE) of the device in Fig. 3b (i.e. the device without PEDOT:PSS). Absorption by the P3HT (the peak at 635 nm and lower) is clearly visible. The small shoulder at 705 nm is attributed to absorption by the PCBM phase. The large change in shape when applying 1 volt of reverse bias indicates that the P3HT:PCBM layer is not entirely active at short circuit, and a larger bias is needed to sweep out more of the photogenerated charges. This effect will impact the more weakly absorbed light (i.e. at 500 nm or at wavelengths longer than 700 nm) stronger than in the peak absorption of the P3HT at 635 nm, changing the shape of the EQE curve. This is a clear indication that devices with thinner active layers will yield better results and we are working on optimizing the layer thickness for this geometry and electrode material.

4.2.3. Conclusions

SWCNT films are an alternative to ITO/PEDOT:PSS as a hole-collecting electrode for organic excitonic solar cells. We demonstrated efficiencies up to 2.6% for a non-optimized device with the structure SWCNT/PEDOT:PSS/P3HT:PCBM/Al and 1.4% for the structure SWCNT/P3HT:PCBM/Al. These are higher than other excitonic devices

employing carbon nanotubes reported to date either as electron or hole acceptors or electrode materials. Additionally, the devices are highly rectifying and show relatively large J_{sc} values. The devices are mainly limited by series resistance caused by either the relatively low conductivity of the SWCNT layer, non-optimized and poorly controlled P3HT:PCBM layer thickness, and contact resistance at the nanotube layer.

4.3. Invisicon in CIGS PV structures with NREL

NREL and Eikos collaborated on Copper Indium Gallium diSelenide (CIGS) type devices, replacing the standard aluminum doped zinc oxide (Al-ZnO) transparent conductor with Invisicon®. These efforts produced working devices on the first attempt. This novel utilization of carbon nanotubes in CIGS devices has produced a paper published in the *Journal of Physical Chemistry C*.

Figure 37: Standard CIGS Cell Construction.

While the standard aluminum doped zinc oxide (Al-ZnO) transparent conducting oxide works relatively well, it limits the device photo-generated current, due to a rather strong free-carrier absorption of near infrared (NIR) photons. Eliminating this absorption is difficult because it requires reducing the free-carrier concentration without affecting conductivity. A preferred transparent conductive coating would provide higher transmittance in the IR portions of the spectrum, while maintaining high electrical conductivity. Carbon nanotube coatings show higher transmittance in the IR, indicating they do not exhibit the same free carrier absorption as standard transparent conductive oxide coatings do.

4.3.1. Experimental Results

High-efficiency ZnO/CdS/CIGS/Mo solar cells usually incorporate a ZnO bilayer consisting of a thin (50–100 nm) intrinsic ZnO layer (*i*-ZnO) capped with a thicker (100–130 nm) *n*-type ZnO layer (in our case, ZnO:Al). We initially tested the SWCNT/*i*-ZnO/CdS/CIGS/Mo device structure to evaluate the coatings as a replacement for the ZnO:Al. In all of the devices, the CIGS absorber layer was grown by evaporation from elemental sources onto molybdenum-coated soda-lime glass. CdS was deposited by chemical-bath deposition. Undoped ZnO was deposited by rf sputtering. The devices were shipped to Eikos to be coated with 50–100 Ω /sq SWCNT film. The coated devices were then returned to NREL, where metal grids were applied, and the cells were mechanically scribed and tested.

Current density-voltage (J-V) data obtained from these initial experiments are summarized in Table 22 for representative cells. Devices were made using different values of sheet resistance for the SWCNT layers, as shown in Table 1. We point out that the device structure, absorber film, and device processing have not yet been optimized, and that further improvements in device performance can be expected by tuning layer thicknesses and compositions.

Table 22: Device results for solar cells with structure of Invisicon® /*i*-ZnO/CdS/CIGS/Mo using varying sheet-resistance values for the SWCNT layers. State-of-the-art ZnO/CdS/CIGS values are shown in the first row for reference.

SWCNT (Ω /sq)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	Eff. (%)	R_s (Ω -cm)	R_{sh} (Ω -cm)
ZnO	0.693	35.34	79.4	19.5	1.449	8798.10
100	0.674	31.21	61.66	12.98	5.826	596.70
75	0.622	29.12	64.93	11.7	3.22	510.78
50	0.598	25.02	62.13	9.30	3.656	265.05

The data in Table 22 show that the new device structure has: (a) lower short-circuit current density (J_{sc}) values as compared to state-of-the-art devices incorporating ZnO:Al, and (b) low shunt resistance. The best device obtained with SWCNT electrodes had an efficiency of 12.98%. Unlike vacuum-deposited ZnO, the SWCNT layers are porous. The layers are very thin and they consist of a three-dimensional network incorporating about 30% voids and a high surface roughness. These attributes may be associated with the low shunt resistance if the layers allow short-circuiting between the metal grid and the *i*-ZnO or CdS beneath the SWCNT film.

Figure 38: Internal quantum efficiency of SWCNT/*i*-ZnO/CdS/CIGS/Mo structures using Invisicon[®] layers with different sheet-resistance values. The 19.5%-efficiency cell data are for a state-of-the-art solar cell (using *n*-ZnO) and are shown for reference.

Figure 38 illustrates that the overall internal quantum efficiency (QE) of the devices incorporating SWCNTs is lower than for standard devices employing ZnO, leading directly to the lower J_{sc} values observed in the SWCNT devices. This is consistent with the finding that although the SWCNT coatings are more transparent in the IR than ZnO:Al, they are less transparent and more absorbing in the visible and ultraviolet (UV) regions for equivalent sheet resistance. The lower optical transmission across the UV, visible, and up to ~1200 nm contributes strongly to the loss in QE, and consequently, J_{sc} and efficiency. In other words, some of the photons that could generate photocurrent are absorbed in the SWCNT layer before they reach the electronic junction of the device.

We employed several strategies to replace the complete ZnO bilayer with SWCNTs and SWCNT/polymer combinations. First, the ZnO bilayer was simply replaced with a 50–100 Ω /sq SWCNT layer applied directly to structures coated with different thicknesses of CdS. All devices made via this initial approach yielded efficiency of less than 5% due to

a lower fill factor (FF) and reduced open-circuit voltage (V_{oc}). However, we found that the device performance was strongly dependent on the CdS layer thickness. Specifically, an increase in CdS layer thickness was observed to mitigate some of the losses in V_{oc} and FF associated with eliminating the *i*-ZnO layer.

The data presented above underscores the importance and role of the *i*-ZnO layer when using SWCNTs and suggest that some sort of physical barrier layer that blocks pinholes to emulate the *i*-ZnO layer may be required between the SWCNT and the CdS to yield an efficient device. This barrier layer should be potentially solution-processible (for compatibility with the SWCNT processing), stable, highly transparent, electrically insulating, cost-effective, and readily available to be useful in CIGS devices. Poly (para-xylylene) (Parylene-N) is a highly insulating and optically transparent polymer that meets many of these criteria, and it was chosen to test the concept of a polymer barrier layer. We tested two solar cell layered structures with Parylene-N that can be described as:

- SWCNT/Parylene/CdS/CIGS/Mo and
- SWCNT/Parylene/thin-SWCNT/CdS/CIGS/Mo.

In the second structure, the thin SWCNT is a 1000 Ω/sq coating, which is shown to be exceptionally transparent. The Parylene-N layer thicknesses were varied between 100 and 200 nm in both structures. Devices fabricated with the first structure did not function, suggesting that a completely insulating barrier layer is not suitable for the devices. Devices made with the second structure were twice as efficient as the devices made with SWCNT deposited directly on CdS, but less efficient than the devices using *i*-ZnO as a barrier layer. This structure was not optimized with respect to sheet resistances or thicknesses of the constituent layers, and further improvements in device performance are expected for these structures.

Figure 39: J-V characteristics of solar cell test structures (a) 100 (Ω/sq) SWCNT/20-nm Parylene/540 (Ω/sq) SWCNT/CdS/CIGS; (b) 100 (Ω/sq) SWCNT/100-nm Parylene/1000 (Ω/sq) SWCNT/CdS/CIGS; (c) 100 (Ω/sq) SWCNT/*i*-ZnO/CdS/CIGS. Efficiency for (a) is <5%, (b) is ~8.4%, and (c) is the ~13%-efficient device from Table I shown for comparison.

Figure 39 shows J-V data for selected devices employing Parylene-N of different thickness sandwiched between two layers of SWCNT. The best device coming out of this combination had an efficiency of 8.4%, Voc of 0.676 V, Jsc of 23.9 mA/cm², and a FF of 45.48%, demonstrating the significant promise of this approach for replacing the ZnO bilayer. Parylene-N is expected to be many orders of magnitude⁹ more resistive than undoped ZnO,¹⁰ and the combined results from the structures described above suggest that some minimum electrical conductivity or a thickness below 100 nm is needed for the barrier layer.

4.3.2. Discussion

It is nontrivial to explain electrical transport in electronic junctions fabricated using SWCNT layers. The difficulty lies in that SWCNT networks are composed of a mixture of ~1/3 metallic and ~2/3 semiconducting nanotubes. The bandgap of pure semiconducting nanotubes is dependent on tube diameter and chirality. Hence, in an attempt to explain electrical transport on the device structures presented above, we propose a simplified band diagram for the layers involved (see Figure 5). In this band

diagram, band bending due to interface states are ignored and the following background data are applied: (i) SWCNTs have shown optical absorption¹¹ discontinuities and optical emission (photoluminescence) spectra¹² consistent with bandgap values in the range ~ 0.5 - 1.0 eV; (ii) To account for the various SWCNT bandgap values we represent in the figure the conduction and valence bands for the SWCNT as boxes; (iii) We assume a Fermi level shift of ~ 0.4 eV toward the valence band (E_V), in accordance with previous studies on acid doped SWCNTs;¹³ (iv) Metallic SWCNT are described as zero-gap semiconductors and their contribution is taken into account by superimposing a metallic density of states at the Fermi level, shown as parallel lines in the figure.

Figure 40: Proposed band diagram for SWCNT/*i*-ZnO/CdS/CIGS device structures. Semiconducting bands in SWCNT are denoted as s-CNT and metallic states by m-CNT.

A priori the conduction band alignment of the semiconducting SWCNT to the *i*-ZnO is not conducive to electron transport in such an interface, hence, it is our reasoning that the metallic SWCNT component dominates conductivity in these layers and they may play

an especially significant role in the devices reported here. Metallic states near the Fermi level would be accessible to electrons from the *i*-ZnO (or CdS or Parylene-N in the other device configurations) providing a plausible explanation for the current transport in these new device structures.

4.3.3. Conclusions

We have demonstrated that ZnO can be replaced with a combination of transparent SWCNT films and polymer layers. SWCNT transparent electrodes warrant further study in thin-film PV devices. It may be possible to increase the optical transmission while maintaining or improving conductivity in the SWCNT coatings by manipulating the tube diameter, length, and chirality. Improvements in network morphology, as well as chemical doping, may also be beneficial. Regardless of advances in the optoelectronic performance, the simplicity of the deposition process for SWCNTs and the potential low cost of the coatings may offset the losses in device efficiency. Manufacturing complexity is a significant challenge to commercializing CIGS thin-film PV technology. If SWCNT coatings could replace multiple layers of the device (*n*-ZnO:Al/*i*-ZnO/CdS), they would greatly enhance the manufacturability and reduce overall PV module cost. SWCNT transparent contacts could be immediately applicable in cell manufacturing processes employing solution growth techniques.

4.4. *Invisicon in CdTe PV structures with NREL*

Stacked or “tandem” PVs with different bandgaps are capable of utilizing a wider range of the solar spectrum than a single bandgap PV, and thus they are expected to have greater photoconversion efficiencies. As conceived, thin-film tandem devices consist of a wide band-gap top cell connected to a narrower band-gap bottom cell. The top and bottom cells may be grown monolithically or mechanically stacked, and they may be either current- or voltage- matched. Suitable pairs of materials for top and bottom cells depend on various aspects of device design. Potential candidates include: CdTe/Hg_xCd_{1-x}Te, CuGaSe₂/Cu(In,Ga)Se₂, Cd_xMg_{1-x}Te/Cu(In,Ga)Se₂, and other combinations of these materials. Although the inherently lower minority carrier lifetimes in thin-film solar cells limit their theoretical efficiency compared to single crystal devices, thin-film tandem devices consisting of current- or voltage- matched state-of-the-art single junction cells could realize up to 28% efficiency. This significantly exceeds the achievable efficiency with single junction devices.¹ One of the main challenges to producing a highly efficient thin-film tandem is developing a top-cell that is both efficient and highly transparent to sub-bandgap light. This requires a transparent back contact to the top cell, which has been difficult to achieve.

Traditional transparent conducting oxides (TCOs) are n-type, and therefore cannot make an ohmic contact to p-type CdTe. They are often used in conjunction with another material to form a composite back contact. Several combinations including p⁺-ZnTe:N/n⁺-ZnO:Al⁶ and thin p-Cu_xTe/n⁺-In₂O₃:Sn have been used successfully in transparent CdTe devices.⁷ Cu_xTe forms an effective back contact to CdTe, but it requires an ITO layer to reduce its sheet resistance when it is thin enough to be sufficiently transparent. While these contacts can be used to make efficient and

transparent devices, the TCO layers still contribute significant free carrier absorption losses in the top cell. $\text{In}_2\text{O}_3:\text{Sn}$ (ITO) and other TCOs exhibit free carrier absorption at wavelengths beyond approximately 800 nm, limiting their utility as transparent back contacts in tandem cells. However, a very high efficiency device (13.9%) that had a sub-bandgap transmittance of about 50% was produced using a composite Cu_xTe /ITO back contact.

SWCNT networks form a transparent contact (TC) that are fundamentally different from traditional TCOs. Device performance and fundamental characterization data show that the networks are preferentially hole conducting while most TCOs are strongly n-type. Free carrier absorption is not apparent in the networks until well beyond 2500 nm. These attributes, combined with our demonstrated success replacing $\text{ZnO}:\text{Al}$ with SWCNT networks in CIGS devices, suggests their potential suitability as interconnects in tandem thin-film PV devices.

CdTe solar cells are already well-developed and are readily produced in a configuration that is suitable for use in mechanically stacked tandems. The structure of the CdTe devices described here is shown in Figure 41.

Figure 41: CdTe top-cell for a mechanically stacked thin-film tandem. SWCNT networks are used as the transparent conductor layer in this work.

The CdTe devices were fabricated according to the procedure developed at NREL, with the exception of the transparent back contact. Briefly, a Cd_2SnO_4 TCO film was deposited onto Corning 7059 glass by rf sputtering. This was followed by sputter deposition of a thin buffer layer of ZnSnO_x and a thin nano-CdS:O film. Next, an approximately 5- μm CdTe film was deposited by close-spaced sublimation (CSS). The device was then treated thermally with CdCl_2 in air. Subsequently, the Cu_xTe back contact was prepared by a three-step process, which includes a CdTe surface etch, thin Cu film deposition, and a post-deposition heat treatment. Several Cu_xTe terminated devices were sent to Eikos, Inc. for deposition of the SWCNT network and protective polymer barrier layer. Metal contact grids were then applied, and the device properties were measured at NREL.

The SWCNT networks used in this work are made from Invisicon[®] ink. Invisicon[®] ink, produced by EIKOS, Inc., is a dispersion of SWCNT applied by numerous methods that self assembles into a networked transparent conductive coating. First, arc-produced SWCNTs are purified by acid reflux, washing, and centrifugation to remove metal catalyst particles and non-tubular carbon.

The purified SWCNTs are dispersed in water and alcohol to form an ink that was spray coated onto heated microscope glass or quartz substrates. This process formed an essentially pure SWCNT coating.

The morphology of these coatings can be described as a randomly distributed network of SWCNT bundles with a high density of void space. The SWCNT coated devices were also dip-coated in a thin conductive polymer in order to protect the SWCNT network during device processing. The SWCNT networks used in this study had nominal sheet resistances 50 or 100 Ω /sq.

Optical transmission and reflection of both the transparent contacts and the devices was measured using a Cary 5G UV-VIS-NIR spectrophotometer between 300 and 1500 nm, which extends beyond the required transparency range for an effective tandem cell. Figure 42 compares the optical transmission of a thin film of ITO with that of 50 and 100 Ω /sq SWCNT networks with the polymer barrier in the visible and near-IR. The ITO was sputter deposited at room temperature.

The SWCNT networks clearly have flatter transmission profiles and significantly lower reflectance compared with ITO, but the 50 Ω /sq SWCNT network has slightly lower transmittance in the visible than the ITO film. However, free-carrier absorption begins to appear in the ITO transmission spectrum around 800 nm, while it remains completely absent in the SWCNT networks.

Figure 42: Reflection and transmission spectra for ITO and two SWCNT networks with different sheet resistances. Both the 50 and 100 W/Sq SWCNT networks were incorporated into transparent CdTe cells successfully.

Figure 42 suggests that incorporating a 100 Ω /sq SWCNT network into the transparent top-cell could result in lower optical losses compared with a device using ITO. Additionally, the SWCNT networks are hole conducting and should form a more ohmic contact to Cu_xTe than ITO. Ohmic contact between a SWNCT network and Cu_xTe was confirmed with a current density vs. voltage (J-V) measurement.

Device efficiency measurements were performed under the standard conditions of 25°C and 100 mW/cm^2 intensity using the AM 1.5 spectrum in an Oriel, Inc. solar simulator. Figure 3a shows the J-V curve for the best transparent device using the SWCNT network in the back contact. This device was made with the 100 Ω /sq SWCNT network, which had an efficiency of 12.4%. Another identical device showed slightly lower efficiency (12.2%) and transmission. Table 23 contains the device parameters for both devices incorporating SWCNT networks and literature data for transparent CdTe devices.

Table 23: Device parameters for transparent CdTe devices. The first two devices use Cu_xTe/SWCNT networks as back contacts, and the third is identical except that ITO is used instead of SWCNT. The fourth device uses a different fabrication procedure and back contact.

Back Contact	J _{sc} (mA/cm ²)	V _{oc} (V)	FF(%)	η (%)
Cu _x Te / 100 Ω/sq SWCNT	21.93	820.2	67.87	12.2
Cu _x Te / 100 Ω/sq SWCNT	22.25	818.1	68.18	12.4
Cu _x Te / ITO	24.97	806.1	69.22	13.9
ZnTe:N / ZnO:Al	22	643	65.1	9.1

The SWCNT network device efficiencies are nominally lower than the devices described by others, and the reason for this is not immediately clear. The SWCNT devices have a higher V_{oc} while J_{sc} and FF are reduced compared with the ITO device. This efficiency is still quite promising for a new device structure, and it also demonstrates that a hole-conducting transparent material can function well as a contact to CdTe/Cu_xTe. The increased V_{oc} in the device incorporating SWCNT network contacts may also be notable, but it must be reproducible over a much larger set of devices than were used here. If the effect is real, it could be due to a number of factors including an effect seen with different back contact metallizations or reduced contact area.

Figure 43: (left) J-V curve for CdTe device with CuxTe/SWCNT back contact. The SWCNT had a sheet resistance of 100 Ω/sq and the contact included a polymer barrier layer. (right) Transmission, reflection, and absorption for the 12.4% efficient device.

The optical transmission, reflection, and absorption spectra for the 12.4% SWCNT device are presented in Figure 43. The transmission of the device is above 40% between 800

and 1500 nm with a peak transmission close to 50% near 900 nm. This is quite high for a device with efficiency greater than 12%. Previous work shows that careful engineering of the backside of the device is required to reduce the total reflectance. A well-matched rear surface anti-reflective coating could increase the transmission as much as 10% if it can be designed to match the SWCNT network.

A comparison of figures suggests that the SWCNT network does not contribute significant optical losses to the device. Absorption decreases as a function of increasing wavelength, whereas a TCO would cause absorption to increase as a function of wavelength due to free carrier effects. This could be a critical reduction in top-cell absorption for mechanically stacked thin-film tandems. Sub-bandgap transmission from the top-cell needs to approach 70% in order to achieve the target efficiency of 25%,¹ and SWCNT back contacts could help achieve that goal.

We have demonstrated the use of SWCNT networks as an effective component of the back contact to a transparent CdTe top cell. We believe that cell efficiencies and optical transmission should increase dramatically as the cell structure and processing are optimized. Work continues in this area to develop and understand highly efficient and transparent CdTe devices using SWCNT networks.

4.5. Commercial Activities

Eikos has engaged with many commercial solar companies under the DOE program. Most companies where we have moved into substantive discussions require that we maintain confidentiality about our involvement. In other programs, Eikos has teamed with Boeing-Spectrolab and Ascent Solar. These activities are an important part of this program, and Eikos will publicly announce any major collaboration with solar companies to ensure that we disseminate our work broadly.

4.6. Conclusions

Eikos has demonstrated that Invisicon® is an excellent substitute for ITO, Al:ZnO, and other transparent conductive oxides in PVs. When considering the manufacturing and cost benefits of a CNT electrode over vacuum deposited oxides, CNTs offer many advantages with similar performance. It should be noted that *none of these devices were fully optimized*. Many of these technologies have been researched for decades to reach current performance levels, and our rapid demonstration of feasibility with moderate to high performance is a sign that CNT electrodes are close to commercial viability. Our processing fits in well with the trend of amorphous silicon, CIGS, and polymer solar cell manufacturers moving away from vacuum processing of active layers towards printing particulate or polymer inks.

5. Invisicon® Application Methods

One of the main purposes of this broad in scope research is to enhance optoelectronic (R/T) performance of Invisicon® coatings, thus making them suitable as transparent conductors for photo-voltaic applications. As flexible, roll-to-roll based low cost PV development is building momentum, materials supporting such technology platforms are needed. Invisicon® is a flexible materials technology rendering it suitable both for devices built using rigid and flexible substrates.

We report progress made in understanding the role of surface energy for achieving uniformly spread coating and the development of high concentration inks with various solvent systems. All this is considered as a necessary path for stable, higher concentration (absorbance) CNT inks compatible with roll-to-roll based materials and process methods specifically for flexible photo-voltaic applications.

5.1. *High Concentration CNT Inks for Coating PET*

During a coating process, air on a given substrate surface is replaced by a liquid coating material. This material needs to have the ability to wet and spread over the substrate surface during coating. It also has to retain its uniformity without curling (beading) during the drying process. Surface properties of the liquid and the substrate determine the wetting and spreading characteristics. More specifically, for spreading to occur, the following condition has to be satisfied:

$$\gamma_{\text{gas-solid}} - (\gamma_{\text{liquid-solid}} + \gamma_{\text{gas-liquid}}) > 0, \quad \gamma = \text{surface tension} \quad (1)$$

If the substrate and coating formulation selected do not satisfy equation (1), coating does not spread. If the coating spreads during the application but the coating composition changes due to drying, the coating may also curl or bead up causing non-uniformity.

As an example, surface energies for IPA and water, at room temperature, are 21 and 72 dyne/cm respectively. When the CNT inks based on certain IPA/water ratios is applied onto a cleaned glass substrate, it spreads evenly without curling. Contrarily, when the same material is applied to a low energy surface such as PET ($\gamma = 44 \text{ erg/cm}^2$), the coating may initially spread satisfactorily. During the drying process, IPA evaporates at a higher rate than water leading to drastic changes in IPA to water ratio. This in turn leads to changes in surface tension of the coating material as water becomes predominant liquid phase. As equation (1) condition is no longer met, liquid begins to crawl (bead) creating isolated water/CNT droplets on substrate surface. Such morphology is characterized with poor uniformity, connectivity and thus low conductivity. Incorporation of surfactants or high boiling point, low surface tension components to the coating may prevent this effect. Notoriously speaking many such materials often impair R/T performance of the CNT based coatings. In this study we report that certain CNT grades can have the same effect as surfactant that prevent liquid crawl (beading) during the coating drying process.

5.1.1. Experimental Test Matrix

Different CNT ink grades and concentrations were applied (41 μm) with #16 Meyer Rod onto PET substrates, Melinex ST505 with adhesion promoter and onto uncoated bare PET and dried under ambient conditions. The drying behavior (beading, spreading) as a function of ink grade, CNT concentration and substrate type was evaluated (Table 8). As controls carrier solvent and its respective components were employed.

Table 24: Influence of Ink Grade and Concentration on Coating Uniformity

Ink Grade, %T	Ink Conc., a.u.	Wetting on ST 505	Wetting on Bare PET
<i>Controls</i>			
Water	0	Beading	Beading
IPA	0	Wetting	Wetting
IPA/water	0	Beading	Beading
<i>Inks</i>			
88.0	3.70	Wetting	Beading
89.0	1.37	Wetting	Beading
92.1	3.80	Wetting	Beading
93.6	5.80	Wetting	Wetting
93.0.	2.90	Wetting	Beading
93.6	1.10	Wetting	Beading
94.7	2.47	Wetting	Wetting
94.7	1.47	Wetting	Wetting
94.7	1.00	Wetting	Wetting
94.7	0.53	Wetting	Beading
94.7	0.26	Wetting	Beading
95.2	0.57	Wetting	Beading

Very low contact angle's nearing zero was measured with test conditions that exhibited uniform wetting and spreading. De-wetting or beading appeared to start from substrate edges moving towards the center leaving behind discrete droplets with high CNT concentration.

Observations and Discussions

As can be readily observed, water is a poor liquid medium for CNT inks as it does not spread either on ST505 or untreated PET. All IPA-containing coatings spread well on both substrates. This is attributed to the lower surface tension of the IPA satisfying equation (1) conditions. With IPA/water compositions, as the ratio of IPA to water decreases due to higher evaporation rate of IPA than water, the surface tension of the coating increases, again, leading to beading and poor wetting. This trend however is favorably influenced by the presence of purified CNT enabling the processing and fabrication of uniform carbon based transparent coatings.

As expected, IPA/water control material beaded readily during drying on both substrates. As CNT became the third component in the same solvent mixture, it wetted well onto ST 505 and in certain cases with untreated PET. In other words, CNT in the solvent has similar effect as a surfactant preventing beading during drying without impairing R/T performance like surfactants do. It can thus be concluded that higher performance CNT ink (expressed by %T) and higher concentration (expressed by a.u.), the more effective is the suspension at preventing beading during CNT ink coating and drying processes.

Several possible mechanisms for the wetting and spreading of water/IPA based nanotube dispersions are proposed.

1. Nanotubes may have adsorbed to low surface energy substrate with a degree of orientation and changed surface energy of the substrate. During drying, the receding liquid phase has a dramatically lowered contract angle on the “covered” or modified substrate surface leading to favorable surface energies.
2. CNT may alter the surface tension of the liquid phase. Measurement of the surface tension of the CNT suspension may confirm this hypothesis.
3. Given that CNT depresses freezing point of certain solvent systems, it is likely that the azeotrope of the suspension is also shifted. During drying, the IPA/water ratio is fixed at the new azeotrope composition, which gives a low overall surface tension. This hypothesis may be tested by measuring the solvent density during the different drying stages. Preliminary density measurements of a CNT ink evaporated at room temperature demonstrated that density was practically unchanged.

Utilization of secondary surface treatment methods such as corona or plasma methods to enhance CNT ink wetting on difficult to coat surfaces such as PET, it now has been demonstrated that certain CNT compositions as such provide intrinsic wetting characteristics. Certain PET substrates such as ST505 have a pretreatment layer that facilitates the wetting of aqueous coatings. This is evident in our experiment as no beading on pre-treated PET test coupons was observed. This treatment layer however adversely affects RT performance of the CNT coating, and thus is undesirable.

5.2. Approaches to High Concentration CNT Inks

One way roll-to-roll coating method differs from spray-coating, proven method to deposit CNT inks uniformly onto substrate, is the requirement for wet coating thickness. Slot-die based methods typically employ wet coating thicknesses from micron to tens of microns. Knowing that requirement, CNT based inks need to be formulated for higher weight loadings in order to maximize throughput and thus optoelectronic performance.

High absorbance ink can be manufactured by simply adding more CNT into the carrier vehicle. Past experiments however, demonstrate that this approach lead to lower yield and degraded ink quality. At elevated concentrations, high purity carbon nanotubes have

increased tendency to flocculate out of solution than lower grade materials. All this leads to poor optoelectronic performance.

Alternative method to producing higher concentration inks is through evaporation. In this case, low concentration CNT ink was evaporated till higher CNT concentration was achieved.

5.2.1. High Concentration through Evaporation

Carbon nanotube inks with absorbance of 1, 2 and 3 were made and left at room temperature to evaporate. Thus produced inks with different concentration (absorbance) were then employed to fabricate CNT coatings onto glass and unmodified, bare PET substrates. As controls, coatings produced from materials that were not evaporated were included in the study. Results from this study are listed in **Table 25**. All coatings were fabricated using a simple Meyer rod approach. In the table, “Target Abs” represents the calculated ink concentration. Ink absorbance after evaporation in the table is represented as “Eva-Abs” represents absorbance after solvent evaporation measured by spectrophotometer. CNT ink composition employed was Eikos proprietary representing a medium grade material.

Table 25: CNT Ink Performance Comparison

Orig. (Target Abs.)	Abs.	Eva- Abs.	Rs, $\Omega/\square$	Rs, $\Omega/\square$	Rs, $\Omega/\square$	Rs, $\Omega/\square$
<i>Substrate:</i>			<i>Glass</i>	<i>Glass</i>	<i>PET</i>	<i>PET</i>
<i>Wet Film Thickness:</i>			<i>40 μ</i>	<i>70 μm</i>	<i>40 μm</i>	<i>70 μm</i>
A. Ink Performance Without Evaporation						
1.47	(1.67)	na	6,680	--	15,640	--
2.06	(1.98)	na	1,951	--	Curling	--
3.06	(4.00)	na	1,551	--	2,671	--
2.47	(2.00)	na	1,800	840	3,000	1,337
3.02	(3.00)	na	--	607	--	1,173
B. Ink Performance After Evaporation						
0.99	(1.00)	1.30	10,610	--	--	--
0.99	(1.00)	2.68	5,665	--	--	--
2.36	(2.00)	3.39	1,276	476	--	738
3.02	(3.00)	3.68	--	455	--	1,049
C. Ink Performance with Additive, No Evaporation						
1.99	(2.00)	na	2,032	--	--	--
4.77	(8.00)	na	740	--	--	--
5.68	(8.00)	na	650	360	--	--

As CNT concentration in the carrier solvent increases, surface resistance (R_s) decreases with both substrates and wet film thicknesses. This trend is evident across all three material sets studied specifically on glass substrate. Low resistance CNT coatings can also be achieved with additives (Test Set C) but only with the use of highly concentrated CNT inks (Abs 8). Use of such materials results to unnecessary loss of purified CNT tubes and thus is not considered practical.

5.2.2. Experimental Discussions and Conclusions

The evaporation approach to making CNT inks enables fabrication of higher concentration inks with high overall quality and stability. An added benefit was the observed improvement in ink yield over standard fabrication method. Standard CNT inks are typically fabricated with a target absorbance of 1. Such inks exhibit desirable process related stability but build conductivity slowly requiring multiple coating runs and/or multiple coating heads. As absorbance approaches 2.7 through evaporation, it becomes unstable evidenced by CNT flocculating out of solution phase thus rendering it unsuitable. As initial absorbance is 2 or 3, approaching 3.4 and 3.8 via evaporation respectively, such concentrated inks remain stable. These materials are ideal for slot-die coating applications building surface conductivity efficiently though performance was only demonstrated on glass substrate. Lower surface resistance coatings can also be achieved by employing heavier wet coating thicknesses (40 vs. 70 μ m).

6. CNT Environmental Performance

A majority of photovoltaic devices are exposed to the elements for their entire useful life. Environmental stability is a critical factor when designing solar cells, as it directly impacts lifetime of the cell, in turn impacting the bottom line price per kilowatt hour. Carbon nanotube coatings can have a change in resistivity caused by their environment; a term Eikos has labeled R_s drift. The change in resistivity changes the properties of the transparent conductive coating in the solar cell in which they are an electrode. Increased resistivity changes the overall resistance (and thus power) of the solar cell, lowering its efficiency.

During its commercial investigations, Eikos found that a generally acceptable levels of R_s drift within the transparent electrode is approximately 20% across environmental test conditions. When R_s drift testing was begun at the start of this work, this requirement was not met. However, as a result of a series of tests and work with treatments, binders, and application techniques, Eikos Invisicon[®] R_s drift now satisfies the requirement. This section summarizes the tests that have been performed, knowledge gained in R_s drift mechanisms, and the conditions under which Invisicon[®] will be used in solar cells to satisfy their manufacturing requirements.

6.1. *Determination of Cause of Environmental Instability*

When work began on the R_s drift task, Eikos sought to first explain its sources and then to remove their effects. After researching past experiments, collating observations, and collectively brainstorming, Eikos produced a fishbone chart, Figure 44. It lists the causes of R_s drift and weights each cause line according to the perceived level of influence. R_s drift is fundamentally caused by environment conditions, with several other factors coming into play.

Figure 44: R_s Drift Ishikawa Fishbone Diagram

6.1.1. Outline a Series of R_s Drift Experiments

Next, a series of R_s drift tests were created to characterize and improve R_s drift caused by environmental instability. This test series examined the most important root causes in the Ishikawa Fishbone, and is listed in Table 26.

Table 26: Rs Drift Experiments

Test	Purpose
R _s Drift Test 1: UV Minimizing	Minimize the effects of UV damage
R _s Drift Test 2: Test Measurement Effects	Determine Effectiveness of test procedures and measurements
R _s Drift Test 3A: UV and Oxygen connection	Understanding Rs Drift caused by ultraviolet in the presence of oxygen
R _s Drift Test 3B: UV and Oxygen connection	
R _s Drift Test 3C: UV and Oxygen connection	
R _s Drift Test 3D: UV and Oxygen connection	UV exposure additives
R _s Drift Test 4: Substrate Test	Understand effect material substrate has on Rs Drift
R _s Drift Test 5: CNT Network Test 1	Test variations across different % concentrations, film thicknesses, ink grades, Initial Rs, and morphology from different application conditions
R _s Drift Test 6: Heat Treatment Test	Characterize the minimization effect of Rs Drift from heat treatments.
R _s Drift Test 7:Environment Effect Process Cube Test	Subject samples to extremes of the environment heat, UV light, and humidity
R _s Drift Test 7:Durability Test	Examine Rs Drift caused by mechanical damage to the samples
R _s Drift Test 8: CNT Network Test 2	Characterize Rs drift effects from nanotube type: metallic or semi-metallic.
R _s Drift Test 9: Binder Test	Test a matrix of binding materials so as to find the best one to increase environmental stability
Rs Drift Series 10: CNT Network Anneal Test	Determine the effect of different morphologies on Rs drift
Rs Drift Series 11+: Future Tests	As needed

6.1.2. Rs Drift Test 1: Minimizing the UV Drift

The purpose of this test was to characterize resistance drift due to sunlight. Eikos Invisicon® ink was sprayed onto PET Film with a Polyester binder. These films were tested with three different light sources, with varying emission spectra, and three different filter film materials, with varying wavelength cut-offs, to determine over which wavelengths resistance damage is occurring.

The majority of the radiant energy related damage is caused within the UVA region. Polycarbonate effectively eliminates wavelengths below 400 nm, but not above. A degree of damage to the CNT layer is observed, as demonstrated by increase in surface resistance within the visible spectrum region. Kapton as a filter, effectively eliminated wavelengths up to 540 nm, beyond which CNT films were found to exhibit no appreciable change in surface resistance and R_s drift. Based on these findings, the

influence of UV-light on CNT coatings can be controlled if not eliminated by the use of appropriate filter materials.

6.1.3. R_s Drift Test 2: Testing Measurement Validity

The purpose of this test is to determine the validity of the procedure and measurement technique used for the R_s drift series of experiments. Electrodes, sample handling, sample size, and repeatability are examined.

Repeatability testing showed that R_s drift differences $<5\%$ (of the total R_s drift) between two samples or values cannot conclusively said to be differentiating enough to draw conclusions. Given this, samples size does not effect R_s drift measurements. Rough handling produces a negligible difference in R_s drift. Gold electrodes do produce different, more attenuated R_s drift changes than silver electrodes.

6.1.4. R_s Drift Test 3A: UV and Oxygen

The purpose of this test was to determine if oxygen is a cause for resistance drift when Invisicon® films are exposed to UV light. Some literature on carbon nanotubes notes that when carbon nanotubes are exposed to UV light in the presence of oxygen, their resistance increases. Eikos conducted this test to evaluate this hypothesis.

The data showed that R_s change versus time in the presence of UV has a sharp transient slope, followed by a lower steady-state slope. If oxygen in the presence of UV causes damage, it is possible that existing oxygen local to the carbon nanotubes causes the large initial R_s change, followed by a smaller R_s change from steady state atmospheric adsorption of oxygen from the environment. To examine these effects, oxygen was desorbed from the carbon nanotubes before, during, or both beforehand and during UV exposure. The method for oxygen desorbing was via low pressure vacuum with argon purge, in the presence of heat to assist in desorbing the oxygen. It was shown that the initial hypothesis – that at least partial oxygen desorption would consistently lower R_s Drift during UV exposure – was proved false.

6.1.5. R_s Drift Test 3B: UV and Oxygen, Cont'd

Experiment 3A produced unexpected results; samples exposed to UV light under argon purge exhibited worse R_s drift than when under air purge. The purpose of this experiment was to help understand the increase in resistance due to the exposure of argon by individually ruling out the possible causes: argon plasma, argon in the presence of heat, and the argon gas itself.

We concluded that it is not likely that argon plasma is forming under UV and causing R_s drift. This test showed argon at 50°C changed R_s very little. Thus, argon and heat alone do not cause the increased R_s drift. Test 3B allowed us to conclude that as nitrogen purge under UV had the same drastic R_s drift; it is not likely that the argon is causing the change. A de-doping of either oxygen or water molecules was determined to be the leading culprit for the large R_s drift. As argon and a 50°C environment alone do not

cause the Drift without the presence of UV, it would seem UV light has the energies to desorb these molecules.

6.1.6. R_s Drift Test 3C: UV and Oxygen, Cont'd

The purpose of this study was to separate doping effects of oxygen and of water on R_s drift under UV exposure. Previous experiments revealed that in the presence of UV, displacing the contents of air with exclusively nitrogen or argon accelerated R_s drift. As the composition of dry air is mostly (99.99%) nitrogen, oxygen, argon, and carbon dioxide, it is possible that the displacement of either oxygen or water molecules, the moist component of air, causes the change of R_s drift. These variables can be individually examined using dry air, which contains oxygen but little water, and moist nitrogen, which contains water but little molecular oxygen. Test 3C separates these two variables for study.

Dry air exhibited slightly worse R_s drift than moist air under UV exposure. It is reasonable to conclude that water provides some doping for carbon nanotubes, lowering R_s drift under UV. However, the full difference measured in previous tests cannot be accounted for by moist air, water doped nanotubes, alone. In testing with nitrogen to replace air, the presence of water molecules lessens the change in R_s Drift. However, over 1080 minutes even moist nitrogen exhibits much larger R_s Drift than dry air, and certainly of moist air. Thus, oxygen is a large component of the R_s Drift under UV. However, it would appear that its absence harms R_s . This would be the case where oxygen is in fact doping the carbon nanotubes and assisting with conduction. These experiments reveal that this is likely the case that oxygen is doping the semiconducting carbon nanotubes, and increasing their conduction. It has been noted that there is a “recovery” effect, where removing the CNT sample from the UV source causes the sheet resistance to decrease, though not back to its original value.

6.1.7. R_s Drift Test 4: UV and Oxygen, Cont'd

The purpose of this experiment was to determine if additives can be used to mitigate R_s drift. Many materials are affected, often detrimentally, by ultraviolet (UV) wavelength light. Anti-Oxidants and UV Absorbers are commonly used additives to attenuate the impact of damaging UV energies. Test 3D is a subset of the Invisicon® UV tests to assess whether these additives benefit our material by mitigating changes in R_s .

The results reveal that both additives cause an increase in R_s drift in the presence of UV. This is opposite of their intended effect, if in fact it were true that oxygen in the presence of UV causes damage to carbon nanotube coatings. The results instead lend support to the hypothesis that oxygen doping is helping our conductance. By adding an anti-oxidant, we reduce oxygen doping. Additives that bind up oxygen will reduce this helpful doping and cause an increase in resistivity. This test suggests that UV absorbers and anti-oxidants are not the cure for the UV effect that produces R_s drift.

6.1.8. R_s Drift Test 4: Substrate test

Test number 4, the substrate test, was included in test #6 for heat treatment and testing. During test number 6, both glass and PET substrates were used, and a long test was performed. Please see that section for more information regarding the effect of substrate on R_s drift.

6.1.9. R_s Drift Test 5: CNT Network Test 1

The purpose of this test was to determine if initial “ink grade” and sheet resistance correlate to the R_s drift observed from UV and heat. Eikos has three different ink grades A, A+, and A++, and can easily tailor sheet resistance across resistivities from 10 ohm/sq to 10 megaohm/sq. For this test, all ink grades were used, and initial R_s was varied between 50 ohm/sq and 10,000 ohm/sq, a sufficiently broad range to determine trends in data results. Table 27 shows the full test matrix performed, and demonstrates the variation in initial R_s and ink grade.

Table 27: Test matrix showing variation across initial R_s and ink grade.

	A++	A+	A	Full test matrix
50				
100				
500				
1000				
10000				
	A++	A+	A	Varying initial R_s
50				
100				
500				
1000				
10000				
	A++	A+	A	Varying Ink Grade
50				
100				
500				
1000				
10000				

The results are shown in absolute values in Table 28 and by percentage change in Table 29. Looking at

Table 30, control samples, left in ambient conditions at approximately 20°C and fluorescent room lighting, we see that little change occurs to the sheet resistance. This is true for all ink grades and all initial conditions for sheet resistance. Table 29 shows the data from the UV test, in terms of percent change in sheet resistance, organized by ink grade. The trend is easily seen that, for higher initial sheet resistances, there is higher R_s drift. However, in Figure 46, percent change from 24 hours of heat exposure, this trend is

less apparent. It is likely then that the mechanism for R_s drift is different for UV than for heat.

Table 28: Resistance for UV, Heat, and Control samples over 24 hours.

		Data Average				
Control		Control	Test 1	Ohms/Square		
		Start	1 hour	2 hour	3 hour	24 Hours
	A++	690	690	690	690	690
	A++	25963	26010	26010	26043	26013
	A++	4163	4163	4163	4170	4170
	A++	2091	2092	2092	2097	2095
	A+	1307	1321	1321	1321	1320
	A+	26620	26617	26617	26683	26653
	A+	507	507	507	508	506
	A+	261	262	262	263	265
	A+	101	101	101	101	100
	A+	51	51	51	51	50
	A	1552	1554	1554	1557	1553
	A	42367	42500	42500	42633	42467
	A	702	703	703	704	702
UV		UV	Test 1	Ohms/Square		
		Start	1 hour	2 hour	3 hour	24 Hours
	A++	599	712	745	763	961
	A++	26147	33630	35700	36950	52300
	A++	4142	5103	5370	5543	7540
	A++	2019	2434	2553	2628	3550
	A+	1309	1582	1660	1705	2147
	A+	27220	37207	39083	40337	50167
	A+	450	539	563	577	722
	A+	2751	3223	3361	3900	4903
	A+	112	127	131	132	164
	A+	61	69	71	71	85
	A	1053	1393	1481	1534	1875
	A	37757	55970	60767	63100	78733
	A	625	801	844	871	1049
Heat		HEAT	Test 1	Ohms/Square		
		Start	1 hour	2 hour	3 hour	24 Hours
	A++	605	761	805	835	1021
	A++	29380	33507	35433	37357	50467
	A++	3850	4524	4792	5014	6500
	A++	1933	2370	2510	2622	3343
	A+	1259	1553	1636	1691	2127
	A+	25813	33107	34680	36407	46967
	A+	425	525	550	566	696
	A+	302	363	379	389	467
	A+	102	121	126	129	155
	A+	57	66	69	71	82
	A	999	1189	1229	1262	1467
	A	34950	40767	42533	44173	53833
	A	590	696	715	732	833

Table 29: Percent change in resistance for UV, Heat, and Control over 24 hours.

Percent						
Control	Control	Test 1	Ohms/Square			
	Start	1 hour	2 hour	3 hour	24 Hours	
	A++	690	0.0%	0.0%	0.0%	0.0%
	A++	2091	0.0%	0.0%	0.3%	0.2%
	A++	4163	0.0%	0.0%	0.2%	0.2%
	A++	25963	0.2%	0.2%	0.3%	0.2%
	A+	51	-0.1%	-0.1%	0.0%	-1.0%
	A+	101	0.1%	0.1%	0.1%	-0.6%
	A+	507	0.1%	0.1%	0.2%	-0.1%
	A+	1307	1.1%	1.1%	1.1%	1.0%
	A+	26620	0.0%	0.0%	0.2%	0.1%
	A	702	0.2%	0.2%	0.4%	0.1%
	A	1552	0.2%	0.2%	0.3%	0.1%
	A	42367	0.3%	0.3%	0.6%	0.2%
UV	UV	Test 1	Ohms/Square			
	Start	1 hour	2 hour	3 hour	24 Hours	
	A++	599	18.8%	24.4%	27.3%	60.5%
	A++	2019	20.6%	26.5%	30.2%	75.8%
	A++	4142	23.2%	29.7%	33.8%	82.1%
	A++	26147	28.6%	36.5%	41.3%	100.0%
	A+	61	13.4%	16.2%	17.3%	39.9%
	A+	112	13.8%	16.9%	18.7%	46.6%
	A+	450	19.7%	25.1%	28.2%	60.4%
	A+	1309	20.9%	26.8%	30.3%	64.0%
	A+	2751	17.1%	21.9%	35.4%	69.0%
	A+	27220	36.8%	43.7%	48.3%	84.2%
	A	625	28.3%	35.1%	39.4%	67.9%
	A	1053	32.3%	40.7%	45.7%	78.1%
	A	37757	48.2%	60.9%	67.1%	108.4%
Heat	HEAT	Test 1	Ohms/Square			
	Start	1 hour	2 hour	3 hour	24 Hours	
	A++	605	25.6%	32.8%	37.8%	68.6%
	A++	1933	22.4%	29.5%	35.3%	72.8%
	A++	3850	17.4%	24.3%	30.0%	68.8%
	A++	29380	14.1%	20.6%	27.1%	71.9%
	A+	57	16.5%	20.9%	23.9%	44.7%
	A+	102	18.4%	23.3%	26.6%	52.0%
	A+	302	20.2%	25.5%	28.7%	54.8%
	A+	425	23.5%	29.4%	33.1%	63.7%
	A+	1259	23.2%	29.7%	34.1%	68.7%
	A+	25813	28.3%	34.4%	41.1%	81.9%
	A	590	18.0%	21.2%	24.0%	41.1%
	A	999	18.9%	22.9%	26.2%	46.7%
	A	34950	16.5%	21.6%	26.2%	54.0%

Table 30: Control samples %Rs change, left to ambient conditions, after 24 hours.

	Control	Test 1			
	Start	1 hour	2 hour	3 hour	24 Hours
Control	A++	690	0.0%	0.0%	0.0%
	A++	2091	0.0%	0.0%	0.3%
	A++	4163	0.0%	0.0%	0.2%
	A++	25963	0.2%	0.2%	0.3%
Control	A+	51	-0.1%	-0.1%	0.0%
	A+	101	0.1%	0.1%	0.1%
	A+	507	0.1%	0.1%	0.2%
	A+	1307	1.1%	1.1%	1.1%
	A+	26620	0.0%	0.0%	0.2%
Control	A	702	0.2%	0.2%	0.4%
	A	1552	0.2%	0.2%	0.3%
	A	42367	0.3%	0.3%	0.6%

Figure 45: Rs percent change results after 24 hours UV light exposure, examining the effects of initial sheet resistance.

Figure 46: R_s percent change results after 24 hours Heat exposure, examining the effects of initial sheet resistance.

Next the results were examined from the perspective of ink grade. Figure 47 and Figure 48 show the same data grouped into “bands” of initial sheet resistance. Four groups, a low resistivity around 50-100 ohm/sq, a second band at 500 ohm/sq, a third at 1000-5000 ohm/sq, and a fourth at 10,000 ohm/sq and greater, are shown. Thus, we can remove the variable of initial sheet resistance, and examine the effect of ink grade on R_s drift caused from heat and UV light exposure. When the sheet resistance variation, there appears to be no discernable correlation of R_s drift to ink grade for UV exposure. Heat exposure data, shown in Figure 48 tells a somewhat different story; there is less R_s drift for lower grades of ink. Again, the data results lead us to conclude that UV and heat R_s drift are caused from different mechanisms.

The test explained much about the effect that UV and heat have on R_s drift. We have determined that, at least in one facet, they are explained and controlled by different mechanisms. For both mechanisms, a higher initial resistivity correlates to a higher R_s drift, especially under UV. Meanwhile, R_s drift caused by UV is not correlated to ink grade, while that caused by heat shows that there is lower R_s drift for lower ink grades.

Figure 47: Rs percent change results after 24 hours UV light exposure, examining the effects of ink grade.

Figure 48: Rs percent change results after 24 hours Heat light exposure.

6.1.10. Rs Drift Test 6: Heat Treatment Test

R_s drift Test 6 was an exhaustive testing on the influence of substrate, heat treatment, and binder on the R_s drift caused by heat and UV conditions. The test in large part concerns the use of a heat treatment step to “anneal” the Invisicon[®] material, and to examine effects of heat and UV given varying heat treatments and use of Binder Alpha. Figure 49 and Figure 50 provide an overview of the test sample conditions and test sample preparation, respectively. This test seeks to answer the following questions:

- How much R_s change occurs from heat treatment?
- How does heat treatment affect R_s Drift:
 - In high temperature environments?
 - When exposed to UV light?
- How do variations in the heat treatment temperature and time affect R_s Drift?
- Does Binder Alpha provide R_s Drift control in both UV AND heat conditions?
- Does the substrate used affect any of the above observations?

└ Test Condition: Heat, UV

- Binder Alpha / No Binder Alpha

- Substrate: Glass and PET

- Heat Treatment

- Time
- Temperature

- Test Condition

- Heat (85°C)
- UV

- Controls

Time (min) \ Temp °C	20	60	180	360
85
100
125
150

Figure 49: Overview of Test Conditions.

■ Binder Alpha / No Binder Alpha x2		■ Samples are 1" x 1"	
■ Substrate: Glass and PET x2		○ Silver Paint Leads	
■ Heat Treatment		○ A++ Ink	
○ Time	x4	○ Prepared on ASC	
○ Temperature	x4	○ 500 ohm/sq (glass samples)	
■ Test Condition x3		○ 300 ohm/sq (PET samples)	
○ Heat (85°C)	(2)	○ No binder	
○ UV	(1)	○ Binder Alpha, 1% where used	
■ Plus controls		■ Sampling done at:	
		○ 1 hr	
		○ 3 hrs	
		○ 1 day	
		○ 3 days	
		○ 1 week	
		○ 2 weeks	
		○ Etc.	

Total = 2 x 2 x 4 x 4 x 3 = 192 + 8 controls = 200 samples

Figure 50: Overview of Test Samples Preparation.

First, we examined the results from the heat treatment testing. A heat treatment anneal sacrifices some R_s drift during sample manufacture, in order to provide for minimized R_s drift during the lifetime of a particular product. Eikos must quantify the changes that occur during the heat treatment. The goal was to meet photovoltaic specifications.

The heat treatment testing produced data on the effect that varying temperatures and duration of exposure have on glass and PET substrates. Observations from this data are summarized as follows:

- PET has less change than Glass
- Binder Alpha attenuates change
- Higher temps and longer exposure times produce greater change
- After performing a large matrix of heat treatments to the samples, they were exposed to heat and UV to simulate the environmental effects of a photovoltaic application. Here are the observations on the results:
- For heat exposure on glass and PET, with and without binder alpha:
- Binder Alpha attenuates change
- Longer heat treatment times give lower R_s change
- Higher heat treatment temps give lower R_s change
- The drift fluctuates with time, going not only up, but also down. This appears to be the result of an additional environmental effect.
- This behavior was common across all heat test samples.

- For UV exposure of CNT on glass and PET, with and without binder alpha:
- Longer exposure gives larger Rs Drift
- **Binder Alpha attenuates change**
- **Longer heat treatment times give lower Rs change**
- **Higher heat treatment temps give lower Rs change**
- Also in regards to binder alpha,
- Without the binder, it is true throughout testing that higher heat treatment temperatures give a lower Rs Drift
- However
- With the binder, high heat treatment temperatures initially led to more Rs drift, which then matched, and finally were lower than that of the lower heat treatments.
 - could be that binder alpha is partially degraded during heat treatment such that the transient benefit is removed under UV, but that the long term benefit remains, ultimately giving a lower Rs drift.
- This behavior was common across all UV test samples.
- From this test, we have been able to make many conclusions. Specifically, from the heat treatment:
 - PET has less change than Glass
 - Binder Alpha (1%) attenuates change
 - Higher temps, longer times produce greater change
 - From the heat testing:
 - Binder Alpha attenuates change
 - Longer heat treatment time gives lower Rs change
 - Higher heat treatment temp gives lower Rs change
 - From the UV testing:
 - Longer exposure gives larger Rs Drift
 - Fairly invariant across heat treatment temperature
 - Longer heat treatment gives:
 - Less Rs Drift (control)
 - Varying Rs Drift (Binder Alpha)
 - Binder Alpha likely degraded by heat
- When this test began, many questions had been posed. The results from this test have provided the answer to many of these questions, as follows:
- How does heat treatment affect Rs Drift?
 - In high temperature environments?
Heat treatment helps minimize Rs drift in high temperature environments.

- When exposed to UV?
Higher temperature heat treatments had no effect on R_s drift under UV. However, longer heat treatments actually seem to add to the R_s drift when binder alpha is used, likely because binder alpha is being degraded in some way.
- How do variations in the heat treatment temperature and time affect R_s Drift?
For the heat test:
 - *Higher heat treatment temps give lower R_s change*
 - *Longer heat treatment times give lower R_s change*
 - And for the UV Test:
 - *Higher heat treatment temps give slightly lower R_s change*
 - *Longer heat treatment times give lower R_s change for controls BUT*
 - *Longer heat treatment times give higher R_s change for Binder Alpha during the start of the test (the binder may be degraded by the heat treatment)*
- Does Binder Alpha provide R_s Drift control in both UV AND heat conditions?
 - *Binder Alpha does help R_s Drift for both UV and heat conditions*
 - *Benefit of Binder Alpha after heat treatment not as good as non-heated Binder Alpha*
- Does the substrate used affect any of the above observations?
 - *Heat Treatment: PET has lower R_s Drift than Glass*
 - *Heat Test: Trends are the same. Heat treatment helps in a similar way.*

6.1.11. R_s Drift Conclusions

Extensive R_s drift testing has helped Eikos understand the cause and effects that create a change in resistivity. Over the course of these tests, heat and UV radiation have proven to be the largest contributors to R_s drift. Eikos has examined and mitigated the factors associated with these environmental effects. Specifically, heat treatments, proper use of binders and application methods and initial process conditions, will minimize R_s drift. While it has not been eliminated completely, it can be controlled for a given application such as photovoltaics, and meet customer requirements for successful devices.

6.2. Environmental barriers

Much of the work on Environmental “Barriers” is described above with Binder Alpha as a binder. Other work was conducted with various metal oxide coatings. These coatings are described in more detail below.

6.2.1. Metal Oxide Binders

Several avenues to addressing the environmental stability concerns of Invisicon[®] films have been identified, as outlined in Section 7. Though the exact root causes and

mechanisms behind the degradation mode are not fully understood, it is believed that CNT doping or functionalization level appears to fluctuate with different environmental conditions such as heat, moisture, UV and their combinations. This directly or indirectly leads to instability in electron transport properties within the CNT matrix, causing fluctuations in resistance. Thus, Eikos, Inc. is searching barrier materials that will prevent changes in doping level, including molecular sorption/desorption, while stabilizing optoelectronic performance under certain environmental constraints.

The fabrication of a coating by this method includes preparation of metal alkoxide precursor solutions in alcohol or other organic solvents. Such solutions could then be deposited onto CNT coated substrates via conventional wet-coating methods. Evaporation of the carrier solvents results in uniform, pin-hole and defect free metal oxide coatings. The chemical process is based on hydrolytic decomposition of metal alkoxides, leading to the formation of hydrated metal oxides, which are then subjected to dehydration and the formation of a metal oxide.

The purpose of the sol-gel experiments was to identify barrier coatings that would not alter opto-electronic properties of Invisicon[®] coatings either due to chemistry or due to test environments (currently heat and UV). Both titanium and aluminum oxides were chosen due to favorable optical transmittance, while zinc oxide was chosen due to UV-blocking characteristics. The impact of metal oxides as barrier layers for CNT under elevated temperatures was not known. As experiments progressed, multilayer barrier systems from the above materials were also evaluated to derive the optimum balance of opto-electronic characteristics across all materials and test platforms.

6.2.2. Experimental Procedure

Metal alkoxide solutions with suitable solvents for each mono or multi-precursor system were prepared (Table 31).

Table 31: Metal Alkoxide Formulations

Metal Alkoxide Barriers		
1 st Barrier Layer	2 nd Barrier Layer	Solvents
Ti (OBu-n)4	None	IPA
Zn(OC2H4OCH3)2	None	4M2P
Al(OBu-sec)3	None	IPA
Ti (OBu-n)4	Zn(OC2H4OCH3)2	IPA, 4M2P
Al(OBu-sec)3	Zn(OC2H4OCH3)2	IPA, 4M2P
Ti (OBu-n)4 + Al(OBu-sec)3	Zn(OC2H4OCH3)2	IPA, 4M2P

IPA= isopropyl alcohol, 4M2P= 4-methoxy-2-propanol

For the purposes of investigating the influences of an alkoxide precursor and subsequent metal oxides on CNT electrodes, a separate set of experiments were conducted to evaluate the influence of solvents and stabilizing acids employed on opto-electronic

properties of CNT films. Each solution concentration was optimized with coating process conditions to achieve a target metal oxide thickness.

Glass slides were then prepared by spray-coating CNT to a surface resistance of 500 Ohms/sq, with silver electrodes underneath. Coatings were prepared by dipping CNT coated glass slides into metal precursor solutions identified in Table 31, listed according to previously established process conditions. Thus coated glass substrates were first pre-dried under ambient temperature, followed by a thermal bake for 2 hours at 120 °C, and stored in a moisture free environment until tested.

The influence of heat (100 °C, static humidity) and ultraviolet light (ambient T, RH)) on the opto-electronic properties of the metal oxide protected CNT films were then monitored. Percent change (%) in surface resistance (R_s) and optical transmittance (%T) were measured as a function of time and compared with CNT coatings without metal oxide layers.

6.2.3. Environmental Stabilization by Metal Alkoxide Coatings

Single layer metal oxide coatings were first deposited over the surface of 500 Ohms/sq CNT films by the dip-coating method. Such compositions were then tested under heat and UV-light, as previously described for RT performance. Monolithic coatings compositions evaluated include a single layer metal oxide protective layer on CNT taking the forms of:

- Glass/CNT/TiO₂
- Glass/CNT/ZnO
- Glass/CNT/Al₂O₃

Unprotected CNT films demonstrated rapid increase in surface resistance with time resulting to approx. 200% increase in R_s at the end of this test (Figure 51).

Figure 51: Heat Stability of CNT/Metal Alkoxide Compositions

All oxides suppressed Rs loss under heat. Aluminum oxide protected CNT coatings trailed the control, thus demonstrating weak protection. CNT protected with TiO₂, on the other hand, demonstrated 25% increase in Rs, while ZnO demonstrated less than a 10% increase during the test. It is thus apparent that certain metal oxide coatings have the potential to becoming a viable approach to minimize heat related degradation of CNT coatings in applications that require elevated temperature stability.

In addition to identifying barrier materials against thermal exposures, there is equally relevant need to prevent damages due to radiant light. Many materials, including polymers, degrade under sunlight. This was assed by exposing CNT materials to simulated sunlight (Q-Panel, UVA-340 lamp) for 115 hours (Figure 52).

Figure 52: UV-Stability of CNT/Metal Alkoxide Compositions

As with thermal energy influence, unprotected CNT films demonstrated rapid increase in surface resistance (Rs) under UV energies. TiO₂ coated CNT trailed behind bare CNT. It is apparent that TiO₂ is, as expected, a poor UV-blocker.

Carbon nanotube films coated with ZnO and Al₂O₃ demonstrated only modest increase in surface resistance; 25% and 50% respectively. These results are considered promising, though barrier materials with substantially improved sunlight protection would be required.

6.2.4. Environmental Stabilization by Hybrid Metal Alkoxide Coatings

Based on the data generated from single-layer metal oxide coating tests, improved performance could be derived from a bi- or a tri-component system based on Ti, Al and Zn. More specifically, this evaluation consists following hybrid structures:

- Glass/CNT/Al₂O₃/ZnO
- Glass/CNT/TiO₂/Al₂O₃
- Glass/CNT/[TiO₂:Al₂O₃]/ZnO

Thermal and UV-stability of the CNT/metal alkoxide coatings was substantially improved by these hybrid coatings (Figure 53 and Figure 54). Bi-layer alkoxides by themselves were promising, while a tri-component multi-layer structure composed of TiO₂ with Al₂O₃ and ZnO demonstrated an exceptional thermal and UV-stabilization effect.

Figure 53: Thermal Stability of CNT/Metal Oxide Films

A barrier layer composed of TiO₂/ZnO did not synergize, though it was expected it would due to the presence of a known UV-blocker; this led to a rapid loss in conductivity under UV-light (Figure 54). Aluminum oxide synergized well with ZnO, as did a tri-component metal oxide hybrid coating composed of TiO₂/Al₂O₃ with ZnO as outer layer.

Figure 54: UV-Stability of CNT/Metal Oxide Coatings

Different sol-gel based metal alkoxide precursor compositions as environmental barrier materials for CNT coatings were investigated. Three single layer, two bi-layer, and one two-component bi-layer barriers were fabricated, and their influence on CNT surface resistance under heat and simulated sun-light were assessed (Table 32).

Table 32: Environmental Stability of CNT/Metal Oxide Structures

Composition	Heat Exposure		UV-Exposure	
	Test time, hrs	% Loss	Test Time, hrs	% Loss
Bare CNT (Control)	500	>100	115	>100
CNT/TiO ₂	500	35	115	>100
CNT/ZnO	500	10	115	25
CNT/Al ₂ O ₃	500	>100	115	45
CNT/TiO ₂ /ZnO	260	20	260	>100
CNT/Al ₂ O ₃ /ZnO	260	25	260	0
CNT/TiO ₂ /Al ₂ O ₃ /ZnO	260	0	260	-10

It is evident that coatings fabricated from CNTs need environmental protection, provided such environmentally harmful conditions are present in a given application. In photo-voltaics specifically, continuous exposure to heat, sunlight, and perhaps moisture are inevitable. Zinc oxide, as a single layer on CNT, demonstrated a promising heat stabilization effect, but was less effective as a UV-blocker. Aluminum oxide with Zinc oxide as an outer layer practically eliminated losses associated with UV-light, at the cost of a slight sacrifice in heat stabilization. Tri-component metal oxide systems

demonstrated no R_s degradation under UV nor heat. Furthermore, this system, was not only stabilized, but also demonstrated a reduction in R_s . This could be attributed to chemical doping of the CNT, often leading to improvements in electrical conductivity within CNT network.

6.2.5. Transmittance Loss from Metal Alkoxide CNT Films

Substantial improvements in minimizing, if not eliminating, heat and UV-light caused changes in R_s of CNT coatings was demonstrated. Undesirable feature associated with metal alkoxide materials is % transmittance (%T) loss, either attributed directly to the oxide or oxide prompted degradation of CNT during environmental testing. This trend was observed with most CNT/metal oxide compositions evaluated (Table 33).

Table 33: Transparency Losses Associated with Metal Oxide Coatings

Coating System	% Loss Due Metal Oxide	% Loss @100 oC*		% Loss due UV**	
		Due Test	Total Loss	Due Test	Total Loss
Bare CNT	-	<2%	<2%	<2%	<2%
CNT/TiO ₂	12-22	2-6	14-28	-	-
CNT/ZnO	10-15	<1	10-13	3-9	13-22
CNT/Al ₂ O ₃	2	<1	3	0-3	<3
CNT/TiO ₂ /ZnO	17-18	7-9	23-24	-	-
CNT/Al ₂ O ₃ /ZnO	10-17	22	27	<1	10-17
CNT/TiO ₂ /Al ₂ O ₃ /ZnO	8-11	2-18	4-28	<1	8-11

* test time 260 hrs; ** test time 144 hrs

As can be readily observed from Table 33, optical transmittance (%T) is substantially less influenced by test environments than surface resistance (Table 32). Certain metal oxide coatings function as thermal barriers for CNT materials, while others perform equally well as UV-blockers, as seen by few % loss due to the test environment. Contrary to all other metal alkoxide formulations evaluated, aluminum oxide demonstrated minimum transmittance loss as a coating as well as during heat aging and UV-exposure, but provided poor protection for electrical stability (Table 32).

Those CNT/metal oxide compositions previously identified, namely ZnO, Al₂O₃/ZnO and TiO₂/Al₂O₃/ZnO, as potential barrier layers, all substantially reduce optical transmittance. Aluminum oxide, under heat aging, caused an additional 22% loss in total transmittance. The only tri-component precursor system evaluated yielded the best balanced R/T performance, though %T loss due to this multi-layer coating is undesirable.

This work successfully demonstrated the utilization of sol-gel based coatings as environmental barrier materials for carbon nanotubes. More specifically, degradation of electrical conductivity due to heat (100 °C) and UV-light (300 – 400 nm) were minimized by developing metal alkoxide precursor compositions suitable for CNT applications, either as single or multi-component coating systems. Certain transparent electrode applications targeted by CNT may be exposed to different environments during their life-time. This certainly is the case with photo-voltaics.

6.2.6. Organic Binders for Transparency Improvement of Metal Oxide-CNT Composites

Sol-gel binders proved to stabilize the resistance of CNT films when exposed to heat, heat and humidity, and UV light. We found that the metal oxide coatings caused a significant decrease in the transparency of the layer, compared with the bare CNT. We attributed the loss of transparency as being due to two potential factors: the metal oxides under exploration are of a high refractive index and therefore will reflect more light, and the microstructural features of the coating were causing the films to have a significant amount of haze. Therefore, we aimed to find a third component to add to the metal oxide-CNT composite to increase transparency by lowering refractive index and reducing haze.

We aimed to achieve the same transparency of CNT on glass without any binders, but with the improvement of heat, humidity, and UV stability. The following compounds were investigated as the third component: polystyrene sulfonic acid (PSS), Binder Alpha and Binder Beta. Preliminary experiments with polyvinylpyrrol – (PVP) have showed that using of this compound dramatically increased sheet resistance after the sol gel coating was deposited, so we eliminated it as a prospective candidate material.

The metal oxide coatings were deposited onto CNT films as described in the previous report. All organic binders were dip coated onto CNT-metal oxide composite coated slides. Binder solvents were chosen based on solubility of the binder and uniform film forming capability. Each sample's resistance and transparency was measured after each step of coating and after an extended heat test at 100 °C. The heat test data are presented below:

Table 34: Effect of resistance and transparency from initially sprayed values during heat tests at 100 °C for varying binder compositions and heating times.

Organic Binder	Oxide Composition	Test Time (hours)	ΔR_s after heating	$\Delta \%T$ after heating
PSS	Al_2O_3 - TiO_2 -ZnO	428	15.5%	-3.5%
Alpha	Al_2O_3 - TiO_2 -ZnO	408	33%	-1.5%
Beta	Al_2O_3 - TiO_2 -ZnO	400	67%	-2.5%
none	Al_2O_3 - TiO_2 -ZnO	408	-5.1%	-9.1%
none	Bare CNT	400	450%	-0.25%

Samples for UV testing were prepared in a similar manner and tested for a similar length of time. The data are presented below:

Table 35: Effect of resistance and transparency from initially sprayed values during UV testing for varying binder compositions and heating times.

Organic Binder	Oxide Composition	Test Time (hours)	ΔR_s after UV	$\Delta \%T$ after UV
PSS	Al_2O_3 - TiO_2 -ZnO	288	-2.4%	>-30%
Alpha	Al_2O_3 - TiO_2 -ZnO	408	37%	+3.3%
Beta	Al_2O_3 - TiO_2 -ZnO	400	31%	-8.1%
none	Al_2O_3 - TiO_2 -ZnO	266	12%	-9.1%
none	Bare CNT	266	450%	-0.75%

As seen in the table above, the PSS binder shows small changes in sheet resistance and transparency during heating, but the samples with the PSS binder became completely yellow during UV exposure. Both Binder Alpha and Binder Beta work well in all tests. However, the addition of Binder Alpha causes a relatively smaller increase in sheet resistance due to binder coating, compared to Binder Beta. Thus, we found that Binder Alpha works under all circumstances to increase transparency of the CNT-metal oxide composite, while maintaining the composite's excellent sheet resistance stability.

6.2.7. Indium Based Protective Coatings

Remarkable progress in the development of barrier coatings for CNT networks that impart exceptional environmental stability has been demonstrated. One such hybrid coating based on Al_2O_3 - TiO_2 -ZnO with low refractive index optical enhancement layer meets RT performance requirements for many applications. However, these hybrid systems are multilayer materials requiring four different chemical components, three

separate coating processes and employ costly raw materials. All combined, this approach may not be suitable to application requiring process simplicity and controlled cost. From this perspective, Eikos set to exploit the use of indium precursor materials as a substitute for previously reported multilayer metal alkoxide based coatings. Indium based barrier materials were explored from three different routes:

- metal alkoxide route with $\text{In}(\text{OR}_3 + \text{Sn}(\text{OR}))_3$
- metal chloride route with InCl_3
- crystalline particle route

Substantial efforts were needed to develop suitable process solution for use that needed to synergize with respective coating processes. Such details are not reviewed in this section. Each route exhibited their unique challenges, benefits and ultimately performance. Variations in performance were noted between glass and PET substrates demonstrating preferentially enhanced behavior in certain material to substrate combinations.

First CNT coated glass and PET substrates were prepared followed by further coating with the metal oxide composition in question. Thus prepared substrates were then exposed to 100 °C for 300 hrs and RT performance monitored. Though changes in R_s due to heat ageing was moderate, averaging 10%, total loss including degradation due to sol-gel chemistry approached 40% both on glass and plastic substrates rendering this material route unsuitable requiring no further testing. Crystalline indium tin oxide particles with cubic bixbuite structure dissolved in three different carrier solvents were prepared and CNT networks coated to a uniform thickness. Thus prepared test coupons were again exposed to a 100°C temperature and R_s monitored over time. These coatings provided no barrier protection to the CNT networks either on glass or PET substrates demonstrating comparable R_s -Drift to that of control or unprotected CNT networks.

Indium tin oxide through metal chloride route was found very successful in enhancing environmental performance of CNT coatings and films. High temperature stability of CNT coating was dependent on InCl_3 solution concentration demonstrating thickness dependency. Different test results for CNT networks protected with ITO via InCl_3 route are demonstrated by Figure 55 and Figure 56.

Figure 55: Thermal Stability of CNT/ITO Hybrid @100 °C (glass)

Under correct film thickness, ITO via metal chloride route is demonstrating exceptional thermal stability with no loss in transmittance not requiring low index of refraction binder materials. Duplicate test on PET substrates, likewise, exhibited performance well below internal limits.

Figure 56: UV-Stability of CNT/ITO Hybrid on Glass

Like thermal stability, R_s -Drift can be controlled under prolonged UV-light exposures. Further stabilization can be achieved by incorporating secondary binder layer onto ITO surface. Again, clear performance improvements were also achieved on PET substrates.

6.3. Accelerated weather testing

The utility of solar cells is judged against a metric proportional to their lifetime multiplied by their efficiency divided by their cost. Lifetime for first generation cells is typically 25 years or more, while thin film cells promise 20+ years, and organic solar cells are 5+ years. As a material used in solar cell construction, Eikos Invisicon[®] carbon nanotube transparent conductors will need to maintain their functionality under extreme weather conditions. **Eikos tested and passed against an organic solar cell environmental stability tests and internally passed tests imposed for thin film environmental stability.**

The low cost of organic solar cells is typically offset by lower efficiency and shorter lifetimes. Nonetheless, materials used in organic solar cells must pass a list of environmental specifications. Eikos prepared environmental stability test samples based on binder coat formulations developed for these purposes. The specification to pass is:

<20% change in 250 hours at:

- Heat 60° C
- Heat/Humidity 60° C, 90% RH
- Light Exposure 1 sun, no UV

Eikos first determined internally that specially formulated Invisicon[®] coating would pass this specification, and then delivered these samples to a solar manufacturer for their tests. This test compared bare CNT, binder coated CNT, and conducting polymer transparent conductors. **Eikos binder coated CNT passed all environmental stability tests**, as can

be seen in Figure 57. In fact, these coating performed far better than their competition in organic solar cells, conducting polymers.

Figure 57: Environmental stability of bare CNT, CNT with binder, and conducting polymer coatings under (a) heat, (b) heat and humidity, (c) and light exposure.

Eikos began preparations to pass the IEC 1646 International Standard tests for thin-film terrestrial photovoltaic modules. These tests for thin film cells are more rigorous than those for organic PV. They include:

- Outdoor exposure test of 60kWh / m² (Test 10.8)
- Thermal Cycling: 200 cycles of dry -40C to 85C (Test 10.11)
- Humidity-freeze test: 10 cycles -40C to 85C @ 85% RH (Test 10.12)
- Damp Heat test: 1000 hours 85C/85% RH (Test 10.13)

This accelerated weather testing guarantees reliable solar cells. For Eikos' coatings, the sheet resistance should change less than 100%, and ideally as little as possible. Eikos' environmental stability testing seeks to emulate conditions as in IEC 1646. For example, our light sensitivity analysis mimics Test 10.8, which is a sunlight exposure test. The preceding section outlined heat and humidity testing at 85 C and 85% R_H, as in Test

10.13. Eikos has investigated independent third party testing of our cells across this IEC 1646 standard. We anticipate from in house testing that our materials will meet all specifications, and are highly reliable for use in solar applications due to steady research developing stabilizing binder coating systems.

7. Invisicon® in PV Manufacturing

7.1. *Coating uniformity*

It is necessary to determine the uniformity of a CNT, depending on the application method. During commercial application of Invisicon®, hundreds of square feet of material will be produced daily. The end use of the material will require an understanding of performance variation across the width of the web in a roll to roll process. The choice of spray, slot-die, gravure, or other printing techniques will dictate the coating uniformity and thus the suitability of the film for certain applications.

The uniformity of the coated material can be measured in two (2) ways: direct measurement or linearity. The former method measures sheet resistance at a defined point. Using a 4-point probe, the voltage is applied locally and resultant current measured. Another method to determine uniformity is to determine the linearity of the resistance across the web width. This method is used in the touch screen industry and is less damaging to the sample.

7.1.1. Linearity Procedure

Briefly, the Linearity Procedure is the following. A sample is coated with Invisicon® to approximately 500 ohms/sq in surface resistance. The coated sample is then placed on a paper grid and fixed with tape on edges. Two (2) silver paint electrodes are applied approximately 10 inches apart. Each electrode is approximately 7" long and 0.25" wide. After the silver paint has solidified (cure, solvent evaporation), copper tape is placed on each electrode overlapping $\frac{3}{4}$ " over the silver electrode. The contact resistance was earlier verified to be less than 5 ohms. The excess tape is folded over so the power supply can be attached. A schematic of the experimental set-up is shown in Figure 58. A 10V DC power supply is applied between the two electrodes. A voltmeter is used to record the voltage per each location on the grid. The negative probe of the voltmeter is fixed at the 0,0 position on the grid.

Figure 58: Schematic of Linearity Procedure

A metric of 1.5% from linearity is used as criteria for an acceptable coating (Figure 59). This was demonstrated by a PET coated ITO sample with a sheet resistance of $300 \Omega/\square$ before and after heat treatment (Figure 60).

Figure 59: Acceptable 1.5% Linearity Variation

ITO As-Received

ITO after Heat Treatment

Figure 60: Histogram of linearity variation of 300 $\Omega/\square$ ITO coated on PET based on 45 data points. Data on left pane is linearity measure of received ITO and data on the right pane is after 18 hour heat treatment at 100°C.

7.1.2. Comparison between Spray and Drawdown Application Methods

The spray coated CNT sample was coated to a sheet resistance of 800 $\Omega/\square$ on A4 size 7 mil PET sheets. The drawdown sample was coated at 70 μm wet thickness, to a sheet resistance of 750 $\Omega/\square$. A considerable amount of the evaluation has occurred on the spray application method (Table 36 & 37, Figure 61) while the draw-down coating methodology is still under development (Table 20, Figure 17).

Table 36: Linearity of Spray Coating Data before Heat Treatment

Individual Linearity at each point				$(V_{\text{actual}} - V_{\text{theoretical}})/V_{\text{theoretical}}$						
	1	2	3	4	5	6	7	8	9	10
Row #1	6.79%	2.79%	1.46%	0.05%	-1.20%	-1.36%	-1.48%	-1.20%	-1.20%	0.00%
Row #2	7.89%	1.90%	0.90%	0.65%	-0.30%	-0.77%	-1.10%	-0.85%	-0.77%	0.00%
Row #3	7.89%	3.40%	0.90%	0.90%	-0.30%	-0.43%	-0.53%	-0.85%	-0.43%	0.00%
Row #4	7.21%	2.71%	1.54%	0.45%	-1.20%	-0.47%	-0.66%	-1.05%	-0.47%	0.00%
Row #5	6.89%	2.90%	0.57%	-0.60%	-0.90%	-0.60%	-0.39%	-0.35%	-0.21%	0.00%

Table 37: Linearity of Spray Coating Data after Heat Treatment (18 hrs @100 °C)

Individual Linearity at each point				$(V_{\text{actual}} - V_{\text{theoretical}}) / V_{\text{theoretical}}$						
	1	2	3	4	5	6	7	8	9	10
Row #1	4.79%	1.80%	0.80%	-0.70%	1.60%	2.03%	2.20%	-1.95%	-1.86%	0.00%
Row #2	7.89%	4.40%	0.57%	-0.35%	-0.70%	-1.43%	1.81%	-1.47%	-1.54%	0.00%
Row #3	7.89%	2.90%	0.57%	0.40%	-0.90%	-0.93%	-0.96%	-2.60%	-0.88%	0.00%
Row #4	5.89%	1.90%	0.90%	-0.35%	1.90%	-1.27%	-1.24%	-0.85%	-1.10%	0.00%
Row #5	4.90%	1.40%	0.90%	-1.10%	-1.50%	-1.10%	-0.96%	-0.72%	-0.65%	0.00%

Figure 61: Histogram of linearity variation of 800 $\Omega/\square$ Invisicon® coated on PET based on 45 data points. Data on left is linearity measure after coating and data on the right is after 18 hour heat treatment at 100°C.

The linearity procedure was then applied to CNT coated PET substrates based on drawdown or blade method. As these two deposition methods are not identical, one would expect disparity in experimental results. It is evident that substantially larger linearity deviation than allowable 1.5% was experienced with drawdown based CNT application method, see Table 38 and Figure 62.

Table 38: Linearity of Drawdown Data before Heat Treatment

Individual Linearity at each point			$(V_{\text{actual}} - V_{\text{theoretical}}) / V_{\text{theoretical}}$							
	1	2	3	4	5	6	7	8	9	10
Row #1	7.88%	14.97%	9.12%	5.04%	2.79%	1.63%	0.09%	-0.57%	-1.20%	0.00%
Row #2	3.29%	9.83%	8.78%	6.54%	4.59%	3.29%	2.22%	1.17%	0.13%	0.00%
Row #3	5.68%	8.33%	8.34%	7.93%	4.49%	3.19%	2.69%	2.32%	1.25%	0.00%
Row #4	2.29%	6.57%	8.23%	7.82%	4.98%	4.25%	2.16%	1.22%	1.59%	0.00%
Row #5	10.96%	11.70%	9.23%	7.82%	6.57%	4.75%	1.74%	-0.77%	-1.95%	0.00%

Figure 62: Histogram of linearity variation of Invisicon® coated on PET based on 45 data points. Data on the left pane is linearity measure on draw down application and data on the right pane is spray application.

7.1.3. Optimizing Coating to Meet Linearity Specifications

In the first experiment, the carbon nanotube concentration and number of coats were evaluated to determine the optimum application parameters. The application flow rate, temperature and substrate speed were constant throughout the evaluation. Table 39 indicates the sheet resistance measured for two concentrations at various coats. The linearity was determined from 45 data points for each sample. Based on the results, between 2 and 7 coats are necessary to achieve acceptable linearity below 1.5%, see Figure 63 and Figure 64. The lack of linearity at the high coating is attributed to undesirable network formation and drying defects due to longer application times.

Table 39. Sheet Resistance measured for two application carbon nanotube concentrations at various application passes (coats).

Ink Concentration (mg/l)	37			75		
Number of Coats	1	4	14	1	2	7
Sheet Resistance ($\Omega/\square$)	1485	272	66	1022	349	66

Figure 63. Linearity of spray applied carbon nanotubes at 37 mg/l. (green box = acceptable linearity deviation)

Figure 64. Linearity of spray applied carbon nanotubes at 75 mg/l. (green box = acceptable linearity deviation)

After the optimum number of passes was determined, the repeatability of the process was evaluated. Standardizing the process such that the desired sheet resistance value was achieved in a least four (4) passes; a sequential run study was conducted. In a two (2) hour period, five (5) paper size samples on PET were fabricated to a sheet resistance value of approximately $300\Omega/\square$. The figure reports the sheet resistance measured and linearity of each run. As shown in Table 40, the linearity is acceptable for all runs except the last run. During the last run, the supply of CNT ink ran out, causing sputtering at the nozzle. Though a new volume of ink was prepared to finish the run, the lack of coating material remaining after coating the previous four (4) samples attributed to poor uniformity performance. Eikos believes the linearity would be acceptable if more material was available. The first sample has different histogram shape and may indicate some “warm-up” period necessary prior to coating production material.

Table 40. Linearity of sequential spray coated runs on PET substrates.

Run #	Sheet Resistance ($\Omega/\square$)	Linearity	# of data $>+/-1.5\%$
1	298		0
2	294		1
3	301		0
4	309		0
5	260		6

The application of a drawn down binder coat was performed on samples from the first three runs in the sequential run experiment. The binder coating is a three component metal oxide sol-gel coating followed by a top coat of PVDF. Although, there is reduction in uniformity, Figure 65, after application of the binder coat; it is believed the

inconsistencies are due to variation in table flatness and application technique. As shown in Run #3 (the last sample coated), the uniformity performance is improved over previous samples applied with binder. Eikos believes the results can be improved with repeated experimentation and optimization of the coating method.

Figure 65. Linearity of spray applied carbon nanotubes with three component metal oxide/PVDF binder coat.

7.1.4. Conclusions and Scale Up

The spray process developed at Eikos can produce uniform coatings for numerous samples with dimensions of 12"x12" and demonstrates a scale-up potential for larger samples and web coating. We have demonstrated that coatings can be spray coated onto A4 PET sheets to meet commercial uniformity and linearity requirements. This advancement is important for commercialization, though further optimization can occur to reduce the overall coating time.

7.2. Patterning methods

Eikos has identified roll to roll thin film and 3rd generation photovoltaics as most synergistic with carbon nanotube transparent conductive coatings. Because Invisicon[®] is applied via a wet process at controllable sheet resistance values; it is well suited to these new low cost technologies. Eikos has developed extensive experience in coating small to large substrates uniformly with CNT networks requiring no patterning. However, in many applications selective deposition schemes will be needed. This requirement has already been observed practically all photovoltaic structures evaluated during this research. Eikos examined both additive (ink jet printing) and subtractive (laser etch) patterning processes

7.2.1. Patterning by Ink Jet Printing

One of the most promising application techniques for emerging organic optoelectronics is ink jet printing. Eikos examined the feasibility of applying Invisicon[®] via ink jet application to PET substrate. This demonstration of an ink jet deposited carbon nanotube transparent conductive coating is especially applicable to dye sensitized and organic bulk

heterojunction type solar cells. This study was highly successful and achieved performance on par with existing application techniques.

Ink jet printers use one of three main technologies: thermal, piezoelectric, and continuous. For the application of carbon nanotube dispersions, piezoelectric ink jet printing is the most viable technique.

Figure 66: Dimatix DMP 2831 Ink Jet Printer.

For this test, Eikos utilized a Dimatix DMP 2831 ink jet printer, as pictured in Figure 66. This printer has 16 nozzles which fire 10 picoliter drops at between 1,000 to 16,000 times a second. The printer has specialized waveforms for driving the piezoelectric print head, and has a print cartridge with 1.5 mL volume. It has a heated platen with 8"x12" printable area, and is controlled by custom PC software.

An advantage of ink jet technology is the precise control of wet coating deposition. On a DMP 2831, the user loads the print area pattern and the software optimizes for depositing over this area with all 16 print heads. For organic photovoltaics, the benefit of precise patterning is that it allows for monotonic integration of individual cells into modules and arrays. Printing has been recognized as a viable application for organic electronics, including organic PVs.

Ink jet printing of carbon nanotubes has recently been demonstrated by universities, but at a low level of performance for conductivity and transparency. To be effective for solar cell applications, Eikos needed to demonstrate RT performance similar to our existing processes. Eikos prepared two distinct ink formulations for ink jet printing. Ink Jet Formulation 1 and Ink Jet Formulation 2 were each sonicated before use, injected into the Dimatix ink cartridge, and tested. The first step in using new inks is to adjust the firing waveform and pulse rate to form clean droplets from each piezoelectric nozzle.

Both of Eikos' formulations performed well on the Dimatix DMP 2831. Table 41 gives the results for each ink formulation, indicating the number of passes needed on the printer to reach a given sheet resistance. Formulation 1 was more dilute, and required many passes to reach sheet resistance values that begin to be useful for photovoltaics. For example, with ten passes of the printer, a sheet resistance of 409 $\Omega/\square$ was reached, with a transparency of 92.1%. Formulation 2 had a longer dry time, even on a heated platen, but

produced useful sheet resistance in fewer passes. In five passes, a sheet resistance of 168 $\Omega/\square$ was reached, at a transparency of 85.5%.

Table 41: RT performance for ink formulation 1 and 2.

Ink	Number of passes	Resistivity ohm/sq	%T	%T @ 500 $\Omega/\square$
1	4	1844	97.5	93.1
1	6	1160	96.1	92.5
1	8	776	96.3	94.8
1	10	409	92.1	93.2
2	3	286	89.5	93.1
2	5	168	85.5	93.6

Figure 67 charts the performance of Ink Jet Formulation 1 and 2 against Eikos' leading RT performance curve and the needs of the solar market. This data was collected in the first Phase of this DOE project. We can see that both formulations have lower performance than the current peak performance. However, two things must be noted: first, that this was an initial attempt at ink jet printing using non optimized formulations, and secondly, that the performance of Invisicon[®] is lower on PET than glass. Thus, while the test was a fair representation for feasibility of roll to roll organic photovoltaic production, it is not a fair comparison against Eikos' methods of production on glass.

Figure 67: RT Performance from Ink Jet on PET.

7.2.2. Ink Jet Printing Scale Up

The demonstration of an ink jet deposited carbon nanotube transparent conductive coating is especially applicable to dye sensitized and organic bulk heterojunction type solar cells. Eikos investigated the scale up path for ink jet printing. Eikos identified three primary producers of ink jet print heads and two primary producers of production level ink jet print systems. Our feasibility test was performed on a prototype system with 16 print head nozzles manufactured by Dimatix (see Figure 68). Though Dimatix produces print heads with 256 print nozzles capable of scaled up operations, Dimatix produces no equipment that could be used for large area manufacturing.

Figure 68: Dimatix 16 nozzle printhead previously used.

Eikos identified three print head manufacturers. Specifically, the majority of piezoelectric printheads are manufactured by Dimatix, Xaar, and Konica. Because Eikos was most familiar with Dimatix brand printheads, the most extensive investigation occurred across their products. Dimatix produces printheads with 80pL drop size down to 10 pL. A listing of printheads includes:

- Nova class, 90dpi, 256 nozzles, ~\$775 cost per printhead
- Galaxy, 30 pL drops, 256 nozzles, ~\$2000 per printhead
- S class, 50 dpi, 128 nozzles

Eikos identified two ink jet printer manufacturers for routes to scale up. Litrex, in Pleasanton, CA, produces prototype and production ink jet print systems. An example production tool in the M Class series is pictured in Figure 69. These massively parallel systems feature upwards of twelve print heads in parallel. With customization offered with either Dimatix, Xaar, or Konica printheads, each featuring up to 256 nozzles firing

80 pL droplets at 10 kHz frequencies, these systems are capable of roll to roll production of megawatts of solar capacity per year.

Figure 69: M Class ink jet printer from Litrex.

ITI (Imaging Technology International), in Boulder, CO manufactures a digital web press with 2" print pass using Xaar print heads. This unit costs \$225,000 as a base model, with additional \$50,000 cost per 2" of print heads. Pictured in Figure 70, this unit is capable of roll to roll processing and could be used for pilot line solar production. The VJet Systems, including the VJet 5000 with a stepper motor and 100 um placement accuracy and starting at \$125,000 and the VJet 7000 with more accurate linear motors for \$200,000, are both useful for monotonic cell fabrication. ITI also custom builds equipment, and would make a roll to roll coater for thin film or organic photovoltaic production as need. Systems can easily be built that have less than 55 um of absolute web weave and with a variety of high throughput ink jet printheads.

Figure 70: Digital Web Press ink jet printer from ITI.

7.2.3. Patterning by Laser Ablation

Removal and patterning of organic layers in thin film devices is a well established technology today. Here Eikos set to evaluate subtractive patterning method to remove CNT from a PET substrate subsequently creating a highly transparent, electrically conducting pattern.

Laser patterning of carbon nanotube coated PET substrates with four different patterns was demonstrated. First relatively thick layer of CNT network with sheet a resistance of $10 \Omega/\square$ was spray-coated onto a PET substrate.

Pattern drawings were then created and supplied to the service provider as a CAD file. Customer provided CAD software was then employed to generate drawings with the desired 0.10 mm line width used in each design. CNT patterns created are shown in Figure 71 below

Figure 71. CAD Designs for CNT Patterns.

A laser scanner system was used for the actual ablation tests. Complete removal of the coating was achieved with a single pass with 28% overlap. The fluence was optimized for each coating thickness to achieve proper 0.1mm line width as well as good edge quality.

Figure 72. Grid 30 with different magnifications; a. represents 50X and b. to d. represent 200X magnification.

All fractal patterns created by the laser ablation approach were found uniform. This is attributed largely to optimized process conditions and improved optical setup. The thinner coatings seem to allow for a better ablation result with cleaner edges and less delamination effects than thicker CNT coatings.

7.2.4. Laser Ablation Patterning Scale Up

Laser ablation technology is used in manufacturing for fine scale subtractive processing. Eikos examined using this subtractive laser etch process with four different patterns of carbon nanotube coated PET substrates. This feasibility study proved successful, and led Eikos to pursue possibilities for scale up in roll to roll photovoltaic manufacturing. Exitech (<http://www.exitech.co.uk/>) the same company Eikos utilized for its feasibility study, creates customized laser etch systems for a variety of applications. The market for laser etch system is large, with numerous companies such as Control Micro Systems (<http://www.cmslaser.com/>), Kern Lasers (<http://www.kernlasers.com/>), Han's Laser Technology (<http://hans-lasertech.fuzing.com/>) and others providing customized solutions for this application method. Though laser ablation techniques are expensive, they are feasible for photovoltaic applications wherein a small amount of material is ablated. For example, Eikos is aware of one amorphous silicon cell roll to roll manufacturer which uses laser etch systems to cut steel backplanes into separate serial cells for monotonic module construction. These techniques have been demonstrated at the coupon scale and would be ready for scale up for manufacturing in PV.

7.2.5. Conclusion

Two fundamentally different CNT patterning methods were investigated for scale up: ink jet printing as an additive process and laser ablation as a subtractive process. Both methods have their unique features and challenges. Laser ablation may be a laborious method for larger area patterning but may find usefulness in fabricating micro-patterns or removing materials from areas requiring clean surfaces. Ink jet printing is a viable manufacturing method for organic electronics such as organic photovoltaics.

7.3. *Process scale-up options*

Substantial efforts were made on developing a sound understanding on all parameters that directly influence optoelectronic performance of Invisicon® on different substrates. Eikos successfully conducted a coating trial with commercial scale web-coating equipment. Results of this experiment are outlined below. The next section summarizes results from recent experiments, conducted with recently identified spray heads that demonstrate the potential for scale-up of the existing spray process.

7.3.1. Roll-To-Roll Coating Methods

The slot die coating trial at Polaroid was conducted on a 5" wide test coater, capable of handling flammable liquids not feasible with the earlier coating equipment. The objectives of this experiment were to demonstrate that continuous slot coating is a feasible process to manufacture high conductivity films on flexible polymeric webs, and to determine how well conductivity performance on a continuous slot coater could be predicted by lab drawdown coating methods employing the most promising carrier solvents.

7.3.2. Experimental Setup

Experimental run and associated process variables were jointly developed with Polaroid scientists. Invisicon® inks were first fabricated at the Eikos laboratory, and transferred by car to a nearby coating laboratory owned by Polaroid. Coating runs were conducted on a 5" wide PET web coater equipped with a 4.75" slot die. CNT inks were pressure fed through in-liner ultrasonic processor into the die without filtering.

Three types of CNT dispersions were used differentiated by type (A+, A++) and concentration or absorbance (1.1, 3.8). Four types of polymer substrates were employed designated as:

- a. ST505
- b. Bare PET
- c. Silica coated PET
- d. TechniMet

All films were 5" wide and 20 ft long and were coated with CNT dispersions. All films were supplied by Polaroid, except TechniMet, purchased separately.

7.3.3. Trial Results and Discussions

Prior to the coating experiment, CNT ink re-dispersion capability at Polaroid was conducted, as it was assumed that transportation may cause CNT to flocculate out from solution. For that purpose, Polaroid provided a Branson 900B flow cell type sonicator. In order to understand the effect of sonication on R/T performance of Invisicon® coatings, a preliminary test matrix was conducted to define optimum power settings for this process.

CNT Inks were delivered to Polaroid in small (mL) and large (L) volumes. Both transportation samples were then evaluated in terms optical transmittance (%T). It was discovered that transportation caused approximately 0.5% loss in %T for both sample volumes. Further sonication and transfer of ink from storage container to coating head caused additional, but not detrimental, degradation. Ink samples taken at the end of the dispensing system and right before the slot head were about 1% lower in transmittance than the freshly made CNT ink. Ink spray-testing results at different stages of the ink life are shown in Table 42.

Table 42: Effect of Sonication on Ink Quality.

Ink type (absorbance)	Paste Specs %T	%T @Eikos	%T @Polaroid	Spray testing at Polaroid, L, %T		Taken before coating head	
				Sonicat Time (min)	%T	In-line sonicator (45% amp.)	%T Before coating head
A+ (1.1)	93.4	92.1	91.7	1	90.5	off	91.2
A+ (4.5)	93.4	90.7	90.3	4	90.3	on	89.4
A++ (3.8)	95.2	92.8	92.1	2	91.7	on	91.6

The flow meter was calibrated with Eikos proprietary solvent blend as control. The same control fluid was then used to establish the coating process, to deliver 20 and 40 micron thick wet coating coverage.

Previous hand-drawdown coating tests have demonstrated that CNT on Technimet film develops surface resistance comparable to that of glass at any given wet ink thickness. CNT films on other polymer substrates have shown lower conductivity. CNT coatings on substrates other than TechniMet substrates also showed that equal total wet thickness coated by multiple passes had better conductivity than coatings developed by one single coating pass. This behavior was confirmed, i.e. certain substrates received two separate CNT coatings.

Table 43 details the experimental test matrix conducted. Total wet thicknesses were calculated from ink flow rate, web speed and coating width. The Rs values were average from three Loresta 4-Point Probe measurements.

Table 43: Experimental Test Matrix.

Sample # - type	Ink type (absorbance)	Wet Film (μm)	# of coats	Rs, (Ω/□)	%T	Coating Uniformity
1-a	A+ (1.1)	20	1	3.0M	98.6	Uniform
2-a	A+ (1.1)	40	1	0.2M	97.6	Wet streak
3-a	A+ (1.1)	2x20	2	0.2M	98.3	Uniform
4-b	A+ (1.1)	40	1	overload	98.1	Severe beading
5-b	A+ (4.5)	20	1	overload		Severe beading
6-a	A+ (4.5)	20	1	23k	97.1	Mottled
7-a	A+ (4.5)	40	1	3,748	93	Mottled
8-c	A+ (4.5)	20	1	5,228	98.2	Uniform
9-a	A+ (4.5)	2x20	2	5,890	94.2	Mottled
10-a	A++ (3.8)	20	1	29k	98.4	Dark spots
11-a	A++ (3.8)	40	1	4,031	95.9	Mottled
12-a	A++ (3.8)	2x20	2	5,113	95.1	Slightly mottled
13-d	A++ (3.8)	20	1	2,888	98.8	Dark spots
14-d	A++ (3.8)	2x20	2	993	95.1	Mottled with dark spots
15-d	A++ (3.8)	40	1	989	96.6	Streaks and dark spots

a. ST505, b= bare PET, c= Silica coated PET, d= TechniMet

A substantial improvement in surface resistance between this and previous web-coating trial was achieved. Previously, Rs values were between 10^3 and 10^7 Ω/□, whereas in this case, Rs on CNT coated TechniMet film <1000 Ω/□ was achieved by a single coating pass.

Furthermore, it is anticipated that R_s can be improved further. More specifically, we have reported previously that drawdown predictions for A++ inks can develop improved surface resistance. Based on conductivity models developed by Eikos, A++ ink with an absorbance of 3.8 should give R_s of approx. $600 \Omega/\square$. As indicated in Table 42, the A++ ink (95.2%T) resulted to 92.8%T; i.e. over 2% below its targeted performance.

For the most part, lab coater data correlated well with hand drawdown results. These two coating methods demonstrated similar effects due to a) substrate type, b) ink type and absorbance and c) total film thickness on resistivity (R_s). As in hand drawdown coating, TechniMet films developed the best R_s performance, followed by silica coated PET. Standard ST 505 showed the worst R_s . Silica coated PET demonstrated great potential for R_s performance but slightly inferior to TechniMet film. CNT ink on bare PET did not wet out, leading to CNT islands that were not connected, resulting in a loss of electrical conductivity.

Most coatings showed mottling, streaks and dark spots. Better ink dispersion, adjustment of drying conditions and viscosity increase are possible ways to improve coating uniformity. It is firmly believed that these are refinement matters related to the web-coating processes rather than inherent problems with the CNT materials.

Substrate surfaces were also characterized with a Zygo interferometer, but no correlation between surface properties and R_s performance of the CNT coatings was evident.

7.3.4. Web Coating Summary

Surface resistance (R_s) $< 1000 \Omega/\square$ was achieved by one coating pass. It is postulated that R_s can be improved further, provided that R/T performance of larger volumes (L) can be maintained at comparable level to smaller volumes (ml). Hand drawdown methods and models correlated well with pilot-line slot coating results. Coating uniformity needs improvement but is a matter of optimizing variables related to web-process.

7.3.5. Effect of Substrate on CNT Coating Conductivity

Earlier work based on Meyer rod drawdown coating methods showed that certain substrates could produce surface conductivities four orders of magnitudes higher than other plastic films. This, with data generated during this reporting period is found in Table 44 below. Although TechniMet film yielded comparable R_s to that of glass; our benchmark performance, it is considered a value-added combination as TechniMet is a high performance and costly substrate.

Table 44: Influence of Substrate and Plasma Treatment on Surface Resistance (Rs). Standard Ink with abs. of 2.3AU unless otherwise stated.

Substrate	Substrate description	Rs (ohms/square)	Coating uniformity
# 4 base no plasma	Gelatin coated PET	6.290E+06	Uniform
#4 with plasma	Gelatin coated PET	5.789E+07	Uniform
# 5 no plasma	Gelatin coated PET	4.004E+07	Uniform
#5 with plasma	Gelatin coated PET	3.515E+06	Uniform
Toray U34	Acrylic coated PET	2.44E+06	Done with 0.866 abs ink, glass is 3.55E+04 with the same ink
ST 505 no plasma	Acrylic coated PET	3.261E+05	Uniform
ST 505 with plasma	Acrylic coated PET	2.153E+06	Uniform
#8 no plasma	Bare PET	5.186E+04	water stain visible
#8 with plasma	Bare PET	6.098E+04	water stain visible
TechniMet roll 1	Aluminum oxide coated PET	3.304E+03	Uniform
Technimet roll1 backside	Bare PET	4.834E+04	Uniform
TechniMet roll 2	Aluminum oxide coated PET	2.803E+03	Uniform
Technimet roll 2 backside	Bare PET	8.864E+04	Uniform
Glass	Microscopic slide	4.166E+03	Uniform

The possible explanation of the dramatic differences in ink volumes needed to achieve comparable conductivity includes surface roughness differences and interfacial interactions between the substrate and that of CNT ink (Figure 73). In this work, we examined the cause of the dramatic effect of different substrates on conductivity, and thus identify ways to optimize slot coating process even further.

Figure 73: Wet Thickness (μm) of different ink grades required to achieve 10⁶ Ω/□.

7.3.6. Influence of PET Sub-Coats on CNT Conductivity

Herein we demonstrate that by rinsing PET film (ST505) with methyl ethyl ketone (MEK) attainable surface conductivity can be improved. It was believed that MEK removes the acrylic coating present on ST505.

In this experiment, ST505 was first rinsed with MEK and IPA. Low grade CNT ink was then prepared to abs of 3.7 and coatings drawn to rinsed PET substrates with a Meyer rod #16. Surface resistance was then measured with a Loresta 4-point probe. Results are tabulated in Table 45.

Table 45: Influence of MEK Rinse on Invisicon® Conductivity

Substrate	Rs (ohm/sq)	Uniformity
ST505 no rinsing (control)	6.230×10^5	Uniform
ST505 rinsed with MEK	4.188×10^4	Uniform
ST505 rinsed with 3:1 IPA/water	3.999×10^4	Uniform
Rinsed Melinex 453 (back) (bare PET)	6581	Beading
Glass control	6068	Uniform

MEK rinse reduced surface resistance (Rs) of CNT coated PET (ST505) by an order of magnitude. Rinsing with 3:1 IPA/water blend gave comparable results. Backside of Melinex 453 representing PET without sub-coats showed very promising surface conductivity.

7.3.7. Optimization of Substrate-Solvent Systems

As quoted in Table 45 above, bare PET produced the highest conductivity among plastic substrates tested. Results, however, are difficult to duplicate due to poor wetting onto that substrate, leaving behind a stain-like non-uniformity.

As IPA has a higher evaporation rate than water, traditional alcohol/water based CNT ink during drying leaves behind water, leading to an increase in surface tension. Now, when substrate surface energy is lower than water (water: 70 dyne/cm, PET: 44 dyne/cm), CNT inks beads up on the substrate leading to curling and beading and thus drying to non-uniform coating. In some cases, this can lead to complete loss of conductivity (Table 10). Substrate and ink surface properties have to be matched in order to produce coatings of good uniformity and high conductivity. Several approaches can be adopted to achieve this goal:

1. *Add high boiling point solvents to the ink to prevent beading up*
2. *Use a substrate with hydrophilic coating*
3. *Change IPA/water ratio of the ink while maintaining good ink dispersion;*
4. *Use a completely different solvent system that does not change surface tension during drying while maintaining good ink dispersion.*

Tests aimed at improving substrate to ink interaction, and conductivity using approaches 1 and 2 above are summarized in

Table 46. Ink used was a low grade ink with abs of 3.7. Two high boiling point solvents, cyclohexanol and propylene glycol monoethyl ether (PGME), were employed at 5% by weight levels. CNT coatings were fabricated by drawdown methods using Meyer rod #16. Most coatings were found to be uniform by visual inspection, unless noted as “beadup”, indicating de-wetting. Surface resistance was measured with a Loresta 4-point probe.

Plastic films employed were backside of Melinex 453 that represents bare PET. ST505 substrate has acrylic sub-coating on both sides. Toray U34, on the other hand, is a smooth PET with acrylic coatings on both sides. Melinex 582 has hydrophilic coating on both sides containing no surfactants. Silica coated PET from Polaroid is hydrophilic, containing no surfactants. All rinsing was done with IPA except for the Polaroid film. The parylene film was constructed by depositing a 250 nm thick parylene-N film on bare PET. Within parylene family of samples, “g” was not cleaned prior to parylene coating; “b” was cleaned with “dirty silane”, “f” was cleaned with IPA prior to parylene coating.

Table 46: Influence of Substrate and Solvent on Conductivity

Substrate	High boiling solvent/ coating uniformity	Rs (ohm/sq)
Glass control	no	5858
Base #8 (bare PET)	No, beadup	3.25E+05
Rinsed Melinex 453 back	No, beadup	6581
Rinsed Melinex 453 back	Pgme, beadup	6346
Rinsed Melinex 453 back	No, severe beadup	>10 ⁸
Melinex 453 back no rinsing	No, severe beadup	>10 ⁸
Paralyene coated g, front side	No, severe beadup	>10 ⁸
Toray U34	no	2.88E+04
Rinsed Toray U34	no	1.47E+04
Melinex 582 (hydrophilic base)	no	1.56E+04
Rinsed Melinex 582	no	1.78E+04
Polaroid silica coated	no	2.19E+04
Water rinsed Pol silica coated	no	3.89E+04
Polaroid silica coated	no	2.89E+04
Glass	cyclohexanol	7857
Melinex 453 back no rinsing	cyclohexanol	1.99E+04
Rinsed Melinex 453 back	cyclohexanol	2.23E+04
Parylene coated g, front side	cyclohexanol	2.90E+04
Parylene coated f, front side	cyclohexanol	1.85E+04
Parylene coated f, back side	cyclohexanol	2.88E+04
Parylene coated b, front side	cyclohexanol	1.64E+04
Parylene coated b, back side	cyclohexanol	1.63E+04
Melinex 582 (hydrophilic base)	cyclohexanol	2.52E+05

Additional coatings were fabricated by draw-down methods on various substrates using different ink grades (approaches 3 and 4) and solvent systems. It has to be noted that all coatings were uniform and no de-wetting or curling was experienced during drying (Table 47).

Table 47: Influence of Substrate, Ink Grade and Solvent on Rs

Substrate	Ink Grade, abs, solvent	High BP Solvent	Rs (ohm/sq)
Rinsed Melinex 453, back side	92%, abs 4 in cyclohexanol	No	1.00E+04
Glass	92% abs 4 in cyclohexanol	No	1.10E+04
Glass	94.9%, abs 1.55 in control	No	3627
Glass	94.9%, abs 1.55 in control	No	4372
Rinsed Melinex 453 back	94.9%, abs 1.55 in control	No	1.13E+04
Rinsed Melinex 453 back	94.9%, abs 1.5 in 5 (IPA):1 (water)	No	6513
Rinsed Melinex 453 back	94.9% abs 1.55 in control	Cyclohexanol	8829
Glass	95.5%, abs 2.35 in control	No	1744
Rinsed Melinex 453 back	95.5%,abs 2.35 in control	No	3665
Dupont Melinex 582	95.5%, abs 2.35 in control	No	4085
Rinsed Toray	95.5%, abs 2.35 in control	No	5686
glass	95.5%, abs 2.35 in control	PGME	2359
Rinsed Melinex 453 back	95.5%, abs 2.35 in control	PGME	5241

Following observations were made from the test results:

1. *Elimination of acrylic top coat by rinsing from PET (Toray, ST505) reduced Rs. Rinsing of non-acrylic PET (bare PET or PET with hydrophilic coating) did not change Rs, implying acrylic coat degraded surface conductivity..*
2. *Lower grade CNT ink in control solvent blend did not spread on bare PET (Melinex 453 backside) and parylene-coated PET. Depending on the severity of the non-wetting, the resulting CNT coatings had fluctuating conductivity from a value of glass control and or above $10^8 \Omega/\square$.*
3. *Addition of high boiling point solvents improved wetting and reduced conductivity. Selection and concentration of high boiling point solvents needs further optimization. Possible candidates identified are propylene glycol and hexylene glycol. These solvents unlike cyclohexanol and PGME, have comparable solubility parameters to control solvents.*
4. *For reasons unknown, higher grade CNT inks (94.9%, 95.5%) in control solvents did not always bead up on bare PET, despite the latter's lower-than-water surface energy. Conductivity of these inks on bare PET was comparable to that on glass. This is promising, requiring further work as the addition of*

high boiling point solvents is not a desirable approach towards enhanced surface conductivity.

5. *In most cases, PET with different sub-coats resulted in degraded conductivity over that on glass based on the same ink grade, with the following two exceptions:*
 - a. *On PET, 94.9% ink grade in 5:1 IPA/water resulted in enhanced conductivity over control solvents. This trend needs to be exploited further.*
 - b. *Electrical conductivity of CNT cast from cyclohexanol onto PET and glass were identical, though slightly lower than the control ink of the same grade and absorbance.*

7.3.8. Experimental Summary

This work demonstrated that by elimination of surfactants, smoothening layers and other polymeric sub-coats from PET surface leads to improved electrical conductivity comparable to that of CNT coated glass (control substrate) by a drawdown coating method. The key to achieving repeatable high conductivity on PET (as high as on glass), including uniform coating, is the elimination of de-wetting. This can be achieved by clean PET surfaces, and modified solvent systems while maintaining optimum ink dispersions.

Experiments demonstrated complex interactions between substrate, high boiling point solvent selection, ink solvent systems, ink grade and concentration. Certain substrate-solvent system combinations implied potential. Further work could be done to better understand these interactions and to optimize the substrate and solvent systems in order to achieve uniform coating and highest conductivity using the minimum amount of ink.

7.3.9. Spray Coating Transfer Method

An experimental spray head was purchased to spray SWNT ink onto a wide variety of substrates. Currently, Eikos uses a spraying system consisting of ultrasonic spray head and air directors to force the spray to the substrate. This system performs well in a batch process application, but doesn't have a large flow and may not be consistent enough to be used in multiple spray head applications. For this reason, larger volume spray head configurations are being considered. For this purpose, a company specializing spray nozzle technologies was contacted to identify suitable hardware for Eikos experiments.

Figure 74 : Air Atomizing Nozzle

The recommended spray head was an air atomizing pressure spray nozzle, as pictured in Figure 74. This nozzle can produce a slot or a round cone spray pattern, depending on the air cap used. Table 48 shows its performance, provided by Spray systems. This spray head can operate over a large range of air and liquid pressures. Such a wide range of conditions enables a broad range of process conditions to be performed.

Table 48: Performance Data for Pressure Spray Nozzle

10 PSI			20 PSI Liquid			30 PSI Liquid			40 PSI Liquid		
Air Press psi	gph	Scfm	Air Press psi	gph	Scfm	Air Press psi	gph	Scfm	Air Press psi	gph	Scfm
18	1.04	1.05	30	1.56	1.43	42	2.06	1.75	55	2.16	2.15
20	0.80	1.15	34	1.10	1.61	44	1.80	1.85	60	1.60	2.38
22	0.62	1.25	36	0.90	1.70	46	1.57	1.94	65	1.15	2.62
24	0.47	1.35	38	0.74	1.79	48	1.35	2.04	70	0.76	2.85
26	0.35	1.45	40	0.60	1.88	50	1.13	2.13	-	-	-
28	0.25	1.55	42	0.47	1.97	55	0.70	2.36	-	-	-

As a first experiment, two PET sheets were taped to a heated aluminum plate that was attached to a programmable X-Y table. The standard coating process requires the X-Y table to pass under the existing spray head multiple times in order to coat wider substrates. With the selected spray head, only the X mode was used as the spray head will coat the sample in one pass. Figure 75 below demonstrates a 13x18" PET sheets placed on the X-Y table ready to be coated with Invisicon ink. The plate is heated to speed with the ink drying process.

Figure 75: PET Sheet placed on a heated 13X18" aluminum plate. The plate is mounted to a programmable X-Y rail.

The spray head was mounted 10 inches above the X-Y table. This setting provided complete coverage for the substrate with the slot air cap spray method. The ink was placed in a pressurized vessel. The spray head has two inlets one for air and the other for liquid.

Initial process pressures selected for liquid and air were 10 and 20 PSI respectively. Plate X-direction speed was set at 1.5 inches per second for a full length of 23 inches. It thus took 15.3 seconds for the full platen length to travel under the spray head one time. A standard grade Invisicon ink (91.6% T @ 500 $\Omega/\square$ on glass) was used for this experiment. It was estimated that about 1.6X more ink for a comparable conductivity on PET substrate would be required. Two PET substrates were then coated with the previously described process conditions. It was discovered that many coatings were required to reach target Rs of 500 $\Omega/\square$. This is not surprising as a substantial amount of ink was wasted as it bounced off from the substrate. This problem can be addressed by adjusting the air and liquid pressure settings and air to ink mix ratios. Reduction in surface resistance with respect to number of CNT coats constructed is demonstrated in Table 49.

Table 49: Conductivity Development Profile

Number of Coats	Process Time, Mins	Rs, $\Omega/\square$
6	1.5	9800
12	3.1	2880
17	4.3	1475
23	5.9	1130
29	7.4	787
35	9.18	632
41	10.5	481

The coating constructed was normalized to 500 ohms/Square @550 nm, representing a low grade CNT ink. Coating uniformity and RT performance was found comparable to the hand sprayed control samples fabricated on glass surfaces. Furthermore, process time was reduced from an average of 40 to 10 minutes. The overall appearance of the Invisicon® coated sheet was satisfactory. The number of passes, or coating layers, can dramatically be reduced by using a higher quality of ink and adjusting the air to liquid ratios and process pressures.

These spray heads could be connected in-line in multiple rows principally to coat substrates of any size, as is currently employed in other coating applications. Additional process refinement obviously would be needed to derive into the optimum balance of process variables and CNT ink quality to that of coating performance. It was demonstrated that “off the self” type spray nozzles hardware is adequate to scale up Invisicon® coating technology too virtually any substrate size.

8. Conclusions

Eikos evaluated the transparent conductor requirements of photovoltaics that are currently manufactured and under development. In this process, we found that our current coatings did not meet the requirements of most commercial PV manufacturers, and thus we spent significant effort on improving the performance of nanotube coatings. Based on literature studies, we focused purification improvements, alterations in reflux conditions, dispersion quality, increasing the amount of metallic CNTs, and deposition of other materials to dope or otherwise increase the conductivity of the CNT coating. We achieved coatings that were greater than 90% transparent at 100 $\Omega/\square$.

In addition to performance improvements, we conducted significant characterization of the CNT coating and studied changes in the coating during environmental exposures. These studies assisted Eikos in developing material solutions to effectively eliminate environmental changes and maintain coating performance.

Eikos fabricated hundreds of solar cells under this program, indicative of a successful collaboration with NREL. We created organic PV, CIGS, and CdTe PVs that were enabled by Invisicon®. Devices demonstrated efficiencies ranging from 2.5% up to 13.0%. Eikos and NREL set several records for efficiency of solar cells that contained CNTs.

To demonstrate manufacturability, Eikos demonstrated multiple deposition techniques of CNT films on a wide variety of substrates. We also showed that the resulting coatings maintain optoelectronic properties using different methods. The coatings can be made to be exceptionally uniform or controllably patterned using additive and subtractive methods. Overall, Eikos has made significant progress in demonstrating the use of CNT coatings for solar cells, and we will continue to push ahead with out commercial partners to move towards commercialization.

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