

Spotless Arc Directed Vapor Deposition (SA-DVD) and Related Method Thereof

RELATED APPLICATIONS

5 The present application claims priority from U.S. Provisional Application Serial No. 61/331,844, filed May 6, 2010, entitled "Spotless Arc Activated Directed Vapor Deposition Concept and Implementation Thereof" and U.S. Provisional Application Serial No. 61/366,711 filed July 22, 2010, entitled "Spotless Arc Activated Directed Vapor Deposition Concept and Implementation Thereof;" the disclosures of which are hereby
10 incorporated by reference herein in their entirety.

FIELD OF THE INVENTION

 The present invention relates generally to the field of physical vapor deposition from
15 point-like vapor sources. More specifically, the invention is in the subfield of plasma-assisted directed vapor deposition.

BACKGROUND OF THE INVENTION

20 Directed Vapor Deposition (DVD) is a physical vapor deposition (PVD) process that combines low vacuum electron beam (EB) evaporation with vapor entrainment in a flowing gas stream (gas jet) to efficiently deposit one or more evaporants upon a substrate. Plasma-activated Directed Vapor Deposition (PA-DVD) is a PVD technology that combines Electron Beam and Plasma Forming technologies to allow the creation of
25 coatings of controlled composition, structure and residual stress. In previous embodiments of PA-DVD, the plasma was created by a hollow cathode discharge. In this process, low voltage electrons together carried by an easily ionized inert gas jet are injected into the region where plasma activation is sought. Injection can occur at any angle to the vapor entraining gas jet. Coaxial concepts that align the plasma forming and vapor entraining
30 gas jets are preferred for many applications.

 However, the plasma activation of a DVD process by means of a hollow cathode discharge, suffers from several drawbacks. First, the plasma source's working gas emitted from the hollow cathode forms a high speed jet whose axis is often at an angle to the

direction of vapor transport. Slow moving or light (i.e. low momentum) vapor particles entrained in the vapor transport jet can be scattered away from the substrate by the working gas jet of the hollow cathode especially when oriented perpendicular to the vapor transporting jet. Second, the approach requires the use of considerable plasma working gas flow rates which has adverse economic consequences: Beside to the gas consumption, it also requires a more powerful vapor transporting carrier gas jet and, therefore, a higher capacity gas pumping system. Third, the hollow cathode plasma source and its supply and control units are costly and laborious to maintain. For instance, a radiation heater coil is used to initiate the discharge in existing installations. These heaters are subject to frequent failure resulting in a need for replacement. Fourth, the slow but steady vaporization of the heater and also of the hollow cathode itself (due to their high operation temperature and ion impingement) create contaminants that are incorporated in the deposited layers. It should be noted that these last four shortcomings of a DVD process by hollow cathode discharge hold true even in more recent hollow cathode technologies which align the hollow cathode discharge with the vapor transport.

There is a need for an improved plasma activation apparatus and method for the DVD process in order to eliminate the disadvantages of the existing, hollow cathode based plasma activation solution and to open up novel pathways for high-rate, economic and clean deposition.

SUMMARY OF THE INVENTION

An aspect of an embodiment of the present invention provides a plasma assisted directed vapor deposition process that utilizes a spotless arc directed vapor deposition (SA-DVD) method for the creation of the plasma in a directed vapor deposition apparatus. Vapor is created by electron or other high intensity directed energy beam evaporation from one or more source materials contained in a water cooled crucible. This vapor is entrained in a transonic helium or other gas jet and transported to a substrate for deposition. The electron or other directed energy beam used for evaporation is simultaneously exploited to weakly ionize the vapor and the jet forming gas (helium, or other gases including combinations of inert and reactant gases). An anode arranged and positioned near the electron beam impingement position and connected to a power supply attracts scattered electrons formed during the directed energy beams interaction with a target surface and

enables the formation of an arc discharge burning towards the surface of the evaporant which acts as the cathode. The arc discharge facilitates intense plasma. This plasma is at first transported towards the substrate by the vapor entraining gas jet through an ion-drag mechanism. However, if the substrate is sufficiently charged (electrically biased), the plasma ions are electrostatically accelerated towards the substrate and this extra momentum aids in vapor transport and deposition on a component surface. Since no plasma forming gas is injected into the deposition, this aspect of an embodiment of the present invention therefore overcomes many issues associated with the use of coaxial hollow cathodes for plasma activation in the DVD process and results in a low cost plasma assistance concept. Instead carrier gas jet is utilized for entraining the vapor plume as part of the process.

An aspect of an embodiment of the present invention therefore overcomes many issues associated with the use of coaxial hollow cathodes for plasma activation in the DVD process. For instance, some of the aspects of some the embodiments of the present invention may pertain to the following:

- The described arc discharge burns in the vapor of the evaporated material and in the gas jet, thus avoiding that additional plasma working gas has to be released into the deposition chamber. The arc plasma is localized and aligned with the shape and propagation of the vapor stream. Thus, no detrimental affection of the directed vapor plume does occur.
- High plasma density, high ion production rate and high degree of ionization (about 50% range) are characteristic for the method. These are aspects provided to reach a raise in the mean energy of condensing particles large enough to match the high deposition rates (about 15 $\mu\text{m}/\text{min}$ range) as well as to the stable functioning of the discharge despite the charge carrier drag-off by the gas jet as encountered in the DVD process.
- The apparatus and method reduces the complexity of the plasma source, avoid wearing parts and eliminate contamination sources, which results in an easy to maintain and low cost plasma activation concept.

A concept of an embodiment of the present invention also allows the vapor to be sprayed over a large area while simultaneously utilizing significant plasma assistance to control the coatings structure and properties.

In an approach, this can be achieved, e.g., either by arranging a group of crucibles, each one equipped with individual or collective anodes and means for generating the vapor transporting gas jets, adjacent to each other as a chain or array, or by sweeping the vapor plume of at least one crucible utilizing means for controlling the direction of the gas jet.

5 Furthermore, if the substrate is pulsed biased, a majority of the positive ions near the substrate can be electrostatically attracted and impact the substrate surface during the period when the substrate is negatively charged. Since the vapor atoms are contained in streamlines that pass near the substrate and have a characteristic speed of motion along the streamline (that is controlled by the jet flow conditions and substrate geometry), the time
10 between pulsed bias pulses can be used control where on a substrate deposition of the ions occurs. This enables the novel ability to control the thickness, structure, composition and residual stress as a function of position on the substrate. It will be of general utility to the field of vapor deposition from point like vapor sources.

An aspect of an embodiment of the present invention provides an apparatus for
15 applying at least one coating onto at least one substrate. The apparatus may comprise: a deposition chamber; at least one evaporant source; at least one energetic beam for impinging the at least one evaporant source forming a vapor plume; at least one anode positioned near the evaporant source for forming an arc discharge between the at least one anode and the at least one evaporant source; and at least one carrier gas forming at least
20 one jet for laterally-confined transport of the vapor plume toward the substrate.

An aspect of an embodiment of the present invention provides a method for applying at least one coating onto at least one substrate. The method may comprise: providing the at least one substrate; providing a deposition chamber; providing at least one evaporant source; impinging the at least one evaporant source with at least one energetic
25 beam to generate a vapor plume; forming an arc discharge between at least one anode and the at least one evaporant source; and emitting at least one carrier gas forming at least one jet in a direction that is at least substantially aligned with the vapor plume for laterally-confined transport of the vapor plume toward the substrate.

These and other objects, along with advantages and features of various aspects of
30 embodiments of the invention disclosed herein, will be made more apparent from the description, drawings and claims that follow.

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing and other objects, features and advantages of the present invention, as well as the invention itself, will be more fully understood from the following description of preferred embodiments, when read together with the accompanying drawings.

5 **FIG. 1** is a longitudinal section schematic view of an embodiment of the spotless arc directed vapor deposition (SA-DVD) apparatus and assembly.

FIG. 2 is an enlarged partial schematic view of an embodiment of the spotless arc directed vapor deposition (SA-DVD) apparatus and assembly as shown in **FIG. 1** (but for having a single evaporant source).

10 **FIG. 3** is a graphical representation that provides the relationship between chamber pressure (Nitrogen pressure, mbar) and the dynamic hardness of the coating deposited on the substrate (GPa) thereby showing an advantage associated with using a (high pressure) DVD embodiment of the spotless arc methodology.

FIG. 4 is a graphical representation that provides the relationship between the jet ion
15 current density (mA/cm^2) versus Jet flow (slm) as it pertains to the use of the carrier gas being ionized (e.g., Ar) or non ionized (e.g., He) and demonstrates the existence of an ion drag phenomenon when transonic gas jets intersect a plasma. . In the particular case study shown, a transverse hollow cathode discharge utilizing Ar as the working gas of the plasma source was crossed by either a He or an Ar carrier gas jet.

20 **FIG. 5** provides a schematic illustration of the effect of pulsed biasing as it pertains to coating a substrate.

FIG. 6 provides a schematic illustration of the streamlines on the carrier gas jet with entrained atoms and ions of the vapor plume.

FIG. 7 provides a schematic illustration of a technique to coat non-planar surfaces
25 either in a conformal or in a trench-filling deposition mode using appropriate bias voltages and carrier gas/vapor particle mixtures.

The accompanying drawings, which are incorporated into and form a part of the instant specification, illustrate several aspects and embodiments of the present invention and, together with the description herein, serve to explain the principles of the invention.
30 The drawings are provided only for the purpose of illustrating select embodiments of the invention and are not to be construed as limiting the invention.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

Turning now to the drawings, an aspect of an embodiment of the present invention, as schematically shown in **FIGs. 1-2**, is a method and apparatus **10** for applying at least one coating onto at least one substrate **20** (e.g., sample), utilizing a plasma assisted directed vapor deposition process. The apparatus may include a deposition chamber **30**, (having an upstream area **33** and a downstream area **35**) at least one evaporant source **40** (e.g., ingots or other types), at least one energetic directed energy (for example electron) beam **50** for impinging at least one of the evaporant sources **40** to form a vapor plume **90**, at least one anode **80** positioned near the evaporant source **40** for forming an arc discharge (not shown) between the anode **80** and the evaporant source **40**, and at least one carrier gas **70** forming at least one jet **71** for laterally-confined transport toward the substrate **20** as generally depicted in the **FIG. 1** as a dashed-line, **72**, confining the vapor plume **90** and/or plasma **105**. At least some of the elements included in the apparatus **10** may comprise a “nozzle” **15**, which may participate in applying at least one coating to at least one substrate **20**. In an approach, the anode **80** is positioned in an elevated position above the evaporant source **40**. In another approach, the anode **80** is positioned above the substrate **20**. The substrate **20** may be biased at about 0 to about +/- 200 Volts, or may be increased or decreased as desired or required.

In an approach, the energetic directed energy beam **50** may be produced by a variety of directed energy devices **52**, such as an electron beam gun, a laser source, or any other directed energy device now or later appreciated in the art. In the case of an electron beam gun **52**, it may be operated in either a low vacuum state, or at a reduced background pressure (i.e., a high vacuum state). For example, a low vacuum state of operation may be about 0.001 to above 100 Torr, but may be other levels as desired or required. The electron beam gun may be approximately a 70kV/10kW type, but not necessarily, as the voltage and wattage may vary as desired or required. The energetic beam **50** may comprise means to alter the beam impingement points among at least one of the evaporant sources **40**. For example, the means may include a solenoid **55** or deflection coil that may be positioned coaxially and/or partially proximal to the evaporant source **40**. The solenoid **55** is capable of at least partially bending the energetic beam **50**. The evaporant source may be a solid or fluid.

In an approach, the solenoid **55** may be positioned and energized such as to magnetically enhance the system's plasma-forming efficiency by causing the electrons to

move along spiral paths which increases the distance moved by the electrons and thus the probability of an ion-forming collision between the electron and an evaporant or gas jet forming atom. In an approach, the solenoid **55** may be provided to at least partially increase the plasma density, as well as facilitate an axial potential gradient for accelerating positive ions toward the substrate **20**.

In an approach, the means for emitting the carrier gas jet **71** may comprise an orifice **73** such as one of the following: pipe, conduit, tube, channel, hose, stem, duct, port, groove, passage, and tunnel. The shaping and transporting of the vapor plume **90** by the carrier gas jet **71** is achieved at least in part by physical and/or electrostatic interactions between the constituents of the vapor plume **90** and the carrier gas jet **71**. In an approach, the momentum of the carrier gas assists in the transport of the vapor plume toward the substrate. Moreover, the carrier gas jet **71** substantially shields the anode **80** from contact with the vapor plume **90** thereby reducing accumulation of evaporant upon the anode **80**. For instance, the shielding provided by the high atomic weight carrier gas reduces the undesirable accumulation of condensed evaporant upon the anode. The carrier gas jet **71** may be positioned at least substantially coaxially with the evaporant source **40**. In an approach, the shielding of the anode's surface against undesired deposition of vapor particles may be provided or improved by a "flushing gas" streaming through fine bore holes (not shown) from inside the anode **80** out into the downstream area **35**. The said bore holes may be arranged such that the flushing gas aids in shaping the vapor plume **90**, e.g., when streaming off the anode **80** radially-inwards.

The direction and/or intensity of the carrier gas jets **71** may be controlled for shaping and/or directing of the plasma **105**, or said vapor plume **90**, or both. The shaping and/or directing may be accomplished by controlling the pressure and/or gas flow rate of the carrier gas jet **71**. In an approach, the carrier gas jets may be positioned in an annular configuration around the evaporant source **40** with the evaporant source **40** being at least substantially coaxially integrated inside the annular configuration of the carrier gas jets **71**. The annular configuration may be a wide variety of array types. In an approach, the shaping and directing is accomplished by controlling the pressure and/or gas flow rate individually in each carrier gas jet of the array. Examples of the carrier gas may include one or more of any combination of the following: inert (e.g., He), reactive, (N₂, H₂, or O₂), or ion-forming (Ar, Xe, or Kr); as well as any other type of suitable carrier gases.

In the various embodiments discussed throughout, the relative pressure and/or gas flow rate of carrier gas jets **71** may be individually controlled for directional sweeping either of plasma, or said vapor plume, or both, from side to side.

In various embodiments, the carrier gas jets may introduce reactant gases. In an approach, the reactant gases may form compounds with the vapor plume atoms or molecules during transport in the carrier gas jets while in a vapor phase. In another approach, the reactant gases may form compounds by a chemical reaction on the deposition surface of the substrate. Alternatively, the reactant gases may form compounds with both modes: with the vapor plume during transport in the carrier gas jets while in a vapor phase; and by a chemical reaction on the deposition surface of the at least one substrate.

In an approach, the energetic beam **50** weakly ionizes the vapor plume **90** thereby forming a plasma **105**. Moreover, an arc discharge between the anode **80** and the evaporant source **40** efficiently ionizes predominantly the vapor particles thus increasing the ionization of the plasma **105** to provide a dense plasma region **100**. The carrier gas jet is predominantly ionized while intersecting the dense plasma region. In an approach, the current of the arc discharge may be changed so as to modulate or control the density of the plasma. In an approach, the balance between the vapor particle ions and carrier gas ions may be controlled by changing the flow and/or composition of the carrier gas. The ionized carrier gas jet has a momentum that can be controlled by electromagnetic forces. Alternatively, the carrier gas could be previously ionized; or a combination of prior ionization as well as ionization while in the dense plasma region. Controlling the ionized carrier gas jet and/or the ionized vapor particles entrained provides a manipulation of the surface topology and internal phases, structures and stresses of at least one coating or portions of coating(s) of the substrate.

In an approach, the anode **80** may be ring-shaped or annular and be positioned at least substantially coaxial with at least one carrier gas jet. In an approach, the anode is segmented to form two or more anode segments, electrically isolated against each other and mechanically arranged such that each segment of the anode corresponds to one of the evaporant sources **40**. When powered by individually controllable current supplies, this approach provides that the ionization of the vapor particles generated at different evaporant sources **40** can be controlled independently of each other.

In an approach, an embodiment of the apparatus **10** may comprise at least one cooling device **42** for cooling the at least one evaporant source **40**. For example, the cooling device **42** may be a crucible, water or fluid cooled crucible, or other devices as desired or required. The crucible may be biased at about 0 to about -10 Volts, or as
5 desired or required.

In an approach, an embodiment of the apparatus **10** may comprise a bias voltage **57** that is applied to the substrate **20** for accelerating ions toward said substrate **20**.

Accordingly, in an approach, an electrostatic ion extraction and acceleration region **58** is provided, as shown in **FIG. 2**. It should be appreciated that the bias voltage **57** may be a
10 DC, AC, or a pulsed voltage of either positive, negative or both signs. The range may be about 0 to about 10^3 V or may be varied as desired or required. An exemplary embodiment having a range of about 100 to about 200 V is shown. Additionally, in an approach a heat source **59** may be provided for advantageous heating of the substrate **20** or impact of the ions may be used to accomplish this heating. The heater or heating may be optional.

15 An aspect of an embodiment of the present invention method and apparatus **10** includes controlling the frequency of the substrate's pulsed bias voltage **57** to alter the deposition location on the substrate **20** so as to control the thickness, structure, composition, residual stress, and/or other coating properties on the substrate **20**.

Moreover, another aspect of an embodiment of the apparatus includes a directed energy
20 beam **50** for impinging at least one of the evaporant source **40** to form a vapor plume **90**. The directed energy beam **50** may also be controlled to alter the directed energy incident upon the evaporation, such as by pulsating the directed energy beam. In this way, it is possible to create a finite length (slug) of vapor that arrives at the substrate location at speed determined by the jet flow conditions. Further yet, an aspect of an embodiment may
25 include coordinating the control of both the substrate bias voltage **57** and the directed energy beam **50**. As result of this coordination, this will further enhance the ability to control the thickness, structure, composition, residual stress, other coating properties and/or location of the region of deposition on the substrate. For instance, controlling may include modifying the phase of the pulsation to both the substrate bias voltage and the
30 directed energy beam.

In an approach, the anode may be configured for creating a magnetic field and for guiding a magnetic flux such that the magnetic field lines in front of the anode are substantially parallel to its surface and radially directed thus forming a closed electron

drift track in circumferential direction which is substantially parallel to the surface of the anode **80**. The magnetic field facilitates an axial potential gradient for accelerating positive ions toward the substrate **20**.

FIG. 3 is a graphical representation that provides the relationship between chamber pressure (Nitrogen pressure, mbar) and the dynamic hardness of the coating deposited on the substrate (GPa) thereby showing an advantage associated with using an embodiment of the spotless arc methodology. By extending the operating pressure of the spotless arc process from that previously envisaged into the higher pressure regime of the DVD process significantly harder coatings can be created.

Turning to **FIG. 4**, **FIG. 4** is a graphical representation that provides the relationship between the jet ion current density (mA/cm^2) versus Jet flow (slm). It shows that the ion current reaching a substrate can be increased when plasma is intersected by a gas jet, and that this effect scales with the atomic weight of the gas jet and plasma particles. This points to an ion drag process in which collisions between the gas jet atoms and the ions directs the ions preferentially towards the substrate resulting in a non electrostatic means for manipulating plasmas.

FIG. 5 provides a schematic illustration of the effect of pulsed biasing approach as it pertains to coating a substrate **20**. **FIG. 5A** illustrates interaction between the coating ions **24** and the non-biased substrate **20** (i.e., wherein no bias voltage is being applied). A plasma sheath **22** of thickness, d_s , is formed and positive charge coating ions **24** in the sheath **22** are attracted to the substrate **20** by a sheath potential. **FIG. 5B** illustrates that as a negative bias voltage is applied (or increased) the thickness, d_s , of the sheath **22** increases. The thickness expands and correspondingly an increased flux of coating ions **24** are attracted from the vapor plume to the substrate **20**. Some ions also collide with coating neutrals, i.e., neutral coating atoms **26**, and scatter them toward the substrate further increasing the fraction of vapor atoms that are deposited on the substrate. **FIG. 5C** illustrates that as the bias voltage is turned off the thickness, d_s , of the sheath **22** initially increases because of prior removal of the ions from the sheath. The thickness expands and correspondently an increased flux of coating ions **24** are attracted to the substrate **20**. Some ions again also collide with coating neutrals, i.e., neutral coating atoms **26**, and scatter them toward the substrate. Most of the ions are deposited to the substrate leaving a positive ion-depleted region **28**. Eventually the plasma sheath collapses back to its original (non biased) value.

FIG. 6 provides a schematic illustration of the streamlines **75** on the carrier gas jet **71** with entrained atoms and ions of the vapor plume. The carrier gas jet **71** provides positive ions to replenish the positive ion depleted region as describe in **FIG. 5C**. The replenishment of vapor depositing atoms or ions occurs by motion of these particles ion the streamlines that flow around the substrate. The particles to be deposited move along the streamlines at a speed that is controlled by the jet flow conditions and the substrate geometry. If the time between bias pulses is large compared with the time for a particle in a stream line to traverse the substrate, the particles near the substrae are fully replenished between pulses. An exemplary pulse rate may be about 10^4 Hz that is 100 μ s between pulses, but may be adjusted as desired or required. The coating ion rich gas jet streamlines may have a particle velocity of about 1,000 m/s (particles move above the substrate a distance of about 1mm per 1 μ s); or may vary as desired or required. A 1mm length above the substrate would therefore be replenished between these pulses. By manipulating the speed of particles in the streamline and the period between pulses, it is possible to create uniform or highly localized deposition and plasma assistance effects from inert gas or condensing atom impacts with the substrate.

FIG. 7 provides a schematic illustration of a technique to coat non-planar surfaces, for example, using a constant bias. Referring to **FIG. 7A**, energetic heavy coating ions **24** collide with previously deposited coatings **25**, for example, a metal coating and resputter coating atoms **27** to regions (e.g., groves) on the substrate that normally receive a low coating atom flux. The resulting accumulated coating **29** due to the resputter coating atoms is illustrated in **FIGS. 7B** and **7C**.

The devices, systems, compositions, apparatuses, and methods of various embodiments of the invention disclosed herein may utilize aspects disclosed in the following references, applications, publications and patents and which are hereby incorporated by reference herein in their entirety:

U.S. Patent No. 5,368,897, Kurihira, et al., "Method for Arc Discharge Plasma Vapor Deposition of Diamond", November 29, 1994.

U.S. Patent No. 4,668,365, Foster, et al., "Apparatus and Method for Magnetron-Enhanced Plasma-Assisted Chemical Vapor Deposition", May 26, 1987.

U.S. Patent No. 5,242,530, Batey, et al., "Pulsed Gas Plasma-Enhanced Chemical Vapor Deposition of Silicon", September 7, 1993.

U.S. Patent No. 5,614,273, Goedicke, et al., "Process and Apparatus for Plasma-Activated Electron Beam Vaporization", March 25, 1997.

U.S. Patent No. 5,780,803, Goedicke, et al., "Process for the Stabilization of Plasma Generation by Means of Electron Beam Vaporizer", July 14, 1988.

5 U.S. Patent No. 6,083,356, Goedicke, et al., "Method and Device for Pre-Treatment of Substrates", July 4, 2000.

International Patent Application No. PCT/US2010/025259, February 24, 2010, entitled "Coaxial Hollow Cathode Plasma Assisted Directed Vapor Deposition and Related Method Thereof;"

10 International Patent Application No. PCT/US2008/073071, filed August 13, 2008, entitled "Thin Film Battery Synthesis by Directed Vapor Deposition"; Haydn N.G. Wadley;

U.S. Patent Application No. 12/733,160, filed February 16, 2010, entitled "Thin Film Battery Synthesis by Directed Vapor Deposition"; Haydn N.G. Wadley;

15 International Patent Application No. PCT/US2006/025978, filed June 30, 2006, entitled "Reliant Thermal Barrier Coating System and Related Methods and Apparatus of Making the Same"; Haydn N.G. Wadley;

U.S. Patent Application No. 11/917,585, filed December 14, 2007, entitled "Reliant Thermal Barrier Coating System and Related Methods and Apparatus of Making
20 the Same"; Haydn N.G. Wadley;

U.S. Patent Application Serial No. 11/788,958 filed April 23, 2007, entitled "Multifunctional Battery and Method of Making the Same, ; U.S. Patent Application Publication No. 2007-0269716, November 22, 2007;

International Patent Application No. PCT/US2001/022266, filed July 16, 2001,
25 entitled "Method And Apparatus For Heat Exchange Using Hollow Foams and Interconnected Networks and Method of Making the Same"; Haydn N.G. Wadley;

U.S. Patent Application No. 10/333,004, filed January 14, 2003, entitled "Heat Exchange Foam"; Haydn N.G. Wadley, U.S. Patent No. 7,401,643, issued 7/22/2008;

U.S. Patent Application No. 11/928,161, filed October 30, 2007, entitled "Method
30 and Apparatus for Heat Exchange Using Hollow Foams and Interconnected Networks and Method of Making the Same"; Haydn N.G. Wadley;

International Patent Application No. PCT/US2005/000606, filed January 10, 2005, entitled "Apparatus and Method for Applying Coatings onto the Interior Surfaces of Components and Related Structures Produced There from"; Haydn N.G. Wadley;

U.S. Patent Application No. 10/584,682, filed June 28, 2006, entitled "Apparatus
5 and Method for Applying Coatings onto the Interior Surfaces of Components and Related Structures Produced There from"; Haydn N.G. Wadley;

International Patent Application No. PCT/US2004/024232, filed July 28, 2004, entitled "Method for Application of a Thermal Barrier Coating and Resultant Structure
Thereof"; Haydn N.G. Wadley;

10 U.S. Patent Application No. 10/566,316, filed February 14, 2006, entitled "Method for Application of a Thermal Barrier Coating and Resultant Structure Thereof"; Haydn N.G. Wadley;

International Patent Application No. PCT/US2003/037485, filed November 21, 2003, entitled "Bond Coat for a Thermal Barrier Coating System and Related Method
15 Thereof"; Haydn N.G. Wadley;

U.S. Patent Application No. 10/535,364, filed May 18, 2005, entitled "Bond Coat for a Thermal Barrier Coating System and Related Method Thereof"; Haydn N.G. Wadley;

20 International Patent Application No. PCT/US2003/036035, filed November 12, 2003, entitled "Extremely Strain Tolerant Thermal Protection Coating and Related Method and Apparatus Thereof"; Haydn N.G. Wadley;

U.S. Patent Application No. 10/533,993, filed May 5, 2005, entitled "Extremely Strain Tolerant Thermal Protection Coating and Related Method and Apparatus Thereof"; Haydn N.G. Wadley;

25 International Patent Application No. PCT/US2003/023111, filed July 24, 2003, entitled "Method and Apparatus for Dispersion Strengthened Bond Coats for Thermal Barrier Coatings"; Haydn N.G. Wadley;

U.S. Patent Application No. 10/522,076, filed January 21, 2005, entitled "Method and Apparatus for Dispersion Strengthened Bond Coats for Thermal Barrier Coatings";
30 Haydn N.G. Wadley;

International Patent Application No. PCT/US2003/012920, filed April 25, 2003, entitled "Apparatus and Method for Uniform Line of Sight and Non-Line of Sight Coating at High Rate"; Haydn N.G. Wadley;

U.S. Patent Application No. 10/512,161, filed October 15, 2004, entitled “Apparatus and Method for Uniform Line of Sight and Non-Line of Sight Coating at High Rate”; Haydn N.G. Wadley;

International Patent Application No. PCT/US2002/28654, filed September 10, 2002, entitled “Method and Apparatus for Application of Metallic Alloy Coatings”; Haydn N.G. Wadley;

U.S. Patent Application No. 10/489,090, filed March 9, 2004, entitled “Method and Apparatus Application of Metallic Alloy Coatings”; Haydn N.G. Wadley;

International Patent Application No. PCT/US2002/13639, filed April 30, 2002, entitled “Method and Apparatus for Efficient Application of Substrate Coating”; Haydn N.G. Wadley;

U.S. Patent Application No. 10/476,309, filed October 29, 2003, entitled “Method and Apparatus for Efficient Application of Substrate Coating”; Haydn N.G. Wadley;

International Patent Application No. PCT/US2001/16693, filed May 23, 2001, entitled “A Process and Apparatus for Plasma Activated Deposition In Vacuum”; Haydn N.G. Wadley;

U.S. Patent Application No. 10/297,347, filed November 21, 2002, entitled “Process and Apparatus for Plasma Activated Deposition in a Vacuum”; Haydn N.G. Wadley; U.S. Patent No. 7,014,889, issued March 21, 2006.

U.S. Patent Application No. 09/634,457, filed August 7, 2000, entitled “Apparatus and Method for Intra-Layer Modulation of the Material Deposition and Assist Beam and the Multilayer Structure Produced There from”; Haydn N.G. Wadley; U.S. Patent No. 6,478,931, issued November 12, 2002.

U.S. Patent Application No. 10/246,018, filed September 18, 2002, entitled “Apparatus and Method for Intra-layer Modulation of the Material Deposition and Assist Beam and the Multilayer Structure Produced There from”; Haydn N.G. Wadley;

International Patent Application No. PCT/US2001/025158, filed August 10, 2001, entitled “Multifunctional Battery And Method Of Making The Same”; Haydn N.G. Wadley;

U.S. Patent Application No. 10/110,368, filed July 22, 2002, entitled “Multifunctional Battery and Method of Making the Same”; Haydn N.G. Wadley; U.S. Patent No. 7,211,348, issued May 1, 2007;

International Patent Application No. PCTUS1999/13450, filed June 15, 1999, entitled "Apparatus And Method For Producing Thermal Barrier Coatings"; Haydn N.G. Wadley;

International Patent Application Publication No. PCT/US1997/11185, filed July 8, 1997, entitled "Production Of Nanometer Particles By Directed Vapor Deposition Of Electron Beam Evaporant"; Haydn N.G. Wadley;

U.S. Patent Application No. 08/679,435, filed July 8, 1996, entitled "Production of Nanometer Particles by Directed Vapor Deposition of Electron Beam Evaporant"; Haydn N.G. Wadley; U.S. Patent No. 5,736,073, issued April 7, 1998;

U.S. Patent Application No. 08/298,614, filed August 31, 1994, entitled "Directed Vapor Deposition of Electron Beam Evaporant"; Haydn N.G. Wadley; U.S. Patent No. 5,534,314, issued July 9, 1996; and

U.S. Patent No. 5,635,087, Schiller, et al., "Apparatus for Plasma-Assisted High Rate Electron Beam Vaporization", issued June 3, 1997.

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Unless clearly specified to the contrary, there is no requirement for any particular described or illustrated activity or element, any particular sequence or such activities, any particular size, speed, material, duration, contour, dimension or frequency, or any particularly interrelationship of such elements. Moreover, any activity can be repeated, any activity can be performed by multiple entities, and/or any element can be duplicated. Further, any activity or element can be excluded, the sequence of activities can vary, and/or the interrelationship of elements can vary. It should be appreciated that aspects of

the present invention may have a variety of sizes, contours, shapes, compositions and materials as desired or required.

In summary, while the present invention has been described with respect to specific embodiments, many modifications, variations, alterations, substitutions, and equivalents will be apparent to those skilled in the art. The present invention is not to be limited in scope by the specific embodiment described herein. Indeed, various modifications of the present invention, in addition to those described herein, will be apparent to those of skill in the art from the foregoing description and accompanying drawings. Accordingly, the invention is to be considered as limited only by the spirit and scope of the following claims, including all modifications and equivalents.

Still other embodiments will become readily apparent to those skilled in this art from reading the above-recited detailed description and drawings of certain exemplary embodiments. It should be understood that numerous variations, modifications, and additional embodiments are possible, and accordingly, all such variations, modifications, and embodiments are to be regarded as being within the spirit and scope of this application. For example, regardless of the content of any portion (e.g., title, field, background, summary, abstract, drawing figure, etc.) of this application, unless clearly specified to the contrary, there is no requirement for the inclusion in any claim herein or of any application claiming priority hereto of any particular described or illustrated activity or element, any particular sequence of such activities, or any particular interrelationship of such elements. Moreover, any activity can be repeated, any activity can be performed by multiple entities, and/or any element can be duplicated. Further, any activity or element can be excluded, the sequence of activities can vary, and/or the interrelationship of elements can vary. Unless clearly specified to the contrary, there is no requirement for any particular described or illustrated activity or element, any particular sequence or such activities, any particular size, speed, material, dimension or frequency, or any particularly interrelationship of such elements. Accordingly, the descriptions and drawings are to be regarded as illustrative in nature, and not as restrictive. Moreover, when any number or range is described herein, unless clearly stated otherwise, that number or range is approximate. When any range is described herein, unless clearly stated otherwise, that range includes all values therein and all sub ranges therein. Any information in any material (e.g., a United States/foreign patent, United States/foreign patent application, book, article, etc.) that has been incorporated by reference herein, is only incorporated by

reference to the extent that no conflict exists between such information and the other statements and drawings set forth herein. In the event of such conflict, including a conflict that would render invalid any claim herein or seeking priority hereto, then any such conflicting information in such incorporated by reference material is specifically not

5 incorporated by reference herein.

CLAIMS

We claim:

1. An apparatus for applying at least one coating onto at least one substrate, said apparatus comprising:

5 a deposition chamber;

at least one evaporant source;

at least one energetic beam for impinging said at least one evaporant source forming a vapor plume;

at least one anode positioned near said evaporant source for forming an arc

10 discharge between said at least one anode and said at least one evaporant source; and

at least one carrier gas forming at least one jet for laterally-confined transport of said vapor plume toward the substrate.

2. The apparatus of claim 1, wherein said at least one evaporant source is a solid.

3. The apparatus of claim 1, wherein said at least one carrier gas jet at least partially assists in shaping and transporting said vapor plume to said at least one substrate.

4. The apparatus of claim 3, wherein the means for emitting said carrier gas jet comprises at least one of the following: pipe, conduit, tube, channel, hose, stem, duct, port, groove, passage, and tunnel.

5. The apparatus of claim 3, wherein said shaping and transporting of said vapor plume by said carrier gas jet is achieved at least in part by physical and/or electrostatic interactions between the constituents of said vapor plume and said carrier gas jet.

6. The apparatus of claim 1, wherein said at least one carrier gas jet at least substantially shields said at least one anode from contact with said vapor plume for reducing accumulation of evaporant upon said at least one anode.

7. The apparatus of claim 1, wherein said at least one carrier gas jet is positioned at least substantially coaxially with said at least one evaporant source.

8. The apparatus of claim 7, wherein said at least one carrier gas jet at least partially assists in shaping and transporting said vapor plume to said substrate.

9. The apparatus of claim 7, wherein upon said at least one carrier gas jet being ionized, said at least one ionized carrier gas jet has a momentum that can be controlled by electromagnetic forces.

10. The apparatus of claim 9, wherein said controlled at least one ionized carrier gas jet provides a manipulation of the surface topology and internal phases, structures and stresses of said at least one coating of said at least one substrate.

11. The apparatus of claim 1, wherein said energetic beam ionizes said vapor plume, forming a plasma.

12. The apparatus of claim 11, wherein said arc discharge increases the ionization of said plasma to provide a dense plasma region.

13. The apparatus of claim 1, further comprising at least one cooling device for cooling said at least one evaporant source.

14. The apparatus of claim 13, wherein said cooling devices comprises a crucible.

15. The apparatus of claim 11, wherein the direction and/or intensity of said at least one carrier gas jets may be controlled for shaping and/or directing of said plasma, or said vapor plume, or both.

16. The apparatus of claim 15, wherein said shaping and/or directing is accomplished by controlling the pressure of said at least one carrier gas jet or controlling the gas flow rate of said at least one carrier gas jet.

17. The apparatus of claim 1, wherein said at least one carrier gas jets are positioned in an annular configuration around said at least one evaporant source with the

evaporant source at least substantially coaxially integrated inside said annular configuration.

18. The apparatus of claim 17, wherein said annular configuration provides an array.

19. The apparatus of claim 17, wherein the direction and/or intensity of said at least one carrier gas jets may be controlled for shaping and/or directing of said plasma, or said vapor plume, or both.

20. The apparatus of claim 19, wherein said shaping and directing is accomplished by controlling the pressure individually in each carrier gas jet or controlling the gas flow rate individually in each carrier gas jet.

21. The apparatus of claim 20, wherein the relative pressure and/or gas flow rate of said carrier gas jets may be individually controlled for directional sweeping either of said plasma, or said vapor plume, or both, from side to side.

22. The apparatus of claim 1, wherein said energetic beam is produced by an electron beam gun or a laser source.

23. The apparatus of claim 1, wherein said energetic beam source further comprises means to alter the beam impingement points among said at least one evaporant sources.

24. The apparatus of claim 1, further comprising a bias voltage applied to said substrate for accelerating ions toward said substrate.

25. The apparatus of claim 24, wherein:
said energetic beam ionizes said vapor plume, forming a plasma; and
said bias voltage electrostatically accelerates ions in said plasma towards said at least one substrate thereby providing an extra momentum and this momentum aids in transporting said vapor plume to said at least one substrate.

26. The apparatus of claim 24, wherein said bias voltage is a DC, AC, or pulsed voltage.

27. The apparatus of claim 26, wherein said pulsed bias voltage is controlled to alter the deposition location on said at least one substrate to control the thickness, structure, composition, residual stress, and/or other coating properties on said at least one substrate.

28. The apparatus of claim 1, wherein said carrier gas jets introduce reactant gases.

29. The apparatus of claim 28, wherein said reactant gases form compounds with said vapor plume during transport in said carrier gas jets while in a vapor phase.

30. The apparatus of claim 28, wherein said reactant gases form compounds by a chemical reaction on the deposition surface of said at least one substrate.

31. The apparatus of claim 1, wherein said at least one carrier gas jets helps to shape said vapor plume and its momentum assists in transport of said vapor plume toward said at least one substrate.

32. The apparatus of claim 1, wherein said anode is annular.

33. The apparatus of claim 32, wherein said anode is positioned at least substantially coaxial with said at least one carrier gas jet.

34. The apparatus of claim 32, wherein said anode is segmented to form two or more anode segments.

35. The apparatus of claim 32, wherein said anode further comprises means for creating a magnetic field and for guiding a magnetic flux such that the magnetic field lines in front of said anode are substantially parallel to its surface and radially directed thus

forming a closed electron drift track in circumferential direction which is substantially parallel to said anode's surface.

36. The apparatus of claim 35, wherein said magnetic field facilitates an axial potential gradient for accelerating positive ions toward said substrate.

37. The apparatus of claim 1, further comprising a solenoid positioned coaxially and at least partially proximal to said evaporant source.

38. The apparatus of claim 37, wherein said solenoid is capable of at least partially bending said energetic beam.

39. The apparatus of claim 37, wherein said solenoid is positioned and energized such as to magnetically enhance said anode's efficiency.

40. The apparatus of claim 37, wherein said solenoid at least partially increases plasma density and facilitates an axial potential gradient for accelerating positive ions toward said substrate.

41. The apparatus of claim 1, wherein said anode is positioned in an elevated position above said evaporant source.

42. The apparatus of claim 1, wherein said anode is positioned above said substrate.

43. A method for applying at least one coating onto at least one substrate, said method comprising:

providing the at least one substrate;

providing a deposition chamber;

providing at least one evaporant source;

impinging said at least one evaporant source with at least one energetic beam to generate a vapor plume;

forming an arc discharge between at least one anode and said at least one evaporant source; and

emitting at least one carrier gas forming at least one jet in a direction that is at least substantially aligned with said vapor plume for laterally-confined transport of said vapor plume toward said substrate.

44. The method of claim 43, wherein said at least one evaporant source is a solid.

45. The method of claim 43, wherein said at least one carrier gas jet at least partially assists in shaping and transporting said vapor plume to said at least one substrate.

46. The method of claim 45, wherein the means for emitting said carrier gas jet comprises at least one of the following: pipe, conduit, tube, channel, hose, stem, duct, port, groove, passage, and tunnel.

47. The method of claim 45, wherein said shaping and transporting of said vapor plume by said carrier gas jet is achieved at least in part by physical and/or electrostatic interactions between the constituents of said vapor plume and said carrier gas jet.

48. The method of claim 45, wherein said at least one carrier gas jet at least substantially shields said at least one anode from contact with said vapor plume.

49. The method of claim 43, wherein said at least one carrier gas jet is positioned at least substantially coaxially with said at least one evaporant source.

50. The method of claim 49, wherein said at least one carrier gas jet at least partially assists in shaping and transporting said vapor plume to said substrate.

51. The method of claim 49, wherein upon said at least one carrier gas jet being ionized, said method comprises controlling the momentum of said at least one ionized carrier gas jet by electromagnetic forces.

52. The method of claim 51, further comprising manipulating the surface topology and internal phases, structures, and stresses of the coating of said at least one substrate using said controlled at least one ionized carrier gas jet.

5 53. The method of claim 43, wherein said energetic beam ionizes said vapor plume, forming a plasma.

54. The method of claim 53, further comprising changing the current of said arch discharge to modulate or control the density of said plasma.

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55. The method of claim 43, further comprising providing at least one cooling device for cooling said at least one evaporant source.

56. The method of claim 55, wherein said cooling source comprises a crucible.

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57. The method of claim 53, controlling the direction and/or intensity of said at least one carrier gas jets for shaping and/or directing of said plasma, or said vapor plume, or both.

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58. The method of claim 57, wherein said shaping and/or directing is accomplished by controlling the pressure of said at least one carrier gas jet or controlling the gas flow rate of said at least one carrier gas jet.

25 59. The method of claim 43, wherein said at least one carrier gas jets are positioned in an annular configuration around said at least one evaporant source with the evaporant source at least substantially coaxially integrated inside said annular configuration.

60. The method of claim 59, wherein said annular configuration provides an array.

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61. The method of claim 59, further comprising controlling the direction and/or intensity of said at least one carrier gas jets for shaping and/or directing of said plasma, or said vapor plume, or both.

62. The method of claim 61, wherein said shaping and directing is accomplished by controlling the pressure individually in each carrier gas jet or controlling the gas flow rate individually in each carrier gas jet.

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63. The method of claim 62, further comprising controlling said relative pressure and/or gas flow rate of said carrier gas jets for directional sweeping either of said plasma, or said vapor plume, or both, from side to side.

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64. The method of claim 43, further comprising altering the beam impingement points among said at least one evaporant sources.

65. The method of claim 64, wherein the means for altering the beam impingement points comprises at least one deflection coil.

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66. The method of claim 43, further comprising applying a bias voltage to said substrate for accelerating ions toward said substrate.

67. The method of claim 66, wherein:

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said energetic beam ionizes said vapor plume, forming a plasma; and
said bias voltage electrostatically accelerates ions in said plasma towards said at least one substrate thereby providing an extra momentum and this momentum aids in transporting said vapor plume to said at least one substrate.

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68. The method of claim 66, wherein said bias voltage is a DC, AC, or pulsed voltage.

69. The method of claim 68, further comprising controlling the frequency of said pulsed bias voltage to alter the deposition location on said at least one substrate to control the thickness, structure, composition, residual stress, and/or other coating properties on said at least one substrate.

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70. The method of claim 43, wherein said carrier gas jets introduce reactant gases.

71. The method of claim 70, wherein said reactant gases form compounds with said vapor plume during transport in said carrier gas jets while in a vapor phase.

5 72. The method of claim 70, wherein said reactant gases form compounds by a chemical reaction on the deposition surface of said at least one substrate.

73. The method of claim 43, wherein said carrier gas jets helps to shape said vapor plume and its momentum assists in transport of said vapor plume toward said at least one
10 substrate.

74. The method of claim 43, wherein said anode is annular.

75. The method of claim 74, wherein said anode is positioned at least substantially
15 coaxial with said at least one carrier gas jet.

76. The method of claim 74, wherein said anode is segmented to form two or more anode segments.

20 77. The method of claim 74, further comprising creating a magnetic field and for guiding a magnetic flux such that the magnetic field lines in front of said anode are substantially parallel to its surface and radially directed thus forming a closed electrons drift track in circumferential direction which is substantially parallel to said anode's surface.

25 78. The method of claim 77, wherein said magnetic field facilitates an axial potential gradient for accelerating positive ions toward said substrate.

79. The method of claim 43, further comprising positioning a solenoid coaxially
30 and at least partially proximal to said evaporant source.

80. The method of claim 43, further comprising providing a solenoid is for bending said energetic beam.

81. The method of claim 79, wherein said solenoid is positioned and energized such as to magnetically enhance said anode's efficiency.

5 82. The method of claim 79, wherein said solenoid at least partially increases plasma density and facilitates an axial potential gradient for accelerating positive ions toward said substrate.

10 83. The method of claim 43, wherein said anode is positioned in an elevated position above said evaporant source.

84. The method of claim 43, wherein said anode is positioned above said substrate.

15 85. The apparatus of claim 27, wherein said energetic beam is controlled to alter the deposition location on said at least one substrate to control the thickness, structure, composition, residual stress, and/or other coating properties on said at least one substrate.

20 86. The apparatus of claim 1, wherein said energetic beam is controlled to alter the deposition location on said at least one substrate to control the thickness, structure, composition, residual stress, and/or other coating properties on said at least one substrate.

25 87. The apparatus of claim 86, wherein said control of said energetic beam provides for a creation of a finite length of vapor plume that arrives at said at least one substrate, whereby said finite length of vapor plume defines a slug.

88. The apparatus of claim 87, wherein said arrival of said slug is controlled by intensity of said carrier gas jet.

30 89. The method of claim 69, further comprising controlling said energetic beam to alter the deposition location on said at least one substrate to control the thickness, structure, composition, residual stress, and/or other coating properties on said at least one substrate.

90. The method of claim 43, further comprising controlling said energetic beam to alter the deposition location on said at least one substrate to control the thickness, structure, composition, residual stress, and/or other coating properties on said at least one
5 substrate.

91. The method of claim 90, wherein said control of said energetic beam provides for a creation of a finite length of vapor plume that arrives at said at least one substrate, whereby said finite length of vapor plume defines a slug.
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92. The method of claim 91, wherein said arrival of said slug is controlled by intensity of said carrier gas jet.