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Continuous Manufacturing of Fine Denier, Conductive Yarns

Dr. Derek Hass

Directed Vapor Technologies International, Inc.

IFAI EXPO

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Composite Fibers

DVTI and its subsidiary, LEAF, have developed a high throughput, roll-to-roll manufacturing process, based on advanced Gas Jet Assisted – Physical Vapor Deposition techniques, for the creation of a new line of conductive and functionalized fibers.

Features:

- Applicable for wide range of multi-filament tows and monofilament fibers
- Proprietary process for enhanced adhesion
- Capability to deposit both simple metals and complex alloys / ceramics onto fibers
- Our advanced deposition process compares favorably with the cost of electroplating deposition

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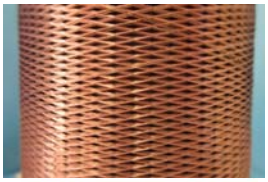
Composite Fibers

Conductive Composite Fibers

- Opportunity to create unique combinations of strength, density, conductivity, flex fatigue resistance.
- The very high density of copper (ρ = 8.9 g/cm^3) creates a significant weight savings opportunities if low density conductors can be utilized as a part of the electrical systems.
- Combinations of low density fiber substrates (polymers, glass, carbon) with high conductivity metals create the opportunity to create unique, light weight conducting materials.

Functionalized Fibers

- Combinations of fiber substrates with metal (single and bi-layer), alloy and ceramic layers can be used to create other types of functional fibers (i.e. energy storage, anti-static, antimicrobial, abrasion resistance, corrosion resistance, controlled bonding)



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Challenge:

Cost effective manufacture of composite fibers resulting in high performance, good outer layer adhesion and materials flexibility

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Conventional Manufacturing Approaches

Plating

- Plating processes are currently being employed to metallize polymeric fibers (such as Kevlar and Zylon), **but have not been demonstrated for many polymeric fibers (such as PEEK)**.
- These approaches have demonstrated some success and are utilized for wire EMI shielding applications, however, issues include:
  - Enhanced adhesion desired for some fiber types and applications. Poor adhesion can limit the thickness of deposited layers and can also be detrimental to flex fatigue performance (de-adhered coating sections act as failure initiation points).
  - A reduction in the fiber strength for some fiber types.
  - Processes for plating fibers can be complicated and often uses environmentally unfriendly materials.
  - Alloys, multilayered coating architectures and complex functional layers are a challenge and often not feasible.

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Conventional Manufacturing Approaches

Physical Vapor Deposition

- Strongly adhered layers can be obtained using physical vapor deposition (PVD) techniques that result in a chemical bond between the coating and the substrate.
- PVD approaches can also apply high quality, highly conductive layers. Wide range of metals, alloys and ceramics can be created.
- However, such approaches typically operate in an ultra-high vacuum, only deposit on line-of-sight regions of substrates and have low deposition rates making them economically unfeasible in composite fiber applications.
- Thus, high throughput PVD processes are desired to enable the affordable creation of high quality functional layers in a feasible manner

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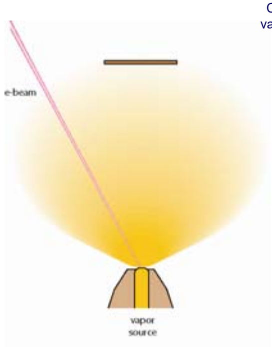
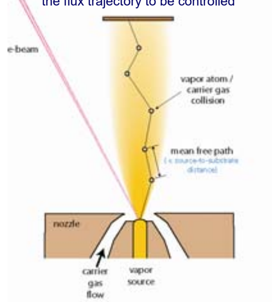
Gas Jet Assisted - PVD

Thermal Evaporation



Gas Jet Assisted – Physical Vapor Deposition

CONCEPT: Gas phase scattering of an evaporated vapor flux (by collisions with supersonic gas) enables the flux trajectory to be controlled



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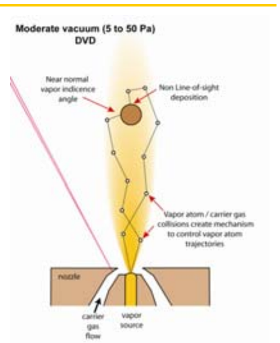
Gas Jet Assisted - PVD

<u>Rationale for DVD:</u>

- increase deposition efficiency of EB-PVD process
- increase deposition rate
- non-line-of-sight coating
- composition and morphology control
- soft vacuum – ease of use

DVD Coated Wire



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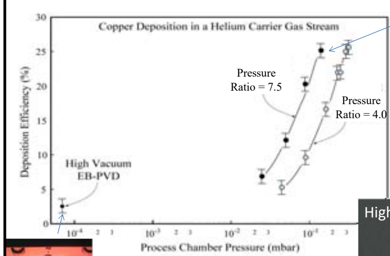
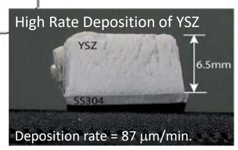
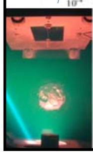
High Rate Deposition







High deposition rate achieved due to:

- High deposition efficiency
- High vapor creation rates

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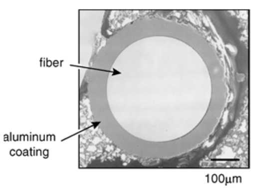
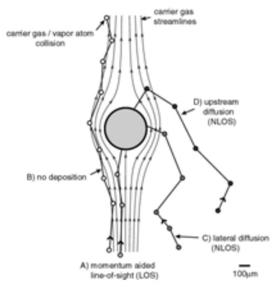
Non Line-of-sight Deposition





Vapor condenses by binary scattering from streamlines that carry flow around the vapor. The local coating thickness depends on the number density of the atoms (I.e. local pressure) and the flow velocity.

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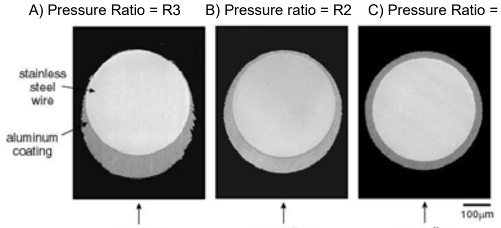
Non Line-of-sight Deposition

A) Pressure Ratio = R3 B) Pressure ratio = R2 C) Pressure Ratio = R1



The coating of a stationary steel wire with aluminum over a constant chamber pressure and a range of gas jet pressure ratios showing the change in the NLOS coating growth rate (top side of the wire) when the pressure ratio is decreased.

The increased growth rate at lower pressure ratios is a result of locally reduced gas jet velocities near the wire which promote lateral diffusion of the vapor atoms from the gas jet streamlines.

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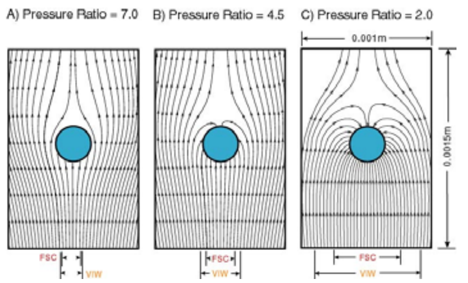
Vapor Atoms Interaction with Cylinder

Simulations showing the trajectories of aluminum vapor atoms around a fiber



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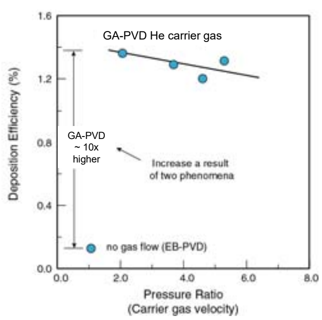
Deposition Efficiency (Fiber Substrate)



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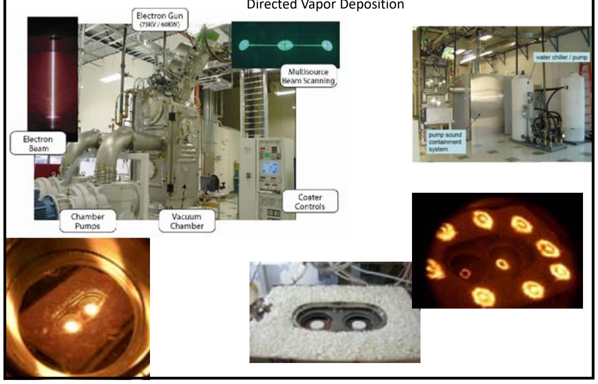
Production Scale GA-PVD Coater

Directed Vapor Deposition



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Gas Jet Assisted - PVD

Processing zones have been identified that enable:

- High vapor creation rates
- Atomistic deposition
- Controllable adatom energy (kinetic and thermal)
- High deposition efficiency
- Scaled coating zone

Result:

- High throughput deposition of high quality films onto a range of substrates

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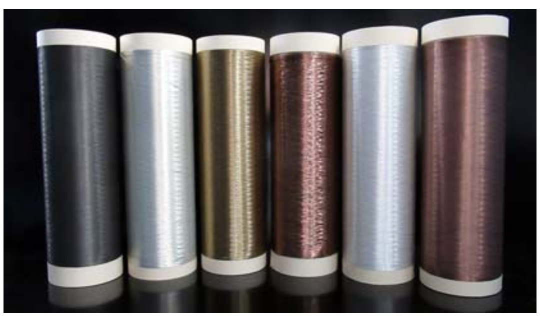
Application: Functional Coatings onto Fibers



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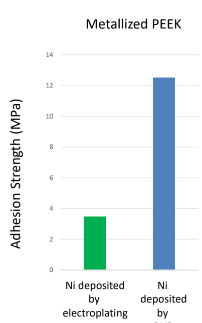
Metallized Polymers with High Adhesion



Values dependent on the material type and surface properties

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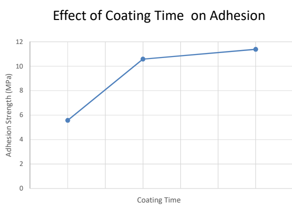
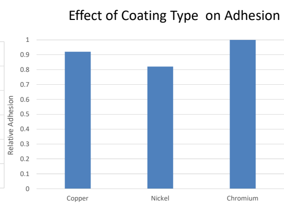
Metallized Polymers with High Adhesion





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Roll-to-Roll Manufacturing

Roll-to-roll manufacturing system enhanced in the DVD environment by:

- 3D Coating Zone
- Atmosphere to Vacuum Technology
- High deposition Efficiency
- NLOS (fiber substrates)
- Composition control for multi-layer deposition

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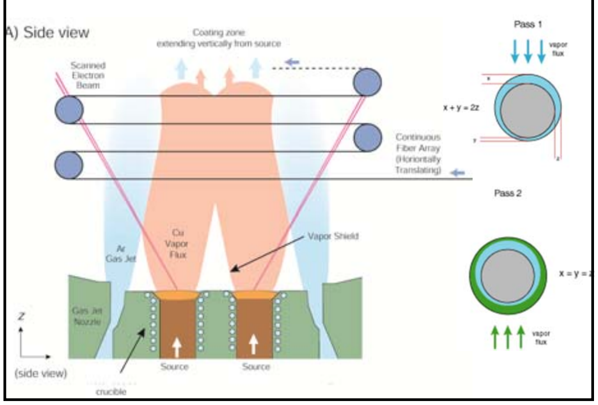
High Throughput Coating of Fibers



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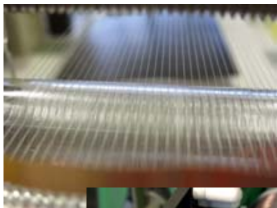
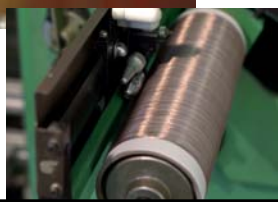
High Volume Manufacture





Multiple pass fiber handling system designed and integrated into DVD coating system

Enables:

- Multi-filament tows
- Low denier fibers and tows
- Fibers with low temperature resistance

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Finesse Product Line

Finesse Ag™: Fine denier, high performance, conductive yarn

- Available with fine denier (sub-100 denier), continuous filament base yarns
- High conductivity (Resistance < 10 ohms/ft.) achieved using strongly bonded silver layer
- Base yarns available include Aramids, PEEK, Nylon 6,6, Vectran, Glass
- Also available using alternate conductive layers and bi-layers (Au, Al, Cu, Sn)
- Nickel free design
- Enhanced adhesion results in high durability during subsequent manufacturing and use.

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Ag on Para-aramid

- Single layer of Ag deposited onto fiber surface
- Resistance < 6 ohms / ft. achieved.

- Good tow infiltration achievable
- Excellent performance in abrasion and oxidation testing

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Coating onto sub-100 Denier Para-aramid

Additional materials combinations

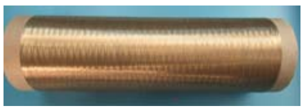
- **Al / Ag Bi-layer:** Provides increased conductivity and enhanced specific conductivity

  Resistance < 3.5 ohms/ ft.

- **Cu / Ag Bi-Layer:** Provide enhanced solderability

  Excellent wettability observed using Pb-Sn solder and R-mA flux

- **Au layer:** Provides enhanced corrosion resistance and elevated temperature durability



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Ag on 150 Denier PEEK Tow

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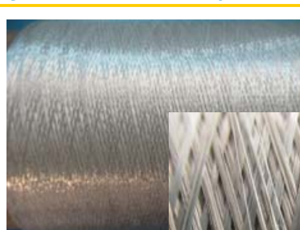
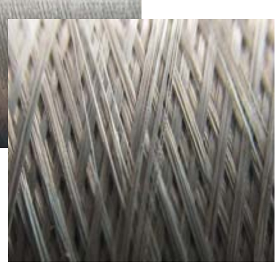
Ag on 200 Denier Nylon6,6





- Resistance = 8 ohm/ft.
- Passed Tape Test

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Cu on PEEK

Copper on 200 micron PEEK

- Resistance: < 5 ohms/ft obtained
- Passed tape test

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Cu-Ni Bilayers on PEEK

Final Nickel Layer

- Resistance: ~150 ohms/ft.
- Passed tape test

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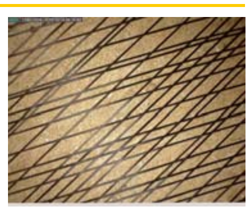
Ta on PEEK

Functional Layers for Radio Opacity

Passed Tape Test



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Coated PEEK - Braiding

- 15,000 ft. of coated PEEK manufactured and braided into tubular shape.
- Conductivity retained following braiding step.

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Tests Conducted on Composite PEEK Fibers

Resistance Spot Check – The resistance of the fiber is spot checked over a one meter length. Coated fiber resistances < 5 Ohms / ft. obtained. Values are thickness dependent

Flex Fatigue Test – The flex fatigue test works by winding and unwinding the fiber around a 10mm diameter tube. A basket is used to hold tension on the fiber.

Thermal Exposure – Sections of copper coated PEEK fibers were exposed to thermal exposures. Section was heated to 200C (60 minutes heating) and then cooled (240 minute cooling). No spallation of the copper coating was observed.

Tensile Strength – Coating process has only a minor effect on the tensile strength.

Elongation Test – Coating remained adhered and conductive following 3% strain on fiber.

Tape Test – Fibers are secured to a surface then a piece of scotch tape is placed on the center of the fiber and pressed down firmly and repeatedly. After more than two minutes the tape is removed and inspected for copper coating on tape.

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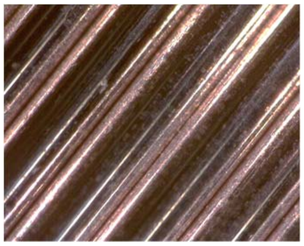
Cu on Polyester



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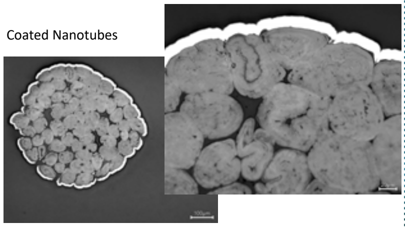
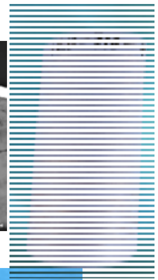
Copper Coating on CNT Yarn

Coated Nanotubes





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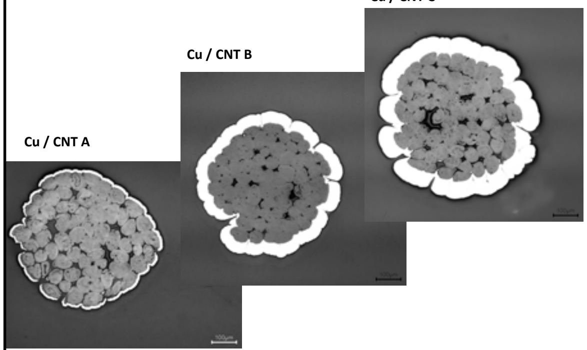
Cu/CNT Microstructure

Cu / CNT C

Cu / CNT B

Cu / CNT A



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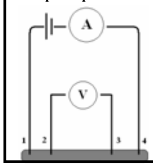
Conductivity Measurements

	V	I	R (Ω)	Test Length (m)	Ω/m	Wire Conductivity	Density (g/cc)	DC Specific Conductivity (Sm^2/kg)
CNT (Uncoated)	0.248	0.103	2.41	0.15	16.1	3.16E+05	0.577*	547.3
CNT (12 micron Cu)	0.125	1.948	0.064168	0.03175	2.021	2.40E+06	1.24	1940
CNT (45.5 micron Cu)	0.0159	1.944	0.008179	0.0026	0.2203	1.36E+07	3.37	4035
CNT (63.6 micron Cu)	0.0105	1.943	0.005404	0.03	0.125	2.23E+07	5.223	4261
Copper Wire	2.155	1.948	1.11	30.6	0.04	5.98E+07	8.91	6680

Four point probe conductivity test



Composite wires > 7X improvement in specific conductivity wrt uncoated CNT

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Advanced Materials

Functional Fibers for Energy Storage, Energy Harvesting

For example, vapor deposition can be used for the creation of:

- Anodes and cathodes of batteries
- Solid electrolytes
- Piezoelectric materials

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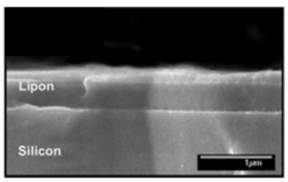
LiPON Electrolytes

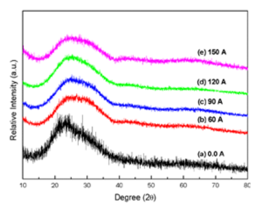
Lithium Phosphorous Oxynitride (LiPON) Electrolytes



Plasma activated DVD process was used to create LiPON films by evaporation of lithium phosphate in a nitrogen containing environment

Concepts for defects control also exist

- Dense LiPON films could be created at high rate (> 300x those of RF-magnetron sputtering)
- Suitable nitrogen incorporation could be controlled by altering plasma conditions
- Ionic conductivities of ~10^{-6} (S/cm) were achieved



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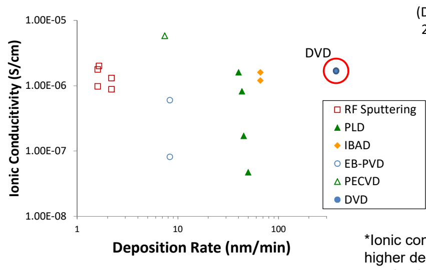
LiPON Solid Electrolyte



Current work*
(Deposition Rates of 2500 – 10,000X RF Sputtering)

*Ionic conductivity for higher deposition rates need to be determined during next steps

J. B. Bates and X. Yu, *J. Vac. Sci. Technol. A*, 14 (1996) 34-37.
S. Zhao et. al., *Thin Solid Films*, 415 (2002) 108-113.
F. Vereda, et. al., *Electrochem. Solid State Lett.* 5 (2002) A239-A241.
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Y. Hamon, et.al., *Solid State Ionics*, 177 (2006) 257-261.
Y.G. Kim, Ph. D. Thesis, University of Virginia, 2008.

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Summary

- Composite fibers (high strength, lightweight fiber + functional outer layer) are of interest in multiple applications. Improved adhesion resulting from advanced deposition processes can enhance the engineering performance of these materials.
- Environmentally friendly, gas jet assisted physical vapor deposition techniques (Directed Vapor Deposition) are suitable for the high throughput application of high quality coatings onto complex substrates.
- Gas jet assisted physical vapor deposition techniques have been used to create a functional coatings onto fibers (polymer, glass, CNT, ceramic). Both monofilament fibers and fiber tows have been demonstrated.
- Results to date indicate good adhesion along with suitable conductivity and flex fatigue performance.
- The enhanced performance of the resulting composite fibers coupled with cost effective production due to the scalability and environmental friendliness of such processes is envisioned to provide value added products across multiple markets.

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Thank You

Directed Vapor Technologies International, Inc.

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Or visit our booth at A961!

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