METHOD AND APPARATUS FOR VAPOR DEPOSITION

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A method and apparatus for vapor deposition employing a conductive, three-dimensional, open cell, reticulated structure having a solid coating of a material that was previously vapor deposited thereon. The solid coating is vaporized to form a deposition gas. A carrier gas is flowed through the three-dimensional, open cell, reticulated structure to yield a controllable partial pressure of the deposition gas thereby forming a mixture of the carrier gas and the deposition gas. The mixture is delivered at a stable flow rate to a temperature controlled substrate. The deposition gas condenses on the surface of the temperature controlled substrate.
METHOD AND APPARATUS FOR VAPOR DEPOSITION

FIELD OF THE INVENTION

The present invention relates generally to the field of physical vapor deposition and more specifically to Organic Vapor Phase Deposition where a source material is heated to a temperature so as to cause vaporization and a vapor plume is created that mixes with and is transported by an inert carrier gas to a substrate where the organic material condenses to form a thin film.

BACKGROUND OF THE INVENTION

There are numerous methods for vapor depositing materials onto the surface of a substrate known in the prior art. Most often, at the start of a production run a crucible is filled with hundreds of grams of material to be deposited on the substrate. The material is placed in the crucible in powdered form. The crucible and its contents are then heated to a temperature that provides the desired vaporization rate.

This approach can achieve a very stable deposition rate using a crystal rate monitor to provide feedback to a slow response temperature control system but exposes much of the material in the crucible to high temperatures for an extended time period. This extended exposure to high temperatures poses a significant risk of thermal decomposition to many materials, particularly organic materials used in OLED (organic light-emitting diode) devices. These methods are additionally unable to rapidly initiate and interrupt vaporization. The chemical distinction between organic and inorganic materials is somewhat arbitrary but typically, in the thin film deposition field, one considers metals and their oxides, nitrides and carbides as being inorganic. By this definition, the risk of decomposition with inorganic materials is very low by comparison. Even the precursors used in metalorganic Chemical Vapor Deposition (MOCVD) (metalorganic chemical vapor deposition) are very thermally stable relative to the organic materials used for small molecule OLED devices. To address these problems, automatic refilling or crucible exchanging systems have been
developed where a small quantity of organic material is introduced on a repeating basis such that it is consumed before significant decomposition occurs as shown in US Pub. No. 20090061090 by Negishi. In some static deposition systems such as taught in US Pub. No. 20100015324 by Negishi, the quantity of organic material introduced per cycle is described as corresponding precisely to the desired deposited film thickness and no attempt is made to control the deposition rate.

Flash vaporization sources have also been developed to address the decomposition issue by metering cooled, powdered organic material to a heated screen element as taught in US Patent no. 7,288,286 by Long or to a porous heating element as taught in US Pub. No. 2009 0039175 by Long and in US Patent no. 6,037,241 by Powell, on an as-needed basis. These sources reduce the thermal exposure time of the organic material to a second or two and allow rapid initiation and interruption of vaporization of single component and multi-component powder mixtures having widely different saturation vapor pressures. To achieve a stable deposition rate however, these systems require fast response feedback systems to compensate for variability in the material feed rate and variability in the vapor generation rate due to variations in powder particle size and packing density. A stable deposition rate, in terms of OLED material deposition, requires material feed accuracy measured in tens of micrograms and feed rate stability in single digit micrograms per second per square meter of substrate surface area.

US Pub. No. 20080193644 by Frob describes a porous heating element that is loadable such that the porous structure is packed with a powdered material to be coated onto a substrate. The powdered material is vaporized when the temperature of the heating element is raised.

The difficulty in precisely metering fine powders due to their tendency to adhere to surfaces and agglomerate, the vaporization variability due to particle size variation and the poor thermal conductivity of powders have motivated the development of solid and liquid fed systems. Transforming the powdered organic material into a solid pellet typically requires further grinding the powders to achieve sub micron particle sizes and sometimes the addition of inert binders before pressing the mixture in a hydraulic press to insure some minimum level of solid integrity. The displacement of the solid pellet is precisely controlled as it is advanced, usually to a
grinding apparatus to recreate a powder stream or aerosol that is then directed to a heating element for vaporization as in US Patent no. 5,820,678 by Hubert. In this method, the majority of the variability of handling powders is moved to the pellet preparation process at some additional cost with the additional caveat that there is an increased likelihood of contamination to the organic material.

Vaporization apparatus based on spraying a stream of atomized liquid droplets have been developed for vaporizing liquid precursors in MOCVD systems. Apparatus of similar concept have been adapted for use with organic materials, such as taught in US Pub. No. 20050227004 by Burrows, US Pub. No. 200601 15585 by Bulovic and US Patent no. 5,204,314 by Kirlin disclose processes involving jetted droplets. These systems benefit from the well developed technology for precisely dispensing even very small quantities of liquids and benefit from the ability of the liquid to rapidly conduct heat from the heating element and vaporize almost immediately.

Vapor depositing OLED materials can be even more problematic. An OLED device includes a substrate, an anode, a hole injecting and transporting layer made of an organic compound, one or more organic luminescent layers with suitable dopants, an organic electron injection and transporting layer, and a cathode. OLED devices are attractive because of their low driving voltage, high luminance, wide-angle viewing and capability for full color, thin emissive displays. Tang et al. described this multilayer OLED device in their U.S. Pat. Nos. 4,769,292 and 4,885,211. High performance OLED devices have been commercialized using manufacturing processes that rely on heating the organic materials to temperatures sufficient to cause sublimation. The organic material vapors are then condensed as thin films on the surface of a substrate to form an OLED device.

An important distinction between the MOCVD systems and the OLED systems is that the MOCVD precursors are liquids whereas the OLED materials are solids below 200°C and can typically only be dissolved to a 1 or 2 percent concentration in solvents. As a result, substantial volumes of solvent vapor are generated as the liquids are vaporized. Systems based on suspensions of the organic material particles in an inert liquid have higher material loading but maintaining suspension homogeneity is problematic. In all cases, it has proven extremely difficult to remove trace contaminants from the liquids that diminish the OLED device
performance and to additionally insure that solvent molecules, potentially incorporated in the deposited films do not decrease device lifetime or efficiency.

The inherent difficulty in removing trace contaminants from liquids is a fundamental reason why OLED materials are subjected to a thermal evaporation purification process that is often repeated several times before the desired purity is achieved. The material resulting from the liquid based chemical synthesis of the desired organic molecule is purified through a thermal vaporization process by heating it in a crucible and directing the vapor to condense along the length of a condensate collection tube having a controlled temperature and temperature gradient. Contaminants having lower volatility than the target molecule tend to condense preferentially at the hotter end of the glass tube while higher volatility contaminants tend to condense preferentially at the colder end of the tube. In principle, with the right temperature and temperature gradient along the condensate collection tube, high purity condensed films can be recovered from a zone near the middle of the tube. The condensate film is removed, as flakes from the walls of the condensate collection tube and is ground into powder form. After one or more purification sublimation cycles, high purity condensate is recovered and is ultimately ground into the final powder form having a specified particle size range.

US Patent no. 5,059,292 to Collins et al. describes a single chamber apparatus and method for in-situ generation of dangerous polyatomic gases and radicals from solid or liquid source materials contained within a porous foamed structure that is used for both storage and evaporation. A cooled cathode is provided for establishing a plasma discharge within the chamber and a heat source is provided to maintain the porous foamed structure within a fixed temperature range chosen such that the source material is removed from the porous foamed structure by evaporation induced by heat from the heat source while at the same time preventing consumption by evaporation of the porous foamed structure itself. The source material is put into the liquid state (by melting from a solid if applicable) and is absorbed in large amounts into the pores of the foamed structure. The foamed structure acts as a large capacity reservoir for the source material and as heat is applied to vaporize the source material from a surface of the foamed structure, new source material continually wicks to the heated surface.
SUMMARY OF THE INVENTION

The prior art fails to teach a vapor deposition method wherein the deposition rate stability on the target is decoupled from any variability in the replenishment vapor flux due to difficulties and variability in metering and vaporizing minute powder quantities on an as-needed basis. This is accomplished through the use of a conductive open cell structure as an intermediate vapor deposition receptacle. The conductive open cell structure of the intermediate vapor deposition receptacle is preferably electrically conductive, but may instead be thermally conductive, or it may be both electrically and thermally conductive. The material to be vapor deposited on the target substrate is first vapor deposited in the open cell structure of the intermediate vapor deposition receptacle such that the intermediate vapor deposition receptacle becomes a vapor deposition material source structure. The vapor deposition material source structure then may be used as a vapor deposition material source for vapor deposition on the final target substrate. With this arrangement, the vapor generation rate stability of the open cell structure of the vapor deposition material source structure determines the deposition rate stability on the target substrate. By utilizing a phase change from gas to solid between the input vapor and the output vapor in the open cell structure, the objective of establishing and maintaining a precise and substantially invariant flux of the output vapor is decoupled from the difficulties of maintaining a stable deposition rate from a vapor on demand flash vaporization system. The term "substantially invariant" is used herein to denote deposition rate stability better than +/- 0.5%. This stability is maintained when the foam is re-vaporizing condensate deposited at a much earlier time (temporal separation) as well as when vapor with a stability of +/- 8% is entering one side of the foam and condensing while vapor with a stability of +/- 0.5% or better is simultaneously exiting the other side of the foam (spatial separation).

The invention allows substantial simplification in the preparation and vaporization of vapor deposition materials, particularly of organic material for making OLED devices through consideration of the organic material purification process and consideration of the variables such as temperature, thermal exposure time, thermal
conductivity, surface area, partial pressure, total pressure and convection that control organic material vaporization and decomposition.

According to one aspect of the present invention a method of vapor deposition is provided comprising vapor depositing a solid coating of a material onto a conductive three-dimensional, open cell, reticulated structure; vaporizing the solid coating to form a deposition gas; flowing a carrier gas through the conductive three-dimensional, open cell, reticulated structure to yield a controllable partial pressure of the deposition gas while vaporizing the solid coating and thereby forming a mixture of the carrier gas and the deposition gas; delivering the mixture at a stable flow rate to a temperature controlled substrate; condensing the deposition gas onto a surface of the temperature controlled substrate; and withdrawing the carrier gas.

According to a second aspect of the present invention a method of vapor deposition is provided comprising vaporizing a selected solid organic or organo-metallic material to form a vapor; transmitting the vapor to a three-dimensional, open cell, reticulated structure, and uniformly distributing the vapor throughout the three-dimensional, open cell, reticulated structure; condensing the vapor to form a solid coating of the selected solid organic or organo-metallic material on the three-dimensional, open cell, reticulated structure; vaporizing the solid coating to form a deposition gas; flowing a carrier gas though the three-dimensional, open cell, reticulated structure to yield a controllable partial pressure of the deposition gas while vaporizing the solid coating and thereby forming a vapor flux that is a mixture of the carrier gas and the deposition gas; delivering the vapor flux at a stable flow rate to a temperature controlled substrate; condensing the deposition gas onto a surface of the temperature controlled substrate; and withdrawing the carrier gas.

According to a third aspect of the present invention a method for supplying a vapor flux at a stable flow rate to a deposition chamber is provided comprising vaporizing a selected solid organic or organo-metallic material to form a vapor; transmitting the vapor to a conductive, three-dimensional, open cell, reticulated foam structure, and uniformly distributing the vapor throughout the three-dimensional, open cell, reticulated foam structure; condensing the vapor to form a solid coating of the selected solid organic or organo-metallic material on the conductive, three-dimensional, open cell, reticulated foam structure; vaporizing the solid coating to form
a deposition gas; flowing a carrier gas though the foam structure to yield a controllable partial pressure of the deposition gas while vaporizing the solid coating; and delivering a mixture of the carrier gas and the deposition gas to a deposition chamber.

According to a fourth aspect of the present invention a vapor deposition apparatus is provided comprising a first conductive, three-dimensional, open cell, reticulated structure having a solid coating of a selected vapor deposition material vapor deposited thereon; means for heating the first conductive, three-dimensional, open cell, reticulated structure solid coating to vaporize the solid coating to form a deposition gas; a first conduit through which a carrier gas is delivered to flow through the first conductive, three-dimensional, open cell, reticulated structure to yield a controllable partial pressure of the deposition gas as the solid coating is vaporized, the vaporized solid coating and the carrier gas forming a mixture; and a second conduit through which the mixture is delivered at a stable flow rate to a temperature controlled substrate within a deposition chamber.

According to a fifth aspect of the present invention the conductive three-dimensional, open cell, reticulated structure is preferably a vitreous carbon foam. A coating of a refractory metal or ceramic material vapor may first be vapor deposited on the conductive three-dimensional, open cell, reticulated structure, the solid coating of the selected vapor deposition material residing on top of the coating of the refractory metal or ceramic material. The solid coating of the selected vapor deposition material has a thickness in the range of from about 1nm to about 2μm and is substantially free of contaminants. The selected vapor deposition material is an organic or organo-metallic material such as OLED materials.

The three-dimensional open cell, reticulated structure is preferably composed of struts or ligaments. The ligaments collectively have a large surface area relative to the deposition target and the ligaments collect the organic material vapor in the form of a conformal, thin condensate coating. The open cell element includes means for generating heat in or conducting heat into the ligaments and a means for controlling the temperature of the ligaments so as to controllably vaporize the conformal organic material coating condensed thereon. The large surface area of contact and the low
thermal contact resistance between the ligaments and the organic material condensed thereon provide a controllable and unusually large organic vapor flux for a given heating element volume and temperature.

An inert gas is caused to flow through the three-dimensional open cell element and around the ligaments, the ligaments providing a tortuous flow path that promotes mixing of the inert gas with the organic vapor generated around the heated ligaments. The flow and temperature of the gas contribute to controlling the rate of generation and transport of the organic vapor toward the deposition target.

The conductive three-dimensional, open cell, reticulated structure is preferably an open cell vitreous carbon foam. Open cell vitreous carbon foam, also called reticulated vitreous carbon foam, is a vitreous carbon structure of three dimensional interconnected polyhedron cells. Vitreous carbon is a glassy carbon as opposed to a graphitic carbon. A cell is typically comprised of 12 to 14 connected struts or ligaments which form a three dimensional polyhedron. An open cell is a cell where no film or solid is connected between the ligaments so that there is free communication in to and out of a cell, and in a group of adjoining cells all cells are interconnected and form a three dimensional interconnected structure. Open cell foam has a structure which typically consists of three dimensional interconnected polyhedron cells with 12 to 14 ligaments composing each cell, and each cell having a spheroidal shape. A method for producing reticulated carbon foam is taught in US Patent no. 6,103,149 to Stankiewicz. Stankiewicz states that the vitreous carbon foam is often coated with other materials via a chemical vapor deposition process. If the underlying vitreous carbon foam has a vast majority of cells with aspect ratios greatly different than 1 the resultant coated foam will have cells with aspect ratios greatly different than 1 and the resultant coated foam may have anisotropic properties. Chemical vapor deposition is used to coat carbon foams with ceramics such as SiC or BN and metals such as W or Ta.

**BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1 depicts a schematic view of an open cell intermediate vapor deposition receptacle within a condensate collection tube of a sublimation purification apparatus, all of which is contained within a deposition chamber.
Figure 1A is a graph illustrating the temperature gradient across the condensate collection tube.

Figure 2 is a magnified view of the open cell intermediate deposition receptacle where the interconnected ligaments composing the foam are clearly visible.

Figure 3 is a highly magnified cross section of a ligament composing the open cell vapor deposition receptacle with a coating of a refractory metal or ceramic and/or vaporizable material thereon.

Figure 4 is a schematic depiction of a vapor deposition apparatus using the open cell vapor deposition material source structure for vapor deposition.

Figure 4A depicts a cross sectional view of an open cell vapor deposition material source structure and accompanying support structure taken along line III - III of Figure 4.

Figure 5 depicts a schematic view of an alternative vapor deposition apparatus to the apparatus of Figure 4 including two open cell vapor deposition material source structures for vapor deposition.

Figure 6 depicts a cross sectional view of an open cell vapor deposition material source structure and accompanying support structure taken along line IV - IV of Figure 5.

Figure 6A depicts a cross sectional view of an open cell vapor deposition material source structure and accompanying support structure taken along line V - V of Figure 5.

Figure 7 depicts a top view of an exemplary apparatus wherein multiple condensate coated foam heating elements can be loaded on a deposition head and sequentially heated to generate a material vapor and wherein a controllable carrier gas flow is directed through the active open cell deposition receptacle to acquire the material vapor in the carrier gas and deposit a material film on a facing substrate surface.

Figure 8 depicts a perspective view of the exemplary apparatus of Figure 7.

Figure 9 is a top view of an exemplary apparatus wherein multiple condensate coated foam heating elements are loaded on more than one deposition head (as depicted in Figure 8) and are sequentially heated to generate multiple material vapors and wherein carrier gas flows are directed through respective active open cell.
deposition receptacles to acquire the material vapors in the carrier gas and deposit multiple material film on respective facing substrate surfaces simultaneously.

Figure 10 is a top view of an alternative exemplary apparatus to the apparatus shown in Figure 9 wherein multiple condensate coated foam heating elements can be loaded in a deposition system and sequentially heated to generate a material vapor and wherein a controllable carrier gas flow is directed through the active open cell deposition receptacle to acquire the material vapor and deposit a material film on a facing substrate surface. An additional gas flow path is provided to enable in-situ replenishment of the condensate coating within one or more of the then inactive intermediate deposition receptacles.

Figure 11 is a section view through the plane indicated as line VII-VII of the apparatus of Figure 10.

Figure 12 is a perspective view of a second alternative exemplary apparatus to the apparatus shown in Figure 8 wherein multiple condensate coated foam heating elements can be loaded in a deposition system and sequentially heated to generate a material vapor and wherein a controllable carrier gas flow is directed through the active open cell deposition receptacle to acquire the material vapor in the carrier gas. An additional gas flow path is provided to enable in-situ replenishment of the condensate coating within one or more of the then inactive intermediate deposition receptacles.

Figure 13 is a bottom plan view of the second alternative exemplary apparatus of Figure 12 showing the gas flow passages in phantom.

Figure 14 is a section view along the plane XII as shown in Figure 13 additionally including the facing target substrate.

Figure 14A is a perspective view of the apparatus depicted in Figures 12 - 14, shown with a larger target substrate positioned adjacent to the open cell foam heating elements.

Figure 15 depicts a schematic view of an alternative vapor deposition apparatus to the apparatus of Figures 4 and 5 including multiple gas inlets and multiple vapor sources that are mixed and delivered to the first and second open cell heater elements on an as-needed basis.
Figure 15A depicts a cross sectional view of an open cell heating element and accompanying support structure taken along line III-III of Figure 15.

Figure 16 is a depiction of the vapor flux stabilization effect of the apparatus depicted in Figure 15 arising from the action of admitting a vapor to the open cell intermediate deposition receptacle, momentarily condensing the vapor and then evaporating the condensate at a steady vapor flux.

Figure 17 is a schematic depiction of a vapor deposition apparatus for vapor deposition onto substrates transported through a vapor deposition chamber on a conveyor and employing multiple vapor deposition heads.

Figure 18 is a schematic depiction of a vapor deposition apparatus for vapor deposition onto extended length substrates transported through a vapor deposition chamber on a conveyor and employing multiple vapor deposition heads.

DETAILED DESCRIPTION OF THE INVENTION

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

An improved vaporization process has been developed that eliminates the need for precise powder metering or the use of liquids or pre-processing of the powder to form pellets. This improved vaporization process reduces thermal exposure of the organic material while it eliminates the need for a fast response control system. The design is guided by the observation that the principal factors governing the vaporization or sublimation of a material; temperature, surface area, partial pressure and total pressure are typically only controlled in a general or macro sense. The limited contact between the walls of a crucible and the organic powder it contains, the large thermal gradient that can exist through organic powders, the variation in powder particle size and the local partial and total pressure gradients within a heated mass of powder all contribute to imprecise vaporization control and the need for crucible temperatures in excess of the theoretical value necessary to attain a given deposition.
rate. The following principles are useful in understanding how the local vaporization conditions can be significantly different from the average vaporization conditions:

First, vaporization rate under high vacuum conditions varies exponentially with the temperature of the organic material. At useful vaporization temperatures for OLED materials, a 1°C change in material temperature can effect a 5% change in vaporization rate.

Second, organic powders are good insulators, especially under high vacuum conditions and those that sublime are especially difficult to heat by solid conduction once they generate an isolating vapor barrier around the particle. Considering the energy lost to vaporization and the insulating properties of the powder, the effective material temperature can be far lower than the heater temperature and a large thermal gradient can exist through the volume of organic material. Both sources of uncertainty in the organic material temperature lead to uncertainties in the deposition rate. Experiments conducted with A1Q3 and NPB, two well known and well characterized OLED materials, provided evidence that temperatures of the foam ligaments between 160°C and 170°C generate deposition rates normally associated with crucible temperatures of 380°C to 390°C. This several hundred degree lower than expected vaporizer temperature for a given vapor flux was verified by three independent measurement methods.

Third, the melting point of materials having dimensions under 10 nm can be tens to hundreds of degrees lower than the bulk material melting point. The amount of melting point depression increases with decreasing particle size because the surface atoms in a nanometer sized particle have fewer neighboring atoms in close proximity compared to atoms in the bulk of the solid and are therefore bound with less cohesive energy. The cohesive energy of an atom is directly related to the thermal energy required to free the atom from the solid and hence its melting point. The melting point depression observed in nanometer size particles pertains also to thin films and particularly to the first stages of thin film formation where single molecules condense and then coalesce with other molecules into sub nanometer size islands before finally forming a continuous film. This phenomenon is believed to contribute to the unexpectedly low vaporization temperatures observed experimentally.
Fourth, vaporization flux under high vacuum conditions is proportional to the exposed surface area of heated organic material. Increasing the surface area of the organic material can allow a reduction in the temperature required to achieve a given deposition rate.

Fifth, variability in the local deposition rate exists because actual vaporization rate is inversely proportional to the local partial pressure surrounding the powder particles. Adjacent and underlying particles can reduce the theoretical vaporization rate of a given particle either by 1) acting as condensation sites if they are cooler or 2) vaporizing, themselves, effectively driving the local partial pressure toward saturation if the vapor escape is impeded.

Sixth, actual evaporation rate is inversely proportional to the total pressure, and the thickness and density of any boundary layer present. Diffusion through a local boundary layer will slow the local vaporization rate by creating an apparent high partial pressure. A carrier gas can be effective in controlling the deposition rate through its influence on total pressure, boundary layer thickness and partial pressure.

Looking at Figure 1, the invention includes the introduction of one or more open cell foam structures 10 into the center region of a sublimation purification apparatus 11 on whose large surface area is deposited a conformal thin film of the purified organic material condensate. As shown in Figure 1, the material to be purified 12 is loaded in a vaporization apparatus 14 within a vacuum chamber 16 and heated by heating elements 18 to a temperature necessary to produce an effective vaporization rate. The vaporization apparatus 14 may be a simple crucible 20 or may use flash vaporization to vaporize the material with little thermal exposure time. Alternatively, the vaporization apparatus 14 may advantageously utilize the apparatus of this disclosure instead of crucible 20 to vaporize the material to be purified. The vapor is directed to pass through a condensate collection tube 22 having a temperature gradient illustrated in the accompanying graph (see Figure 1A) such that the temperature of condensate collection tube 22 is higher at the end nearest the vaporization apparatus 14 and lower at the opposite end. Intermediate to the two ends of the condensate collection tube 22 is placed one or more open cell foam elements 10 whose temperature is controlled and maintained at a desired condensation temperature Tc such that vapor having the desired molecular structure preferentially condenses on
the open cell foam element 10. The foam element 10 can be placed as in Figure 1 with the face of the one or more foam elements positioned normal to the axis of the condensate collection tube 22 or the foam element 10 can have a polyhedral or tubular shape and be positioned concentric within the condensate collection tube 22. The foam element 10 can also take the form of flat plates arranged to generally conform to the walls of the condensate collection tube 22. The vacuum chamber 16 is maintained at a desired pressure by vacuum pump 21 in combination with pressure sensor 24 and pressure controller 26. Figure 2 is a magnified view of the open cell, polyhedral structure of the foam element 10 composed of interconnected struts or ligaments 28. Such foam, made from glassy carbon, is commercially available from ERG Aerospace. These foam materials can be coated with metals and ceramics through a chemical deposition process.

Figure 3 is a highly magnified view of a cross section of a ligament 28 of the foam having a generally triangular shape that is surrounded in this illustration by a very thick coating of condensed material 30.

Collecting the purified organic material condensate in this manner eliminates the step of removing condensate from the inside of the collection tube in the sublimation purification apparatus and then grinding the condensate to a prescribed particle size and particle size range as is typically done in preparing OLED materials for vapor deposition. The improved method of collecting the condensate directly from the purification sublimation apparatus 11 greatly reduces the health risks of collecting and processing fine powders and additionally eliminates losses and contamination in the removal, grinding and particle sizing processes.

The condensate infused open cell foam element 10 is removed from the sublimation purification apparatus 11 and placed in a vapor deposition apparatus 32 as shown in Figure 4. A carrier gas is directed from an input tube 34 through a mass flow controller 36 and an optional gas heater 38. The carrier gas enters the deposition apparatus 32 through an input duct 40 and is directed uniformly over the surface of the open cell foam element 10 by a gas distribution manifold or plenum 42. Electrical energy for heating is brought in to the foam element 10 through wires 44, 45 and contacts 46, 48 such that foam element 10 functions as a heating element. In this manner, the temperature of foam element 10 is controlled to vaporize the material
condensed on the surfaces within the open cell foam element 10 at a rate that is well correlated to the pressure inside vacuum chamber 50, carrier gas flow rate and the temperature of foam element 10 because of the intimate thermal contact between the dense conformal condensate film and the surface of the open cell foam element 10. A substrate holder 52 controls the temperature of substrate 54 and the interior of the vacuum chamber 50 is maintained at a desired pressure by vacuum pump 56 in combination with pressure sensor 58 and pressure controller 60. The gas distribution manifold 42 may be heated by heating elements 62 to a temperature sufficient to prevent condensation on the internal surfaces of gas distribution manifold 42 of vapor molecules back diffusing through the carrier gas flow.

Those skilled in the art will recognize that the target, temperature controlled substrate for the embodiments described herein may take many forms. The target substrate would most commonly be a borosilicate glass panel having a thickness between 0.3 and 0.7 mm which is polished on both faces for display applications. For lighting applications which tend to be more sensitive to cost, the target substrate would most commonly be a soda-lime glass panel with a thickness between 0.5 and 1 mm which is polished on at least one face. It is also known to use a flexible substrate made from glass, aluminum or stainless steel foil. These foils are typically between 25 and 100 microns thick. Polymeric substrates such as PET and PEN have also been used after a moisture barrier film coating has been first deposited as a support layer for the OLED material.

Looking at Figure 4A, there is shown a cross section view of vapor deposition apparatus 32. Heater 10 is sandwiched between electrodes 64, 66. The electrodes 64, 66 are preferably a conductive metal foil, and current flows through electrodes 64, 66 to the ligaments of heater 10 to cause heat to be produced. Electrical cable leads 68, 70 connect to electrodes 64 and 66, respectively. Electrodes 64, 66 preferably take the form of conductive foils. A variety of metals can be used for the electrodes 64, 66. Conveniently, titanium, tantalum, tungsten, or molybdenum or coatings of these materials on softer metals such as copper or silver can be used due to their relative chemical inertness at elevated temperatures. Compliant elements 72, 74 are heat resistant and optionally thermally conductive material. Compliant elements 72, 74 can conform to the surface texture of heater 10 and create local deformation of
conductive foils 64, 66 when the heater 10 is pressed against the compliantly supported conductive foils 64, 66. One example of useful compliant material is GRAFOIL®. UCAR Carbon Company Inc. of Wilmington, DE., manufactures GRAFOIL® Flexible Graphite as a rolled sheet product that exhibits good heat resistance and typically exceeds 97% elemental carbon by weight.

The sandwich configuration shown in Figure 4A provides low contact resistance between the heater 10 and the conductive foils 64 and 66, insuring that at least 90 percent of the heat is generated in the ligaments of heater 10 instead of at the interface between the electrodes 64, 66 and the heater 10. Nano-particulate silver paint can also be used to lower the electrical contact resistance between the electrodes 64, 66 and the carbon foam material of the heater 10. Because the silver particles are of a nanometer size, they soften and melt at temperatures hundreds of degrees less that the melting temperature of bulk silver. This behavior is very size dependent and facilitates the establishment of excellent electrical contact between the electrodes 64, 66 and the carbon foam material of the heater 10. The heater 10 and foils 64, 66 and compliant elements 72, 74 are clamped together by contacts 76, 78. Contacts 76, 78 may be electrically conductive and be attached to electrodes 64, 66, respectively to carry current to the heater 10. Alternately, the contacts 76, 78 could be electrical insulators or have an electrically insulating coating but act as thermal conductors to cool heater 10. Isolating element 80 electrically and thermally isolates the heating structure from the vapor manifold or plenum 42 and the entire assembly is unitized by clamping structure 84. A thermocouple 86 or infrared sensor can be used to measure the temperature of heater 10 and provide feedback to control the current delivered to heater 10. It is also possible to measure the voltage and current delivered to heater 10 as a function of temperature to determine the effective electrical resistance. Most materials have a measurable temperature coefficient of resistance and after calibration; it is possible to infer the average temperature temperature based on the effective resistance.

Figure 5 depicts an alternative vapor deposition apparatus 100 similar to the apparatus 32 shown in Figure 4. A carrier gas is directed from an input tube 102 through a mass flow controller 104 and an optional gas heater 106. The carrier gas enters the vapor deposition apparatus 100 through an input duct 108 and is directed uniformly over the surface of the open cell foam element 10 by a gas distribution
manifold or plenum 110. Electrical energy for heating is brought in to the foam element 10 through wires 112, 113 and contacts 114, 116 such that foam element 10 functions as a heater. In this manner, the temperature of foam element 10 is controlled to vaporize the material condensed on the surfaces within the open cell foam element 10 at a rate that is well correlated to the pressure within vacuum chamber 118, carrier gas flow rate and the foam temperature because of the intimate thermal contact between the dense conformal condensate film and the surface of the open cell foam element 10. A substrate holder 120 controls the temperature of substrate 122 and the interior of the vacuum chamber 118 is maintained at a desired pressure by vacuum pump 124 in combination with pressure sensor 126 and pressure controller 128. The gas distribution manifold or plenum 110 may be heated by heating elements 130 to a temperature sufficient to prevent condensation on its internal surfaces of vapor molecules back diffusing through the carrier gas flow. In this embodiment, the gas distribution function within gas distribution plenum 110 is accomplished with a second open cell foam structure or heating element 132 similar or identical to the open cell foam element 10 used to re-vaporize the condensed material. However, second open cell foam structure or element 132 does not have vapor deposition coating thereon. Instead of acting as a source of vapor deposition material in the vapor deposition process, second open cell foam structure 132 serves to evenly distribute the carrier gas across the upstream face of the open cell foam element 10. The open cell foam structure 132 may be heated by passing electrical current through contacts 134, 136 and current delivery wires 138, 139. As such, second open cell foam structure 132 may optionally be used to preheat the carrier gas. The combination of the gas distribution manifold 110, heating elements 130, and an optional gas heater 106, input duct 108, wires 112 and contacts 114 and 116, along with the open cell heating elements 10, 132 may be referred to herein as a vapor deposition head 140. Open cell foam structures are well known to randomly change the direction of a steady flow of gasses passing through them and thereby produce a spatially uniform output flow over the entire area of the output face of the foam even when the input flow is focused over less than 1 percent of the area of the input face of the foam. The configuration shown in Figure 5 is especially advantageous in that a single open cell foam element 132 provides uniform carrier gas flow to the heating
and vaporizing open cell foam element 10, can provide heating of the carrier gas, and can be heated to a controlled temperature to prevent condensation on its surfaces as well as the surfaces of the gas distribution manifold 110 from vapor molecules generated from open cell foam element 10 that back diffuse through the carrier gas flow. This method achieves precise vapor deposition rates based on heater temperature and carrier gas flow without the need to accurately prepare and dispense powders, without the need to introduce liquids, and without the need for a fast response control system. In working with a condensate film as opposed to powders, this method additionally reduces the exposed surface area of the organic material that can be subject to infiltration of water vapor and other contaminants. When the organic material infused in the open cell foam is exhausted, a new foam element with a fresh charge of organic material may be introduced.

Three dimensional, open cell reticulated foam structures are commercially available having 90 to 97% open porosity. In these open cell reticulated foams, only the edges of the polyhedral shaped cells remain. The edges of the cells or ligaments most often have a generally triangular cross section and collectively present a large surface area relative to the volume of the foam. A one micron thick organic condensate enveloping each ligament in 250 cm³ of foam volume would constitute 1 gram of condensed organic material. Relative to systems vaporizing powders, the intimate mechanical contact between the conformal condensed organic film and the ligaments in the open cell foam structure provides superior temperature uniformity and heat transfer to the entirety of the organic material as well as improved control and correlation between the temperature of the ligaments and the vaporization rate of the organic material.

The open cell foam can be made from glassy carbon, for example, and therefore can be used as a responsive electrical resistance heater because it is electrically conductive. Further, the very low mass of the open cell foam allows for a very fast heating response. While glassy carbon is relatively inert, refractory metals (e.g. niobium, tantalum, tungsten, molybdenum, and rhenium), inert metals (e.g. gold and platinum), and ceramic compounds (e.g. the oxides, nitrides, carbides, borides, and silicides of the metals) may be deposited over the glassy carbon structure by CVD to produce a conformal coating, retaining the resistance heating characteristics of the
glassy carbon while improving the thermal conductivity, the mechanical strength and
the maximum service temperature of the foam in air. By introducing a coating on the
glassy carbon, it is also possible to control the emissivity of the foam element to, for
example, minimize the energy absorbed and emitted through thermal radiation. A
perspective view of a section of the foam structure is depicted in Figure 2.

Looking at Figure 6, there shown a cross section view of vapor deposition
apparatus 100 passing along line IV - IV in Figure 5 through heater 10. A parallel
cross section through heater 132 in Figure 5 along line V-V is shown in Figure 6A.
Both Figures 6 and 6A show identical functional elements to those shown in Figure
4A. Heater 10 is sandwiched between electrodes 142, 144. The electrodes 142, 144
are made of a conductive metal foil, and electrical current flows through the electrodes
142, 144 to the ligaments of heater 10 through electrodes 142, 144 to cause resistance
heat to be produced in the ligaments. Electrical cable leads or wires 112, 113 connect
to electrodes 142, 144, respectively. Electrodes 142, 144 preferably take the form of
conductive foils. A variety of metals can be used for the electrodes 142, 144.
Conveniently, titanium, tantalum, tungsten, or molybdenum or coatings of these
materials on softer metals such as copper or silver can be used due to their relative
chemical inertness at elevated temperatures. Compliant elements 146, 148 are heat
resistant and, optionally, thermally conductive material. Compliant elements 146,
148 can conform to the surface texture of heater 10 and create local deformation of
electrodes 142, 144 when the heater 10 is pressed against the compliantly supported
142, 144. One example of useful compliant material is GRAFOIL®. UCAR Carbon
Company Inc. of Wilmington, DE., manufactures GRAFOIL® Flexible Graphite as a
rolled sheet product that exhibits good heat resistance and typically exceeds 97%
elemental carbon by weight.

The sandwich configuration shown in Figure 6 provides low contact resistance
between the heater 10 and the electrodes 142, 144, insuring that at least 90 percent of
the heat is generated in the ligaments of heater 10 instead of at the interface between
the 142, 144 and the heater 10. Nano-particulate silver paint can also be used to lower
the electrical contact resistance between the electrodes 142, 144 and the carbon foam
material of the heater 10. Because the silver particles are of a nanometer size, they
soften and melt at temperatures hundreds of degrees less that the melting temperature
of bulk silver. This behavior is very size dependent and facilitates the establishment of excellent electrical contact between the electrodes 142, 144 and the carbon foam material of the heater 10. The heater 10 and foils 142, 144 and compliant elements 146, 148 are clamped together by contacts 114, 116. Contacts 114, 116 may be electrically conductive and be attached to electrodes 142, 144, respectively to carry current to the heater 10. Alternately, the contacts 114, 116 could be electrical insulators or have an electrically insulating coating but act as thermal conductors to cool heater 10. Isolating element 150 electrically and thermally isolates the heating structure from the plenum 110 and the entire assembly is unitized by clamping structure 152. A thermocouple 86 or infrared sensor can be used to measure the temperature of heater 10 and provide feedback to control the current delivered to heater 10. It is also possible to measure the voltage and current delivered to heater 10 as a function of temperature to determine the effective electrical resistance. Most materials have a measurable temperature coefficient of resistance and after calibration; it is possible to infer the average heater temperature based on the effective resistance.

In Figure 6A, electrical cable leads or wires 138, 139 connect to electrodes 135, 137, respectively. Electrodes 135, 137 preferably take the form of conductive foils. A variety of metals can be used for the electrodes 135, 137. Conveniently, titanium, tantalum, tungsten, or molybdenum or coatings of these materials on softer metals such as copper or silver can be used due to their relative chemical inertness at elevated temperatures. Compliant elements 131, 133 are heat resistant and, optionally, thermally conductive material. Compliant elements 131, 133 can conform to the surface texture of heater 132 and create local deformation of electrodes 135, 137 when the heater 10 is pressed against the compliantly supported 131, 133. One example of useful compliant material is GRAFOIL®. UCAR Carbon Company Inc. of Wilmington, DE., manufactures GRAFOIL® Flexible Graphite as a rolled sheet product that exhibits good heat resistance and typically exceeds 97% elemental carbon by weight.

The vaporization rate of the organic material from the three-dimensional, open cell, reticulated element is essentially constant over a wide range of condensed material mass within the foam structure but varies as a function of the temperature of the three-dimensional, open cell, reticulated element, as a function of the chamber
pressure and as a function of the carrier gas flow rate. The large interaction surface area between the organic material and the open cell foam heater and the intimate and uniform thermal contact with the entirety of the conformal organic material coating greatly increase the vapor flux generated for a given temperature of the foam heater structure. In addition, the over 90% open porosity of the foam structure provides a low resistance flow path for the vapor to escape from the foam structure and for an inert carrier gas to further assist in evacuating the organic vapor from the foam. Allowing the free escape of organic vapor from the condensate surface and optionally facilitating the escape with the use of a carrier gas fosters a low partial pressure environment at the condensate surface that further improves the vaporization rate for a given heater temperature. Because the decomposition of organic materials is strongly correlated with temperature, a reduction of the vapor generator source temperature by 50°C or more, as has been demonstrated with the device of this disclosure for a given vapor flux, provides a substantial reduction in the decomposition of organic materials. The disclosed geometry enables precise control of the temperature, the partial pressure, and the total pressure over virtually the entire volume of organic material at a very local level. The temperature of the inert carrier gas can be the same or different from that of the foam material. If the carrier gas is cooler than the foam material, it is possible to effect cooling of the foam and therefore provide the capability to rapidly interrupt, initiate or modify the vaporization rate of the organic material. If the carrier gas is hotter than the foam, it can be used to provide at least part of the vaporization energy and again interrupt, initiate or modify the deposition rate based on the gas flow rate. It is further possible for the carrier gas to be a mixture of an inert gas and an organic vapor such that the flow exiting the foam consists of multiple organic material vapors.

The flow rate of the carrier gas and its effect on the local pressure provide greater control of the deposition rate than is attainable by temperature control alone. Recalling that the vaporization rate varies exponentially with temperature, a 1°C temperature change can effect a 5% deposition rate change but over some range, the deposition rate varies nearly linearly with the flow rate of a carrier gas.

It can be shown that a 20 nm thick film on a fifth generation substrate (1.43 m² surface area) contains only 36 milligrams of organic material, and that 1 gram of
condensed organic material infused in each 250 cm³ of foam volume per micron of condensate thickness can be used to coat at least 12, fifth generation size substrates, even with a deposition efficiency of only 50%. A one micron condensate thickness adds less than a 10 PPM change to the surface area of a 250 cm³ volume of open cell foam, allowing excellent deposition rate stability for a given foam temperature even as the organic material is consumed. For a high throughput application, producing 2000 m² of coated substrates per day, the amount of organic material deposited per layer on average is 50 grams per day. If the deposition efficiency is greater than 50%, the daily required organic condensate volume could be infused in a foam block measuring 30 cm x 30 cm x 5 cm thick.

Multiple operating modes are possible. For example, multiple condensate coated or infused foam heating elements 10 (as described with reference to Figures 1, 4, 4A, and 6) can be loaded in a deposition source supply head 300, shown in Figures 7 and 8, and sequentially heated to generate vapor and thereby enable longer deposition periods than would be practical with a single foam element. The deposition source supply head 300 comprises a rotor 302 and a stator 304 that can rotate one relative to the other. In one embodiment, the rotor 302 rotates about the stator 304 and in another embodiment; the stator 304 rotates within the rotor 302. The deposition source supply head 300 shown in this exemplary embodiment is a hexagonal prism and includes a frame 306 mounted each face 307 thereof. In each frame 306 is supported a condensate coated or infused foam heating element 10. Heating element 10 is supported within frame 306 similar to the how the heating element 10 is supported within frame or clamping structure 152 as depicted in Figure 6. For purposes of brevity, the electrodes, electrical cable leads, compliant elements, contacts, electrical isolating element, and vapor manifold described with reference to Figure 6 are not shown in or described with reference to Figures 7 and 8 (with the exception of a single contact 309 which is visible in Figure 8). However, those skilled in the art will recognize the need for such elements to be present so that heating element 10 can actually function as a heater. An inert carrier gas flowing through feed tube 308 enters duct 310 in stator 304 that is in rotatable but gas sealing cooperation with rotor 302. The inert carrier gas passes through duct 312 in rotor 302 and is distributed uniformly over the surface of the active open cell foam heating element 10.
The carrier gas mixes with the vapor generated within open cell foam heating element 10 upon heating and is transported to a substrate 314 supported on a temperature controlled substrate holder 316 where the vapor condenses to deposit a controlled thickness film. The deposition source supply head 300 is rotatable such that each heating element 10 on rotor 302 may be positioned to align with duct 310 in stator 304 such that gas flows from feed tube 308, into duct 310, then duct 312 and through the aligned heating element 10. The carrier gas mixes with the vapor generated by evaporating material within heating element 10, the mixture passes into a deposition chamber (not shown) containing the target substrate 314 and the vapor condenses on the surface of the target substrate 314. Figure 8 shows a perspective view of the deposition source supply head. While each face 307 of rotor 302 is depicted as being planar, and each heating element 10 is depicted as having planar surfaces, those skilled in the art will understand that the support faces 307 may have other shapes. For example, each heating element 10 may take a curvilinear form, and support faces 307, or the frames 306, or both may be either or at least adapted to receive curvilinear heating elements. In this manner, the apparatus can be adapted to vapor deposit onto substrates that curved or non-planar surfaces. Alternatively, each of the condensate infused heating elements 10 can contain a different vaporizable material such that a single substrate 314 sequentially receives coatings of different materials as rotor 302 carries different condensate infused heating elements 10 into alignment with carrier gas duct 312 and substrate 314.

One skilled in the art will appreciate that a rotatable multi-faceted prism 320 as shown in Figure 9 can be used in combination with one or more deposition source supply heads 300. A substrate holder 322 and a target substrate 324 can be mounted on each face of a rotatable multi-faceted prism 320 and be rotated into facing alignment with one of several condensate infused heating elements 10 on one or more deposition heads 300 such that single or multiple film depositions can be accomplished in a continuous manner on successive substrates 324. The apparatus shown in Figure 9 could, for example, deposit twelve different layers on a continuous succession of substrates. In this embodiment, a single gas feed tube 308, stator 304 and duct 310 are shown in deposition heads 300 but one skilled in the art will understand that multiple gas feed tubes, stators, and ducts can be arranged within
rotor 302, each in fluid communication with a different condensate infused heating element 10, to simultaneously evaporate infused, vaporizable material on multiple substrates simultaneously. If there were multiple, multi-faceted prisms 320 holding substrates arranged around one deposition source supply head having multiple gas feed tubes then multiple substrates (on different substrate holding prisms) could receive coatings simultaneously. The substrate holding prisms could remain stationary while a single deposition head sequenced through six different materials on its six faces to build six layer film stacks on one of the substrates per substrate holding prism. Alternately, the deposition head could remain stationary while the multiple substrate holding prisms sequenced through their six substrates each to deposit the same material on each of the six substrates before the deposition head is rotated to begin depositing a new material on each of the six substrates. It is also possible to recharge expended and idle foam heating elements 10 with condensate in-situ as shown in Figure 10. In this embodiment, multiple condensate coated or infused foam heating elements 10 can be loaded in a deposition source supply head 400, shown top view in Figure 10. These heating elements 10 can be sequentially heated to generate vapor and thereby enable longer deposition periods than would be practical with a single foam element. The deposition source supply head 400 comprises a rotor 402 and stator portions 404, 406 that can rotate one relative to the other. In one embodiment, the rotor 402 rotates about stator portions 404, 406 and in another embodiment; the stator portions 404, 406 rotate within rotor 402. The deposition source supply head 400 shown in this exemplary embodiment is a hexagonal prism and includes a frame 408 mounted each face thereof. Frames 408 are identical to frames 306 described with reference to Figure 7. In each frame 408 is supported a at least one condensate coated or infused foam heating elements 10. Heating elements 10 is supported within frames 408 similar to the how the heating element 10 is supported within frame 22 as depicted in Figure 6. For purposes of brevity, the electrodes, electrical cable leads, compliant elements, contacts, electrical isolating element, and vapor manifold described with reference to Figure 6 are not shown in or described with reference to Figures 10 and 11. However, those skilled in the art will recognize the need for such elements to be present so that heating element 10 can actually function as a heater. An inert carrier gas flowing through feed tube 410
enters duct 412 in stator portion 404 that is in rotatable but gas sealing cooperation with rotor 402. The inert carrier gas passes through duct 414 in rotor 402 and is distributed uniformly over the surface of the active open cell foam heating element 10. The carrier gas mixes with the vapor generated within open cell foam heating element 10 and is transported to a substrate 416 supported on a substrate support 418 contained within a deposition chamber (not shown) where the vapor condenses to deposit a controlled thickness film. The deposition source supply head 400 is rotatable such that each heating element 10 on rotor 402 may be positioned to align with a duct 412 in stator portion 404 such that gas flows from feed tube 410, into duct 412, then duct 414 and through the selected aligned heating element 10. The carrier gas mixes with the vapor generated by evaporating material within heating element 10, the mixture passes into a deposition chamber (not shown) containing the target substrate 416 and the vapor condenses on the surface of the substrate 416.

In the embodiment shown in Figure 10, a replenishment vapor flux is generated from a second vapor source (not shown), passes through feed tube 410 and into duct 420 in stator portion 406 that is in rotatable but gas sealing cooperation with rotor 402. The replenishment vapor passes through duct 422 in rotor 402 and is dispersed uniformly into the volume of the foam heating element 10 (being maintained at a temperature that will promote condensation of the replenishment vapor). As the replenishment vapor expands into the lower temperature and pressure region within the foam, it cools and the vapor condenses on the cooler ligaments of the foam to form a solid coating thereon. The foam acts as a condensate accumulator, storing enough organic material in the solid state to subsequently coat many substrates. The addition of a replenishment vapor flux in the apparatus shown in Figure 10 can maintain the deposition function of the apparatus as a source of vaporized material indefinitely. In this embodiment, it is not necessary for the replenishment vapor source to have a particularly steady or controlled vapor flux.

Figure 11 shows a cross section through the apparatus of Figure 10 along the plane VII to more clearly illustrate the vapor path through the apparatus. The rotor 402 is rotated to align a selected heating element 10 supported within a frame 408 with ducts 412, 414 so that deposition vapor can be generated in the selected heating element 10 and transmitted to a target substrate 416. Similarly, rotor 402 is rotated to
align a selected heating element 10 supported within a frame 408 with ducts 420, 422 so that replenishment vapor can be delivered to a spent heating element 10 to re-coat the spent heating element with a coating of the deposition material. After the spent heating element 10 has been re-charged with vapor deposition material, it can be rotated back into a position of alignment with ducts 412, 414.

An alternate, exemplary vapor deposition apparatus including a vapor deposition head 500 is shown in Figures 12, 13 and 14 which is similarly capable of sequentially heating and vaporizing material from one or more open cell foam elements 10 and which is capable of having a separate station to replenish the condensate coating on the one or more exhausted open cell foam elements. A controlled carrier gas flows through feed tube 502 and into duct 504 in stator portion 506. The carrier gas passes through duct 508 in rotor 510 and mixes with material vaporized in open cell foam heating element 10. The material vapor then condenses on the surface of substrate 512 supported on substrate holder 514 (shown in Figure 14) in facing alignment to foam heating element 10 individually supported with a respective frame 511 attached to rotor 510. A replenishment vapor of selected vapor deposition material may be admitted through feed tube 516 and into duct 518 in stator portion 520. The replenishment vapor then passes through duct 522 in rotor 510 and condenses on the ligaments of open cell foam heating element 10 then aligned with duct 518. This configuration shares all of the functional capabilities of the apparatus shown in Figures 7 and 10 in that multiple material infused foam heating elements 10 may be sequentially heated to generate a material vapor that mixes with a carrier gas for deposition on a substrate 512 in facing alignment analogous to the functionality of the apparatus shown in Figure 7; the one or more substrate holders 514 supporting respective substrates 512 may themselves be supported on a rotatable table (not shown) allowing one or more deposition heads 500 to simultaneously deposit material on substrates 512 supported by one or more substrate support tables analogous to the functionality of the apparatus shown in Figure 9, and a replenishment vapor of a selected vapor deposition material can be introduced to replenish deposition material in expended foam elements 10 positioned outside of active deposition positions analogous to the functionality of the apparatus shown in Figure 10.
This configuration can enable additional functionality however when each of
the foam heating elements 10 is used simultaneously to generate material vapors that
mix with separate carrier gas flows to deposit a mixture of materials on a facing
substrate surface. The multiple foam elements 10 may remain stationary relative to
the target substrate during the deposition process and rely on gas mixing to create a
spatially uniform material concentration in the deposited film or may additionally
utilize rotational, translation or other relative motion between the foam heating
elements 10 and the substrate to create the desired material concentration uniformity
over the surface of the substrate. This mode of operation can most easily be
visualized from Figure 14A for a substrate 524 having dimensions slightly smaller
than rotor 510 that is located with its center concentric with the axis of rotor 510 and
a short distance off-spaced from foam heating elements 10. A rotary coupling could
be used to communicate multiple gas flows from stationary gas sources to the multiple
rotating foam heating elements. In this configuration, each of the three (in this case)
foam heating elements can evaporate a different organic material at different
evaporation rates to provide a film on the stationary substrate that is a controlled
mixture of the three organic materials. Three separate gas feed tubes would be used in
this example. Both the rotor and stator would rotate together in this embodiment so
that the carrier gas continues to flow to its respective foam element. Further, those
skilled in the art will recognize that the substrate may be rotated as an alternative to
rotating the foam elements. Typically the substrate must be temperature controlled
and this would similarly require a rotary coupling for the coolant flow.

Experimentally, foam having a pore cell size of approximately 1 mm and a
thickness in the vapor flow direction of 1 cm proved effective in storing and releasing
organic vapors when heated to temperatures between 100°C and 200°C in a vacuum
chamber under a range of pressures from 10 to 200 Pa. In addition to demonstrating
the suitability of the open cell foam as a means of re-evaporating a condensate
coating, an experiment was conducted to determine if a replenishment vapor could be
continuously delivered to a foam element that was actively generating a vapor flux.
These experiments demonstrated that it is possible, by varying the temperature profile
in the flow direction through a 1 cm thick open cell foam element, to use the foam
element as a vapor selective sieve or valve. In a first temperature condition, the foam
allows the free passage of replenishment vapor molecules through, as well as the
generation of vapor from condensate within the foam. In a second temperature
condition, the foam prevents the passage of more than a fraction of 1 percent of
replenishment vapor molecules and inhibits the generation of vapor from condensate
within the foam. In both of these conditions, the carrier gas flows through the foam
virtually unimpeded. This behavior as a vapor selective sieve is observed even though
there is sufficient open area to allow an observer to "see" through the foam element.

In this pressure and temperature range, the mean free path, defined as the average
distance a molecule travels before colliding with another molecule is smaller but on
the same order of magnitude as the average pore size in the foam. It is believed that
the short collision distance due to the mean free path to pore size correlation explains
why the percentage of vapor molecules passing through the foam unimpeded is nearly
zero and is much smaller than would be expected from the large line-of-sight open
area. The ability to selectively allow or prevent the passage of vapor while offering
nearly no resistance to the flow of the carrier gas is important to the operation of
carrier gas assisted deposition systems from two perspectives. From a first
perspective, it is useful to be able to switch the incoming vapor flow off when the
desired film thickness has been deposited on the substrate and to do so without
disturbing the carrier gas flow and therefore the pressure in the deposition chamber.
The vapor typically represents only a few percent of the total gas flow but the
deposited film thickness signal from the crystal rate monitor is strongly influenced by
changes in its ambient pressure. By selectively inhibiting only the vapor flow, it is
possible to maintain a constant chamber pressure and therefore a reliable film
thickness monitor reading. From a second perspective, after passing over the
substrate, the carrier gas must be exhausted and there is always some vapor in the
exhaust gas downstream of the substrate. It is useful to capture this residual vapor to
prevent unwanted deposition in the exhaust system and to do so without significantly
impeding the flow of the exhaust carrier gas.

Although the first 1 cm thick foam element experiment failed to demonstrate
the ability to generate a steady re-evaporated vapor flux that is completely
independent from a concurrent replenishment vapor flux, it demonstrated that the open
cell foam is a much more effective vapor sieve than its visual appearance would suggest.

There is shown in Figure 15 an alternative embodiment vapor deposition apparatus 600 in which replenishment of the coating on the open cell foam element 602 is performed in situ. A continuous flow of replenishment vapor from one or more vapor generator sources 604, 606, each with a respective carrier gas inlet 608, 610, and a respective gas flow controllers 612, 614 is directed to a vapor mixer 616 having an optional dilution carrier gas inlet 618, a gas flow controller 620 and gas temperature controller 622. From the vapor mixer 616, the gas mixture is transmitted through conduit 624 into gas inlet tube 626 of gas distribution manifold or plenum 628. Open cell foam structures 602, 630 reside within gas distribution manifold or plenum 628 which may be heated by heating elements 631 to a temperature sufficient to prevent condensation on the internal surfaces of gas distribution manifold or plenum 628 of vapor molecules back diffusing through the carrier gas flow. Electrical energy for heating is brought in to the foam elements 602, 630, through wires 632, 633 and contacts 634, 635 such that foam elements 602, 630 function as heaters. The gas flow is directed to uniformly flow into the foam structures or elements 602, 630 and condense uniformly on the ligaments of the foam structures 602, 630. Foam structures 602, 630 are essentially the same as the open cell foam element 10 depicted in and discussed with reference to previous Figures with the exception that open cell foam heating element 630 does not have a coating of a vapor deposition material deposited thereon.

A substrate holder 636 controls the temperature of substrate 637 and the interior of the vacuum chamber 638 is maintained at a desired pressure by vacuum pump 639 in combination with pressure sensor 640 and pressure controller 642. In this embodiment, the gas distribution function within plenum 628 is accomplished with the second open cell foam structure or element 630 similar or identical to the open cell foam element 602 used to re-vaporize the condensed material. However, second open cell foam structure or element 630 does not have vapor deposition coating thereon. Instead of acting as a source of vapor deposition material in the vapor deposition process, second open cell foam structure 630 serves to evenly distribute the carrier gas across the upstream face of the open cell foam element 602.
The open cell foam structure 630 may be heated by passing electrical current through contacts 644, 646 and current delivery wires 648, 650. As such, second open cell foam structure 630 may optionally be used to preheat the carrier gas. The combination of the gas distribution manifold or plenum 628, heating elements 602, 630, gas inlet tube 626, electrical wires 648, 650 and contacts 644, 646, along with the open cell heating elements 602, 630 is referred to herein as a vapor deposition head 652.

In this embodiment, there is a temperature gradient established through the thickness of the foam structures 602, 630 in the vapor flow direction such that the temperature is highest where the replenishment vapor enters the foam structure 630 and the temperature is lowest on the surface of the foam structure 602 opposite the target substrate 654 supported on substrate holder 656 within deposition chamber 658. Substrate holder 656 controls the temperature of substrate 654 and the interior of deposition chamber 658 is maintained at a desired pressure by vacuum pump 662 in combination with pressure sensor 664 and pressure controller 666. It is possible to achieve this thermal gradient by dimensioning the cross section of the foam elements 602, 630 through which an electrical current passes to establish a higher current density near the replenishment vapor inlet. It is also possible to use two or more individually controllable foam elements 602, 630 to achieve the required thermal gradient. Naturally, some thermal gradient through the thickness of the foam elements 602, 630 is achieved due to the presence of the heated replenishment vapor manifold on one side and the presence of a much cooler substrate 637 on the other side. As the replenishment vapor molecules enter the open cell foam structure along with carrier gas molecules having a mean free path about equal to the cell dimensions, they collide frequently with each other and with the ligaments of the foam structure. The vapor molecules colliding with the ligaments in progressing through the thickness of the foam have a probability of condensing with each collision and have an increasing probability of condensing on the increasingly cooler ligaments. With a single foam element having a one centimeter thickness, the vapor specific sieve behavior discussed previously was observed but generating a steady re-evaporated vapor flux completely independent from a concurrent replenishment vapor flux was not achieved. By adding a second, 1 cm thick foam element or by using a thicker foam element, the probability
of condensing collisions is increased and the temperature differential in the flow
direction can be increased such that virtually all of the replenishment vapor molecules
are forced to condense before travelling through the entire foam thickness. Complete
isolation between instabilities in the replenishment vapor flux and the output vapor
flux can be achieved because the replenishment vapor first condenses, if only
momentarily, before being re-evaporated at a highly stable and controllable rate. The
momentary condensation regime is most desirable where extremely thermally
sensitive materials are used. The momentary condensation regime is also most
desirable where the replenishment vapor consists of more than one material and
especially when the saturation vapor pressures of the more than one material are
dissimilar. In this manner, the infinitesimal enveloping organic material coating of the
foam structure is renewed or maintained by a continuous or intermittent flux of
replenishment organic material vapor distributed uniformly over the surface of the
open cell foam structure. This replenishment vapor substantially condenses in the
form of a conformal, thin condensate coating on the foam ligaments directly. This
embodiment allows continuous deposition onto a moving substrate such as in roll to
roll production as long as the average replenishment vapor flux is equal to the average
deposition flux. With this embodiment, a widely fluctuating input vapor rate supplied
to the open cell foam structure such as by flash vaporization or through a typical
vaporization in a crucible, can be transformed into a vapor output rate from the open
cell foam structure to the target substrate with less than 1 percent variation.

Looking at Figure 15A, there is shown a cross section view of vapor
deposition apparatus 600. Heater 630 is sandwiched between electrodes 668, 670.
The electrodes 668, 670 are made of a conductive metal foil, and electrical current
flows through the electrodes 668, 670 to the ligaments of heater 630 through
electrodes 668, 670 to cause resistance heat to be produced in the ligaments.
Electrical cable leads or wires 648, 650 connect to electrodes 668, 670, respectively.
Electrodes 668, 670 preferably take the form of conductive foils. A variety of metals
can be used for the electrodes 668, 670. Conveniently, titanium, tantalum, tungsten,
or molybdenum or coatings of these materials on softer metals such as copper or silver
can be used due to their relative chemical inertness at elevated temperatures.
Compliant elements 672, 674 are heat resistant and, optionally, thermally conductive
material. Compliant elements 672, 674 can conform to the surface texture of heater 630 and create local deformation of electrodes 668, 670 when the heater 630 is pressed against the compliantly supported electrodes 668, 670. One example of useful compliant material is GRAFOIL®. UCAR Carbon Company Inc. of Wilmington, DE., manufactures GRAFOIL® Flexible Graphite as a rolled sheet product that exhibits good heat resistance and typically exceeds 97% elemental carbon by weight.

The sandwich configuration shown in Figure 15A provides low contact resistance between the heater 600 and the electrodes 668, 670, insuring that at least 90 percent of the heat is generated in the ligaments of heater 630 instead of at the interface between the electrodes 668, 670 and the heater 630. Nano-particulate silver paint can also be used to lower the electrical contact resistance between the electrodes 668, 670 and the carbon foam material of the heater 630. Because the silver particles are of a nanometer size, they soften and melt at temperatures hundreds of degrees less than the melting temperature of bulk silver. This behavior is very size dependent and facilitates the establishment of excellent electrical contact between the electrodes 668, 670 and the carbon foam material of the heater 630. The heater 630, electrodes 668, 670 and compliant elements 672, 674 are clamped together by contacts 644, 646. Contacts 644, 646 may be electrically conductive and be attached to electrodes 668, 670, respectively to carry current to the heater 630. Alternately, the contacts 644, 646 could be electrical insulators or have an electrically insulating coating but act as thermal conductors to cool heater 630. Isolating element 676 electrically and thermally isolates the heating structure from the plenum 628 and the entire assembly is unitized by clamping structure 678. A thermocouple 680 or infrared sensor can be used to measure the temperature of heater 630 and provide feedback to control the current delivered to heater 630. It is also possible to measure the voltage and current delivered to heater 630 as a function of temperature to determine the effective electrical resistance. Most materials have a measurable temperature coefficient of resistance and after calibration; it is possible to infer the average heater temperature based on the effective resistance.

A sensor 682 can be used in-situ to measure the vapor flux emanating from the foam structure 602 and this signal can be used to control the power delivered to foam element 602 or both foam elements 602 and 630 such that the output vapor flux can be
controlled to very precise flux values that remain substantially invariant over long time intervals despite temperature and pressure variations in the system. Sensor 682 can be a quartz crystal oscillator or other in-situ deposited film thickness measurement sensor that measures the rate of deposition of the material vapor on the active face of the sensor. The feedback loop to the foam element 602 and or 630 can be of a very low bandwidth, measured in tens of seconds because of the inherently stable output flux from the foam element 602. The action of the foam element can be compared to that of an electrical capacitor such that a relatively constant output signal is obtained even when the input signal is highly variable. This behavior is depicted graphically in Figure 16, which shows a widely variable input rate 684 of replenishment deposition vapor to an open cell foam heating element 10 to form a vapor deposition coating thereon. Yet the output rate 686 of deposition vapor generated by heating the foam heating element 10 is very stable. The control system could advantageously also contain a cascaded control loop to adjust the average replenishment vapor flux of vapor sources 604 and 606 based on a persistent positive or negative control signal in the primary loop controlling the power delivered to the foam element 602.

We have described the use of the open cell foam structures in fairly general terms but the illustrations show the foam elements being used in what may be analogized to showerhead-type arrangement, with individual foam elements having a generally square shape. It is also possible to use the foam in the form of a long rectangle such as would be applicable for a linear manifold used with in-line and roll-to-roll deposition. Figure 17 depicts an in-line deposition system 700 where multiple vapor deposition heads 702 are arranged in series. Each vapor deposition head 702 is substantially identical to the vapor deposition head 140 shown in Figure 5, or alternatively, the vapor deposition heads shown in Figure 15. A plurality of substrates 704 supported on a conveyor system 706 are transported in proximity to vapor deposition heads 702 and receive a coating of the respective deposition materials emanating from each vapor deposition heads 702 to produce a layered coating on substrates 704. The substrates 704 are shown as being delivered from a substrate supply magazine 708, transported on a substrate conveyor system 706 in close proximity to vapor deposition heads 702 and delivered to a receiving substrate magazine 710. One skilled in the art will appreciate that the substrates 704 may be
delivered to conveyor system 706 by means other than magazine 708, transported by means other than conveyor system 706, and the coated substrates 705 may be received by means other than magazine 710. The vapor deposition heads 702, conveyor system 706, substrate supply magazine 708, and receiving substrate magazine 710 are contained within a vacuum chamber 712. The pressure in the vacuum chamber 712 is controlled through a feedback system comprising a pressure sensor 714, a pressure controller 716 and a vacuum pump 718.

Figure 18 depicts an in-line deposition system 800 where multiple vapor deposition heads 802 are arranged in series. Each vapor deposition head 802 is substantially identical to the vapor deposition head 140 shown in Figure 5, or alternatively, the vapor deposition heads shown in Figure 15. An extended length substrate 804 supported on a conveyor system 806 is transported in proximity to vapor deposition heads 802 and receives a coating of the respective deposition materials emanating from each of the vapor deposition heads 802 to produce a layered coating on substrate 804. The substrate 804 is shown as being delivered from a roll 808, transported on a substrate conveyor system 806 in close proximity to vapor deposition heads 802 and delivered to a receiving roll 810. One skilled in the art will appreciate that the substrate 804 may be delivered to conveyor system 806 by means other than roll 808, transported by means other than conveyor system 806, and the coated substrate 805 may be received by means other than roll 810. The vapor deposition heads 802, conveyor system 806, substrate supply roll 808, and substrate receiving roll 810 are contained within a vacuum chamber 812. The pressure in the vacuum chamber 812 is controlled through a feedback system comprising a pressure sensor 814, a pressure controller 816 and a vacuum pump 818.

The term "extended length substrate" as used herein is intended include a substrates having a length that is greater than the length of the deposition chamber. This necessarily includes the roll-to-roll configuration shown in Figure 18.

The roll-to-roll configuration depicted in Figure 18 demonstrates that the present invention is applicable to batch and continuous deposition processes on both discrete and extended substrates. The flexible substrate can be made from glass, aluminum or stainless steel foil. These foils are typically between 25 and 100 microns...
thick. Polymeric substrates such as PET and PEN can also be used after a moisture barrier film coating has been first deposited as a support layer for the OLED material.

In each of these embodiments, the deposition rate stability on the target substrate is determined by the vapor generation rate stability of the open cell foam structure and is decoupled from any variability in the replenishment vapor flux due to difficulties and variability in metering and vaporizing minute powder quantities on an as-needed basis. By utilizing a phase change from gas to solid between the input vapor and the output vapor in the open cell foam, the objective of establishing and maintaining a controllable, precise and invariant flux of the output vapor is decoupled from the difficulties of maintaining a stable deposition rate from a vapor on demand flash vaporization system.

The invention allows substantial simplification in the preparation and vaporization of organic material for making OLED devices through consideration of the organic material purification process and consideration of the variables such as temperature, thermal exposure time, thermal conductivity, surface area, partial pressure, total pressure and convection that control organic material vaporization and decomposition.

In the practice of the present invention the thickness of the solid coating of material vapor deposited onto the surface of the three-dimensional open cell reticulated structure is preferably less than 5µm. The preferred thickness will vary, however, by the material being deposited. The more thermally robust materials will support longer thermal exposure times and can therefore be coated to a greater thickness to enable longer deposition autonomy. The least thermally robust materials will likely only support sub-micron thicknesses to insure that they are consumed before they decompose. These sensitive materials are good candidates for use with the continuous vapor replenishment mode of operation.

In the practice of the present invention the solid coating of material vapor deposited onto the surface of the three-dimensional open cell reticulated structure is substantially pure. The term "substantially pure" is used herein to denote of at least 99.5% purity and less than 10 PPM of halogens such as fluorine, chlorine, bromine. This is a significant improvement over the typical solution purification of OLED materials, which may vary by material and synthesis method used. However, it is
believed that solution purification of OLED materials is generally limited to less than 97% or 98% purity. This may not seem like a large numerical difference but the performance and especially the lifetime of OLED devices can be degraded 10% by chlorine concentrations as low as 30 PPM.

OLED materials that can be vapor deposited with the present invention include, by way of example, TiOPC, NPB, LiQ, TcTa, Bphen, DMQA, DBQA, Rubrene, TMDBQA, Ir(ppy)3, Ir(ppy)2(acac), Ir(mppy)3, CBP, A1Q3, DCJTB, Ir(piq)3, Ir(piq)2(acac), Ir(2-phq)3, Ir(2-phq)2(acac), Ir(BT)2(acac), DCM, F4-TCNQ, Perylene, Pentacene.

While the present invention has been discussed primarily as a method for vapor depositing OLED materials, it is possible to vapor deposit metals and ceramics. Glassy carbon is an example of a non-graphitizing carbon that is a carbon which cannot be transformed into crystalline graphite even at temperatures of 3000°C and above (Franklin, Proc. Roy. Soc. A, 209, 196, 1951, Harris, Int. Mater. Rev., 42, 206. 1997). In addition to very high thermal stability, its distinguishing properties include its extreme resistance to chemical attack: it has been demonstrated that the rates of oxidation of glassy carbon in oxygen, carbon dioxide or water vapour are lower than those of any other carbon (Jenkins and Kawamura, Polymeric Carbons - Carbon Fibre, Glass and Char (Cambridge: Cambridge University Press). 1976). It is also highly resistant to attack by acids. Thus, while normal graphite is reduced to a powder by a mixture of concentrated sulphuric and nitric acids at room temperature, glassy carbon is unaffected by such treatment, even after several months.

The inertness of glassy carbon makes it a useful crucible material for melting and vaporizing a wide range of organic and inorganic materials including metals. The process described here for controllably vaporizing organic materials can therefore be used to controllably vaporize a wide range of materials whose vaporization temperatures are below 3000°C. This capability encompasses most of the elements from the periodic table including elements from groups I, III and VI that are notable for photovoltaic applications. Copper, indium, gallium and selenium could be vaporized to deposit CIGS, cadmium telluride could also be vapour deposited by this method to achieve a uniform film coating on a continuously moving substrate for use in high volume fabrication of photovoltaic devices.
While the intermediate vapor deposition receptacle is described herein as a conductive three-dimensional, open cell, reticulated structure, preferably an open cell vitreous carbon foam, it should be understood that the intermediate vapor deposition receptacle can be formed differently. As an example, it may be comprised of multiple layers of carbon fiber mesh or lattice overlaid on one another to yield a conductive, open, three-dimensional reticulated structure with a multitude of tortuous flow paths therethrough. The tortuous flow paths promote mixing of the gas with the organic vapor generated around the heated ligaments or fibers, and the flow and temperature of the inert carrier gas contribute to controlling the rate of generation and transport of the organic vapor toward the deposition target substrate.

PARTS LIST

10  open cell foam structures
11  sublimation purification apparatus
12  material to be purified
14  vaporization apparatus
16  vacuum chamber
18  heating elements
20  crucible
21  vacuum pump
22  condensate collection tube
24  pressure sensor
26  pressure controller
28  struts or ligaments
30  coating of condensed material
32  vapor deposition apparatus
34  input tube
36  mass flow controller
38  gas heater
40  input duct
42  gas distribution manifold or plenum
44, 45 wires
46, 48 contacts
50  vacuum chamber
52  substrate holder
54  substrate
56  vacuum pump
58  pressure sensor
60  pressure controller
62  heating elements
64, 66 electrodes
68, 70 cable leads
72, 74 compliant elements
76, 78 contacts
80  isolating element
84  clamping structure
86  thermocouple
100 vapor deposition apparatus
102  input tube
104  mass flow controller
106  gas heater
108  input duct
110  gas distribution manifold or plenum
112, 113 wires
114, 116 contacts
118  vacuum chamber
120  substrate holder
122  substrate
124  vacuum pump
126  pressure sensor
128 pressure controller
130 heating elements
131, 133 compliant elements
132 second open cell foam structure or heating element
134, 136 contacts
135, 137 electrodes
138, 139 wires
140 vapor deposition head
142, 144 electrodes
146, 148 compliant elements
150 isolating element
152 clamping structure
154 heater
300 deposition source supply head
302 rotor
304 stator
306 frame
307 support faces
308 feed tube
309 contact
310 duct
312 duct
314 substrate
316 substrate holder
320 multi-faceted prism
322 substrate holder
324 target substrate
400 deposition source supply head
402 rotor
404, 406 stator portions
408 frames
410 feed tube
412 duct
414 duct
416 substrate
418 substrate support
420 duct
422 duct
500 vapor deposition head
502 feed tube
504 duct
506 stator portion
508 duct
510 rotor
512 substrate
514 substrate holder
516 feed tube
518 duct
520 stator portion
522 duct
524 substrate
600 vapor deposition apparatus
602 open cell foam element
604, 606 vapor generator sources
608, 610 carrier gas inlets
612, 614 gas flow controllers
616 vapor mixer
618 dilution carrier gas inlet
620 gas flow controller
622 gas temperature controller
624 conduit
626 gas inlet tube
628 gas distribution manifold or plenum
630 open cell foam structure
heating elements
wires
contacts
substrate holder
substrate
vacuum chamber
vacuum pump
pressure sensor
pressure controller
contacts
wires
vapor deposition head
target substrate
substrate holder
deposition chamber
deposition chamber
vacuum pump
pressure sensor
pressure controller
electrodes
compliant elements
isolating element
clamping structure
thermocouple
sensor
variable input rate
output rate
in-line deposition system
vapor deposition heads
substrates
coated substrates
conveyor system
708  substrate supply magazine
710  receiving substrate magazine
712  vacuum chamber
714  pressure sensor
716  pressure controller
718  vacuum pump
800  in-line deposition system
802  vapor deposition heads
804  substrate
805  coated substrate
806  conveyor system
808  substrate supply roll
810  substrate receiving roll
812  vacuum chamber
814  pressure sensor
816  pressure controller
818  vacuum pump
CLAIMS:

1. A method of vapor deposition comprising:
   (a) vaporizing a solid coating of a material that was previously vapor deposited on a three-dimensional, open cell, reticulated structure to form a deposition gas;
   (b) flowing a carrier gas through the three-dimensional, open cell, reticulated structure to yield a controllable partial pressure of the deposition gas while vaporizing the solid coating and thereby forming a mixture of the carrier gas and the deposition gas;
   (c) delivering the mixture at a stable flow rate to a temperature controlled substrate;
   (d) condensing the deposition gas onto a surface of the temperature controlled substrate; and
   (e) withdrawing the carrier gas.

2. A method of vapor deposition comprising:
   (a) vapor depositing a solid coating of a material onto a three-dimensional, open cell, reticulated structure;
   (b) vaporizing the solid coating to form a deposition gas;
   (c) flowing a carrier gas through the three-dimensional, open cell, reticulated structure to yield a controllable partial pressure of the deposition gas while vaporizing the solid coating and thereby forming a mixture of the carrier gas and the deposition gas;
   (d) delivering the mixture at a stable flow rate to a temperature controlled substrate;
   (e) condensing the deposition gas onto a surface of the temperature controlled substrate; and
   (f) withdrawing the carrier gas.

3. A method according to claim 1 or 2 or in particular according thereto wherein:
   the selected solid material is an organic or ogano-metallic material.

4. A method according to one of the preceding claims or in particular according thereto wherein:
the conductive three-dimensional, open cell, reticulated structure is a vitreous carbon foam.

5. A method according to one or more of the preceding claims or in particular according thereto wherein:
   the solid coating of the material onto the three-dimensional, open cell, reticulated structure has a thickness in the range of from about 1nm to about 2µm.

6. A method according to one of the preceding claims or in particular according thereto wherein:
   the three-dimensional, open cell, reticulated structure is electrically conductive.

7. A method according to one of the preceding claims or in particular according thereto wherein:
   the solid coating of the material onto the three-dimensional, open cell, reticulated structure is substantially free of contaminants.

8. A method according to one of the preceding claims or in particular according thereto further comprising:
   vapor depositing a coating of a refractory metal or ceramic material on the three-dimensional, open cell, reticulated structure, the solid coating of the selected vapor deposition material residing on top of the coating of the refractory metal or ceramic material.

9. A method according to one of the preceding claims or in particular according thereto further comprising:
   replenishing the selected solid material on the conductive three-dimensional open cell, reticulated structure via vapor deposition after the solid coating thereon has been spent.

10. A method according to one of the preceding claims or in particular according thereto further comprising:
replenishing the selected solid material on the three-dimensional, open cell, reticulated structure via vapor deposition while the solid coating thereon is being vaporized and deposited on the surface of the target substrate.

11. A method according to one of the preceding claims or in particular according thereto wherein:
   the three-dimensional, open cell, reticulated structure is electrically conductive and the vaporizing step is performed by applying a voltage across the three-dimensional, open cell, reticulated structure.

12. A method according to one of the preceding claims or in particular according thereto wherein:
   the three-dimensional, open cell, reticulated structure is thermally conductive and the vaporizing step is applying heat to the three-dimensional, open cell, reticulated structure.

13. A method according to one of the preceding claims or in particular according thereto wherein:
   the conductive three-dimensional, open cell, reticulated structure is a resistance heater.

14. A method of vapor deposition according to one of the preceding claims or in particular according thereto further comprising:
   (a) supplying a replenishment deposition vapor to the three-dimensional, open cell, reticulated structure; and
   (b) condensing the replenishment deposition vapor on the three-dimensional, open cell, reticulated structure to replenish the solid coating.

15. A method of vapor deposition according to one of the preceding claims or in particular according thereto comprising:
   (a) simultaneously supplying a replenishment deposition vapor to the three-dimensional, open cell, reticulated structure; and
(b) condensing the replenishment deposition vapor on the three-dimensional, open cell, reticulated structure to replenish the solid coating.

16. A method according to one of the preceding claims or in particular according thereto further comprising:

   measuring a material deposition rate onto the temperature controlled substrate and providing feedback to control the electrical current delivered to the heater.

17. A method for supplying a vapor flux at a stable flow rate to a deposition chamber comprising:
   (a) vaporizing a selected solid organic or organo-metallic material to form a vapor;
   (b) transmitting the vapor to a three-dimensional, open cell, reticulated foam structure, and uniformly distributing the vapor throughout the three-dimensional, open cell, reticulated foam structure;
   (c) condensing the vapor to form a solid coating of the selected solid organic or organo-metallic material on the conductive, three-dimensional, open cell, reticulated foam structure;
   (d) vaporizing the solid coating to form a deposition gas;
   (e) flowing a carrier gas though the foam structure to yield a controllable partial pressure of the deposition gas while vaporizing the solid coating; and
   (f) delivering a mixture of the carrier gas and the deposition gas to a deposition chamber.

18. A method according to one of the preceding claims or in particular according thereto wherein:

   the selected solid material is an OLED material.

19. A vapor deposition apparatus comprising:
   (a) a first three-dimensional, open cell, reticulated structure having a solid coating of a selected vapor deposition material vapor deposited thereon;
   (b) means for heating the first three-dimensional, open cell, reticulated structure solid coating to vaporize the solid coating to form a deposition gas;
(c) a first conduit through which a carrier gas is delivered to flow through the first three-dimensional, open cell, reticulated structure to yield a controllable partial pressure of the deposition gas as the solid coating is vaporized, the vaporized solid coating and the carrier gas forming a mixture; and
(d) a second conduit through which the mixture is delivered at a stable flow rate to a temperature controlled substrate within a deposition chamber.

20. A vapor deposition apparatus according to claim 19 or in particular according thereto further comprising:
   a power supply for supplying an electrical current to the first conductive, three-dimensional, open cell, reticulated structure.

21. A vapor deposition apparatus according to claim 19 or 20 or in particular according thereto further comprising:
   a vapor deposition rate sensor for measuring a material deposition rate onto the temperature controlled substrate and providing feedback to control the electrical current delivered to the heater.

22. A vapor deposition apparatus according to claim 19 to 21 or in particular according thereto wherein:
   the solid coating is a solid organic or organo-metallic material.

23. A vapor deposition apparatus according to claim 19 to 22 or in particular according thereto wherein:
   the solid coating is a metal or ceramic material.

24. A vapor deposition apparatus according to claim 19 to 23 or in particular according thereto wherein:
   the first conductive, three-dimensional, open cell, reticulated structure is electrically conductive.
25. A vapor deposition apparatus according to claim 19 to 24 or in particular according thereto wherein:
   the means for heating is a power source for applying a voltage across the first electrically conductive, three-dimensional, open cell, reticulated structure, the first electrically conductive, three-dimensional, open cell, reticulated structure thereby acting as a resistance heating device.

26. A vapor deposition apparatus according to claim 25 or in particular according thereto wherein:
   the means for heating is a heater for applying heat to the first three-dimensional, open cell, reticulated structure.

27. A vapor deposition apparatus according to claim 19 to 26 or in particular according thereto wherein:
   the first conductive, three-dimensional, open cell, reticulated structure is a vitreous carbon foam.

28. A vapor deposition apparatus according to claim 19 to 27 or in particular according thereto further comprising:
   a uniform coating of a refractory metal on the first conductive, three-dimensional, open cell, reticulated structure, the solid coating of the selected vapor deposition material residing on top of the uniform coating of the refractory metal.

29. A vapor deposition apparatus according to claim 19 to 28 or in particular according thereto further comprising:
   a uniform coating of a ceramic on the first conductive, three-dimensional, open cell, reticulated structure, the solid coating of the selected vapor deposition material residing on top of the uniform coating of ceramic.

30. A vapor deposition apparatus according to claim 28 or 29 or in particular according thereto wherein:
   the refractory metal is tungsten, tantalum or molybdenum.
31. A vapor deposition apparatus according to claim 29 or in particular according thereto wherein:
   
   the ceramic includes silicon carbide or boron nitride

32. A vapor deposition apparatus according to claim 19 to 31 or in particular according thereto wherein:
   
   the vaporization rate of the selected material from the three-dimensional, open cell, reticulated structure is substantially constant over a wide range of condensed material mass within the first three-dimensional, open cell, reticulated structure but varies as a function of the temperature of the first conductive, three-dimensional, open cell, reticulated structure and as a function of the carrier gas flow rate.

33. A vapor deposition apparatus according to claim 19 to 32 or in particular according thereto wherein:
   
   the carrier gas is an inert gas that flows through the first three-dimensional, open cell, reticulated structure, the first three-dimensional, open cell, reticulated structure comprising a plurality of ligaments, the ligaments providing a tortuous flow path that promotes mixing of the carrier gas with the vaporized solid coating generated around the ligaments, and the flow and temperature of the gas contributing to controlling a rate of generation and transport of the vaporized solid coating toward the deposition target.

34. A vapor deposition apparatus according to claim 19 to 33 or in particular according thereto further comprising:
   
   an exhaust port through which the carrier gas is withdrawn from the chamber.

35. A vapor deposition apparatus according to claim 19 to 34 or in particular according thereto further comprising:
   
   a heated plenum, the first conductive, three-dimensional, open cell, reticulated structure residing with the heated plenum.
36. A vapor deposition apparatus according to claim 19 to 35 or in particular according thereto further comprising:
   a second three-dimensional, open cell, reticulated structure residing above the first conductive, three-dimensional, open cell, reticulated structure within the plenum.

37. A vapor deposition apparatus according to claim 19 to 36 or in particular according thereto wherein:
   the first three-dimensional, open cell, reticulated structure is thermally conductive.

38. A vapor deposition apparatus according to claim 24 to 37 or in particular according thereto further comprising:
   a first pair of electrodes electrically connected to the first conductive, three-dimensional, open cell, reticulated structure

39. A vapor deposition apparatus according to claim 38 or in particular according thereto wherein:
   each of the first pair of electrodes is a conductive foil sheet, the conductive foil sheets positioned on opposite sides of the heater.

40. A vapor deposition apparatus according to claim 39 or in particular according thereto further comprising:
   a respective compliant element interfacing with each of the first pair of electrodes each respective compliant element conforming to a surface texture of heater to create local deformation of conductive foil sheets.

41. A vapor deposition apparatus according to claim 40 or in particular according thereto further comprising:
   a contact element positioned adjacent to each conductive foil sheet for clamping together the heater, the foil sheets and the compliant elements.
42. A vapor deposition apparatus according to claim 39 to 41 or in particular according thereto wherein:
   each of the contact elements is electrically conductive.

43. A vapor deposition apparatus according to claim 39 to 42 or in particular according thereto wherein:
   each of the contact elements is thermally conductive.

44. A vapor deposition apparatus according to claim 19 to 43 or in particular according thereto further comprising:
   a temperature sensor for measuring the temperature of the first conductive, three-dimensional, open cell, reticulated structure and providing feedback to control the electrical current delivered to the first conductive, three-dimensional, open cell, reticulated structure.

45. A vapor deposition apparatus according to claim 19 to 44 or in particular according thereto further comprising:
   a vapor deposition rate sensor for measuring a material deposition rate onto the temperature controlled substrate and providing feedback to control an electrical current delivered to the first conductive, three-dimensional, open cell, reticulated structure.

46. A vapor deposition apparatus according to claim 36 to 45 or in particular according thereto wherein:
   the second conductive, three-dimensional, open cell, reticulated structure is electrically conductive.

47. A vapor deposition apparatus according to claim 36 to 46 or in particular according thereto wherein:
   the second conductive, three-dimensional, open cell, reticulated structure is thermally conductive.
48. A vapor deposition apparatus according to claim 19 to 47 or in particular according thereto wherein:

the selected material is an OLED material.

49. A vapor deposition apparatus according to claim 19 to 48 or in particular according thereto further comprising:

(a) a plenum in which first conductive, three-dimensional, open cell, reticulated structure resides; and
(b) at least one vapor generator source for supplying a replenishment deposition gas to the plenum, the replenishment deposition gas condensing to form a new solid coating of deposition material on the first conductive, three-dimensional, open cell, reticulated structure.

50. A vapor deposition apparatus according to claim 19 to 49 or in particular according thereto further comprising:

at least one vapor generator source for supplying a replenishment deposition gas to the plenum, the replenishment deposition gas condensing to form a new solid coating of deposition material on the first conductive, three-dimensional, open cell, reticulated structure.

51. A vapor deposition apparatus according to claim 19 to 50 or in particular according thereto further comprising:

at least one vapor generator source for supplying a replenishment deposition gas to the plenum, the replenishment deposition gas condensing to form a new solid coating of deposition material on the first conductive, three-dimensional, open cell, reticulated structure.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

INV. C23C14/12 C23C14/24 H01L51/00 C23C14/22

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23C H01L B05D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>A</td>
<td>WO 2006/100058 A2 (CREAPHYS GMBH [DE]); FR0EB HARTMUT [DE]; DRECHSEL JENS [DE]) 28 September 2006 (2006-09-28) page 8, line 3 - line 14 page 15, line 1 - line 12 figure 1 A</td>
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Further documents are listed in the continuation of Box C. See patent family annex.

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Date of the actual completion of the international search 13 March 2012

Date of mailing of the international search report 21/03/2012

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Kudelka, Stephan

Form PCT/ISA210 (second sheet) (April 2005)
C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>US 2006/115585 AI (BULOVIC VLADIMIR [US] ET AL) 1 June 2006 (2006-06-01) figure 7a</td>
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