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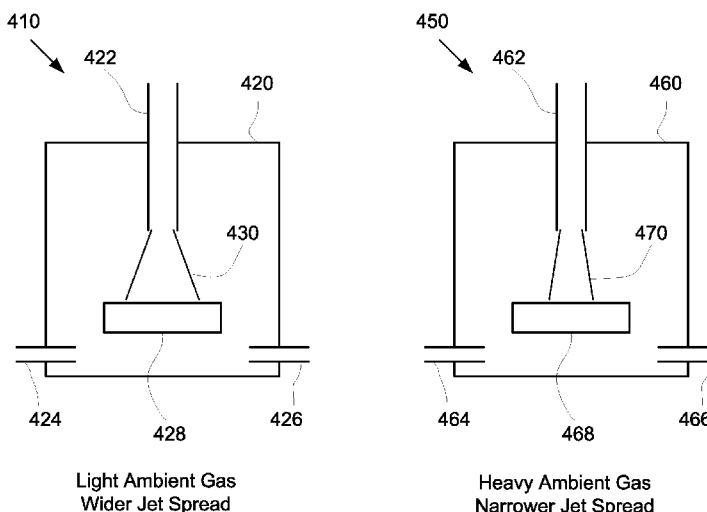


FIGURE 4

(57) Abstract: A method of depositing organic material is provided. A chamber is provided having a substrate disposed therein. An organic material is deposited over the substrate by ejecting from a nozzle (422, 462) directed at the substrate: a first gas; and a vapor of the organic material carried by the first gas. During the depositing an organic material, a second gas is provided in the chamber. The flow rate of the second gas is at least 5 % of the sum of the flow rates of all gases flowing into the vacuum chamber. The second gas has a molecular weight at least 20 % greater than the molecular weight of the first gas. The second gas is provided in the chamber via an aperture (424, 464) remote from the nozzle.



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## ORGANIC VAPOR JET PRINTING

[0001] The claimed invention was made by, on behalf of, and/or in connection with one or more of the following parties to a joint university corporation research agreement: Regents of  
5 the University of Michigan, Princeton University, The University of Southern California, and the Universal Display Corporation. The agreement was in effect on and before the date the claimed invention was made, and the claimed invention was made as a result of activities undertaken within the scope of the agreement.

### FIELD OF THE INVENTION

10 [0002] The present invention relates to organic vapor jet printing (OVJP).

### BACKGROUND

[0003] Opto-electronic devices that make use of organic materials are becoming increasingly desirable for a number of reasons. Many of the materials used to make such devices are relatively inexpensive, so organic opto-electronic devices have the potential for  
15 cost advantages over inorganic devices. In addition, the inherent properties of organic materials, such as their flexibility, may make them well suited for particular applications such as fabrication on a flexible substrate. Examples of organic opto-electronic devices include organic light emitting devices (OLEDs), organic phototransistors, organic photovoltaic cells, and organic photodetectors. For OLEDs, the organic materials may have performance  
20 advantages over conventional materials. For example, the wavelength at which an organic emissive layer emits light may generally be readily tuned with appropriate dopants.

[0004] OLEDs make use of thin organic films that emit light when voltage is applied across the device. OLEDs are becoming an increasingly interesting technology for use in applications such as flat panel displays, illumination, and backlighting. Several OLED  
25 materials and configurations are described in U.S. Pat. Nos. 5,844,363, 6,303,238, and 5,707,745, which are incorporated herein by reference in their entirety.

[0005] One way to deposit OLEDs and other organic devices is Organic Vapor Jet Printing (OVJP). The general principle of OVJP has been described in U.S. Patent No. 7,404,862, issued July 29, 2008, U.S. Patent 7,744,957 issued June 29, 2010, U.S. Patent No. 7,431,968  
30 issued October 7, 2008, U.S. Patent No. 7,722,927 issued May 25, 2010, and U.S. Patent Application No. 12/034,683, filed February 21, 2008, all of which should be incorporated by reference.

[0006] As used herein, the term "organic" includes polymeric materials as well as small molecule organic materials that may be used to fabricate organic opto-electronic devices. "Small molecule" refers to any organic material that is not a polymer, and "small molecules" may actually be quite large. Small molecules may include repeat units in some circumstances.

5 For example, using a long chain alkyl group as a substituent does not remove a molecule from the "small molecule" class. Small molecules may also be incorporated into polymers, for example as a pendent group on a polymer backbone or as a part of the backbone. Small molecules may also serve as the core moiety of a dendrimer, which consists of a series of chemical shells built on the core moiety. The core moiety of a dendrimer may be a  
10 fluorescent or phosphorescent small molecule emitter. A dendrimer may be a "small molecule," and it is believed that all dendrimers currently used in the field of OLEDs are small molecules.

[0007] As used herein, "top" means furthest away from the substrate, while "bottom" means closest to the substrate. Where a first layer is described as "disposed over" a second  
15 layer, the first layer is disposed further away from substrate. There may be other layers between the first and second layer, unless it is specified that the first layer is "in contact with" the second layer. For example, a cathode may be described as "disposed over" an anode, even though there are various organic layers in between.

[0008] More details on OLEDs, and the definitions described above, can be found in US  
20 Pat. No. 7,279,704, which is incorporated herein by reference in its entirety.

#### SUMMARY OF THE INVENTION

[0009] A method of depositing organic material is provided. A chamber is provided having a substrate disposed therein. An organic material is deposited over the substrate by ejecting  
25 from a nozzle directed at the substrate: a first gas; and a vapor of the organic material carried by the first gas. During the depositing an organic material, a second gas is provided in the chamber. The flow rate of the second gas is at least 5% of the sum of the flow rates of all gases flowing into the vacuum chamber. The second gas has a molecular weight at least 20% greater than the molecular weight of the first gas. The second gas is provided in the chamber  
30 via an aperture remote from the nozzle.

[0010] Preferably, the flow rate of the second gas is at least 30% of the sum of the flow rates of all gases flowing into the vacuum chamber. More preferably, the flow rate of the

second gas is at least 60% of the sum of the flow rates of all gases flowing into the vacuum chamber.

[0011] Preferably, during the depositing of an organic material, the total pressure in the vacuum chamber is between 1 mTorr and 1 Torr.

5 [0012] The first gas is preferably N<sub>2</sub>. The second gas is preferably selected from the group consisting of Ar, Kr, freons,, Xe, CO<sub>2</sub> and WF<sub>6</sub>.

[0013] The second gas may be a single material. The second gas may be a mixture of different gases, each having a molecular weight at least 20% greater than that of the first gas..

10 [0014] The second gas preferably has a molecular weight at least 100% greater than the molecular weight of the first gas. The second gas may be a mixture of materials each having a molecular weight at least 100% greater than the molecular weight of the first gas.

[0015] The chamber may be a vacuum chamber.

15 [0016] A method of depositing organic material is provided. A chamber is provided having a substrate disposed therein. An organic material is deposited over the substrate by ejecting from a nozzle directed at the substrate: a first gas; and a vapor of the organic material carried by the first gas. During the depositing an organic material, a second gas is provided in the chamber. The second gas has a molecular weight at least 20% greater than the molecular weight of the first gas. The second gas is provided in the chamber via an aperture remote from the nozzle. The nozzle has an aperture having a smallest dimension. The organic material is deposited over the substrate as a patterned feature having a shape defined by the shape of the aperture. The partial pressure of the second gas in the chamber during the depositing of the organic material is sufficient to reduce by a factor of 2 the amount of organic material deposited at a distance of one smallest dimension from the edge of the patterned feature, relative to an otherwise identical deposition performed without the second gas.  
25

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0017] FIG. 1 shows an organic light emitting device.

30 [0018] FIG. 2 shows an inverted organic light emitting device that does not have a separate electron transport layer.

[0019] FIG. 3 shows cross sections of four different nozzle geometries taken in a direction perpendicular to gas flow.

[0020] FIG. 4 shows two chambers in which material is being deposited, one with a light ambient gas and the other with a heavy ambient gas.

5 [0021] FIG. 5 shows plots of emission ratios vs. distance from a deposition edge, which provides a measure of how much overspray occurred during deposition.

#### DETAILED DESCRIPTION

[0022] Generally, an OLED comprises at least one organic layer disposed between and  
10 electrically connected to an anode and a cathode. When a current is applied, the anode injects holes and the cathode injects electrons into the organic layer(s). The injected holes and electrons each migrate toward the oppositely charged electrode. When an electron and hole localize on the same molecule, an "exciton," which is a localized electron-hole pair having an excited energy state, is formed. Light is emitted when the exciton relaxes via a photoemissive  
15 mechanism. In some cases, the exciton may be localized on an excimer or an exciplex. Non-radiative mechanisms, such as thermal relaxation, may also occur, but are generally considered undesirable.

[0023] FIG. 1 shows an organic light emitting device 100. The figures are not necessarily drawn to scale. Device 100 may include a substrate 110, an anode 115, a hole injection layer  
20 120, a hole transport layer 125, an electron blocking layer 130, an emissive layer 135, a hole blocking layer 140, an electron transport layer 145, an electron injection layer 150, a protective layer 155, and a cathode 160. Cathode 160 is a compound cathode having a first conductive layer 162 and a second conductive layer 164. Device 100 may be fabricated by depositing the layers described, in order. The properties and functions of these various  
25 layers, as well as example materials, are described in more detail in US 7,279,704 at cols. 6-10, which are incorporated by reference.

[0024] More examples for each of these layers are available. For example, a flexible and transparent substrate-anode combination is disclosed in U.S. Pat. No. 5,844,363, which is incorporated by reference in its entirety. An example of a p-doped hole transport layer is m-  
30 MTDATA doped with F.sub.4-TCNQ at a molar ratio of 50:1, as disclosed in U.S. Patent Application Publication No. 2003/0230980, which is incorporated by reference in its entirety.

Examples of emissive and host materials are disclosed in U.S. Pat. No. 6,303,238 to Thompson et al., which is incorporated by reference in its entirety. An example of an n-doped electron transport layer is BPhen doped with Li at a molar ratio of 1:1, as disclosed in U.S. Patent Application Publication No. 2003/0230980, which is incorporated by reference in its entirety. U.S. Pat. Nos. 5,703,436 and 5,707,745, which are incorporated by reference in their entireties, disclose examples of cathodes including compound cathodes having a thin layer of metal such as Mg:Ag with an overlying transparent, electrically-conductive, sputter-deposited ITO layer. The theory and use of blocking layers is described in more detail in U.S. Pat. No. 6,097,147 and U.S. Patent Application Publication No. 2003/0230980, which are incorporated by reference in their entireties. Examples of injection layers are provided in U.S. Patent Application Publication No. 2004/0174116, which is incorporated by reference in its entirety. A description of protective layers may be found in U.S. Patent Application Publication No. 2004/0174116, which is incorporated by reference in its entirety.

**[0025]** FIG. 2 shows an inverted OLED 200. The device includes a substrate 210, a cathode 215, an emissive layer 220, a hole transport layer 225, and an anode 230. Device 200 may be fabricated by depositing the layers described, in order. Because the most common OLED configuration has a cathode disposed over the anode, and device 200 has cathode 215 disposed under anode 230, device 200 may be referred to as an "inverted" OLED. Materials similar to those described with respect to device 100 may be used in the corresponding layers of device 200. FIG. 2 provides one example of how some layers may be omitted from the structure of device 100.

**[0026]** The simple layered structure illustrated in FIGS. 1 and 2 is provided by way of non-limiting example, and it is understood that embodiments of the invention may be used in connection with a wide variety of other structures. The specific materials and structures described are exemplary in nature, and other materials and structures may be used. Functional OLEDs may be achieved by combining the various layers described in different ways, or layers may be omitted entirely, based on design, performance, and cost factors. Other layers not specifically described may also be included. Materials other than those specifically described may be used. Although many of the examples provided herein describe various layers as comprising a single material, it is understood that combinations of materials, such as a mixture of host and dopant, or more generally a mixture, may be used. Also, the layers may have various sublayers. The names given to the various layers herein are not intended to be strictly limiting. For example, in device 200, hole transport layer 225 transports holes and

injects holes into emissive layer 220, and may be described as a hole transport layer or a hole injection layer. In one embodiment, an OLED may be described as having an "organic layer" disposed between a cathode and an anode. This organic layer may comprise a single layer, or may further comprise multiple layers of different organic materials as described, for example, with respect to FIGS. 1 and 2.

[0027] Structures and materials not specifically described may also be used, such as OLEDs comprised of polymeric materials (PLEDs) such as disclosed in U.S. Pat. No. 5,247,190 to Friend et al., which is incorporated by reference in its entirety. By way of further example, OLEDs having a single organic layer may be used. OLEDs may be stacked, for example as described in U.S. Pat. No. 5,707,745 to Forrest et al, which is incorporated by reference in its entirety. The OLED structure may deviate from the simple layered structure illustrated in FIGS. 1 and 2. For example, the substrate may include an angled reflective surface to improve out-coupling, such as a mesa structure as described in U.S. Pat. No. 6,091,195 to Forrest et al., and/or a pit structure as described in U.S. Pat. No. 5,834,893 to Bulovic et al., which are incorporated by reference in their entireties.

[0028] Unless otherwise specified, any of the layers of the various embodiments may be deposited by any suitable method. For the organic layers, preferred methods include thermal evaporation, ink-jet, such as described in U.S. Pat. Nos. 6,013,982 and 6,087,196, which are incorporated by reference in their entireties, organic vapor phase deposition (OVPD), such as described in U.S. Pat. No. 6,337,102 to Forrest et al., which is incorporated by reference in its entirety, and deposition by organic vapor jet printing (OVJP), such as described in U.S. patent application Ser. No. 10/233,470, which is incorporated by reference in its entirety. Other suitable deposition methods include spin coating and other solution based processes. Solution based processes are preferably carried out in nitrogen or an inert atmosphere. For the other layers, preferred methods include thermal evaporation. Preferred patterning methods include deposition through a mask, cold welding such as described in U.S. Pat. Nos. 6,294,398 and 6,468,819, which are incorporated by reference in their entireties, and patterning associated with some of the deposition methods such as ink-jet and OVJP. Other methods may also be used. The materials to be deposited may be modified to make them compatible with a particular deposition method. For example, substituents such as alkyl and aryl groups, branched or unbranched, and preferably containing at least 3 carbons, may be used in small molecules to enhance their ability to undergo solution processing. Substituents having 20 carbons or more may be used, and 3-20 carbons is a preferred range. Materials

with asymmetric structures may have better solution processibility than those having symmetric structures, because asymmetric materials may have a lower tendency to recrystallize. Dendrimer substituents may be used to enhance the ability of small molecules to undergo solution processing.

- 5 [0029] Devices fabricated in accordance with embodiments of the invention may be incorporated into a wide variety of consumer products, including flat panel displays, computer monitors, televisions, billboards, lights for interior or exterior illumination and/or signaling, heads up displays, fully transparent displays, flexible displays, laser printers, telephones, cell phones, personal digital assistants (PDAs), laptop computers, digital cameras,
- 10 camcorders, viewfinders, micro-displays, vehicles, a large area wall, theater or stadium screen, or a sign. Various control mechanisms may be used to control devices fabricated in accordance with the present invention, including passive matrix and active matrix. Many of the devices are intended for use in a temperature range comfortable to humans, such as 18 degrees C. to 30 degrees C., and more preferably at room temperature (20-25 degrees C.).
- 15 [0030] The materials, structures and methods described herein may have applications in devices other than OLEDs. For example, other optoelectronic devices such as organic solar cells and organic photodetectors may employ the materials, structures and methods. More generally, organic devices, for example organic transistors, may employ the materials and structures.
- 20 [0031] Organic Vapor Jet Printing (OVJP) is a desirable method for depositing organic materials in many circumstances. OVJP may allow for the deposition of organic molecules in shapes or patterns defined by the nozzle through which the jet is formed, without the use of a mask, photoresist, or similar patterning techniques based on blocking off or hiding parts of the substrate onto which deposition is not desired.
- 25 [0032] In general, the nozzle or nozzles of an OVJP system are in fluid communication with a source of carrier gas and a source of organic molecules.
- [0033] As used herein, a “nozzle” is a mechanism that directs, guides, or otherwise controls the flow of material after it exits the mechanism.
- [0034] Some, but not all, OVJP systems involve deposition in a chamber. Many OVJP
- 30 systems also involve a substrate holder adapted to support a substrate beneath the nozzle, and to move relative to the nozzle. The nozzle, the substrate holder, or both may move. Where a



chamber is used, the nozzle and substrate holder may be within the chamber. The use of a chamber allows for better control of ambient conditions, such as background pressure, gas composition, and temperature. As used herein, “beneath” the nozzle means disposed in the direction that the nozzle points, i.e., that the nozzle points at the substrate. The nozzle may be oriented in any number of directions in the substrate.

[0035] OVJP has been practically demonstrated using a single carrier gas (usually nitrogen) to transport organic vapor into a nozzle from where it is deposited on a substrate in close proximity to the nozzle, making a thin film with lateral dimensions defined by the size of the nozzle. Although it is often simplistically stated that the width of the deposited thin film is equal to the size of the nozzle, it is recognized in more sophisticated analyses that, absent a physical mask over the substrate, less than 100% of the organic molecules ejected from the nozzle will deposit beneath the nozzle itself. The material which deposits outside of the nozzle area is called “overspray.” Given the sensitivity of organic devices to contamination (in particular the sensitivity of organic light emitting devices to the presence of light emitting molecules of lower exciton energy), a small amount of overspray (< 0.1%) could be problematic. It is therefore desirable to minimize overspray.

[0036] It has already been disclosed that the addition of a coaxial stream of organic-free gas around the nozzle (known as “guard flow”) can reduce overspray, see U.S. 7,744,957. However, the coaxial arrangement adds complexity to the OVJP nozzle. A simpler method of reducing overspray is herein disclosed, accomplished simply by introducing into the deposition chamber with a “blanket” gas with an atomic mass significantly greater than the carrier gas.

[0037] FIG. 3 shows cross sections of four different nozzle geometries taken at the aperture in a direction perpendicular to the gas flow. The arrow in each aperture represents the “smallest dimension” of the aperture. In mathematical terms, at the smallest dimension, the arrow length is either at a local maximum (for the circle, oval and triangle) or is constant (for the rectangle) with respect to translation of the whole arrow in a direction perpendicular to the arrow, and the “smallest” dimension is the smallest local maximum or constant for which this occurs. Figure 3 shows cross sections of apertures 310, 320, 330 and 340 having circular, oval, rectangular and triangular cross sections, respectively. A rectangular aperture is the most preferred shape for depositing lines, and is also a relatively easy shape to obtain in a nozzle etched in silicon. However, other shapes may be used.

[0038] A method of depositing organic material is provided. A chamber is provided having a substrate disposed therein. An organic material is deposited over the substrate by ejecting from a nozzle directed at the substrate: a first gas; and a vapor of the organic material carried by the first gas. During the depositing an organic material, a second gas is provided in the chamber. The flow rate of the second gas is at least 5% of the sum of the flow rates of all gases flowing into the vacuum chamber. The second gas has a molecular weight at least 20% greater than the molecular weight of the first gas. The second gas is provided in the chamber via an aperture remote from the nozzle.

[0039] Preferably, the flow rate of the second gas is at least 30% of the sum of the flow rates of all gases flowing into the vacuum chamber. More preferably, the flow rate of the second gas is at least 60% of the sum of the flow rates of all gases flowing into the vacuum chamber.

[0040] It has been demonstrated (see Figure 5 and related discussion) that the presence of the second gas, which may be referred to as a “blanket” gas, reduces overspray relative to a method where, instead of the heavier blanket gas, only the carrier gas is present. One characteristic of the second gas is that it is introduced into the chamber via an aperture remote from the nozzle. By “remote,” from a nozzle, it is meant that the aperture through which the blanket gas is introduced is at least two “smallest dimensions” of the nozzle aperture away from the nozzle aperture. In most embodiments, it is likely that the aperture through which the blanket gas is introduced is much further away. The blanket gas is different from a “guard flow,” which, in its most common embodiment, is introduced into the chamber via an annular ring around the nozzle through which carrier gas is introduced, i.e., the specific location at which the guard flow is introduced matters to the fluid dynamics of gas ejected from the nozzle. In its purest sense, the *specific* location from which a “blanket gas” is introduced does not matter, because the presence of the blanket gas in the ambient gas of the chamber affects the fluid dynamics of gas ejected from the nozzle, resulting in a narrower jet spread. As a result, the use of a heavy blanket gas may be easier to implement than the use of a guard flow.

[0041] By “heavy,” it is meant herein that the blanket (or second) gas has a molecular weight that is at least 20% greater than that of the carrier (or first) gas. A molecular weight that is at least 20% greater is expected to have an effect, as demonstrated with respect to Figure 5 and the related experiment, because Ar has a molecular weight of 18, compared to

the molecular weight 14 of N<sub>2</sub>. From the perspective of narrowing jet spread, the heavier the blanket gas relative to the carrier gas the better. A molecular weight for the blanket gas that is at least 100% greater than the molecular weight of the carrier gas is preferred.

**[0042]** It is preferred that the blanket gas be inert in terms of device performance. The blanket gas should not react with materials in the device being fabricated. Suitable gases that are inert and heavy include Ar, Kr, freons, Xe, CO<sub>2</sub> and WF<sub>6</sub>. N<sub>2</sub> is preferred for use as a first gas because it is inert and light. He may also be used as a carrier gas, which opens up new possibilities for “heavier” blanket gases. For example, N<sub>2</sub> is heavier than He, and N<sub>2</sub> may be used as a blanket gas when He is the carrier gas.

**[0043]** The blanket gas may be a single gas meeting the weight criteria, or it may be a mixture of gases that each meet the weight criteria, whether it is 20% or 100% greater than the molecular weight of the carrier gas. While it is preferred for simplicity that a single gas be used, the blanket gas has its desired effect because it is composed of molecules that are heavy relative to the carrier gas, and this effect should occur whether all of the blanket gas molecules are the same or not.

**[0044]** It is expected in most embodiments that the carrier gas will be a single gas, preferably N<sub>2</sub>. However, embodiments of the invention may be practiced with a carrier gas having multiple gas components. In this situation, the “molecular weight” of the carrier gas should be considered as the molar average molecular weight.

**[0045]** Preferably, during the depositing of an organic material, the total pressure in the vacuum chamber is between 1 mTorr and 1 Torr. This is a preferred range of pressures for OVJP generally. OVJP, including OVJP with the use of a blanket gas, may be practiced at higher and lower pressures as well. But pressures lower than the bottom of the range are less preferred because OVJP by its nature introduces gas into the chamber during deposition, such that lower vacuum levels may require most expensive vacuum equipment as compared to similar vacuum levels in other processes, such as thermal evaporation. Higher pressures may readily be used, but carrier gas should generally be removed so that deposition can occur over a period of time at a controlled equilibrium in the chamber, and it is reasonably easy to obtain a 1 Torr pressure.

**[0046]** The chamber is preferably a vacuum chamber. However, there are embodiments of OVJP that can be practiced at atmospheric or higher pressures, and the use of a blanket gas would be applicable to those embodiments.

[0047] One way to quantify the amount of blanket gas in the chamber is by flow rate. At equilibrium, it is expected that the relative flow rates of the various gases introduced into the chamber will correspond to the partial pressures of the gases at a location remote from any of the apertures where gas is being introduced, i.e., the “ambient” gas in the chamber. However, flow rates are much easier to control and measure than partial pressures.

[0048] Another way to quantify the amount of blanket gas in the chamber is by measuring the effect of overspray. One goal of embodiments of the invention in the context of OLEDs is to reduce the amount of impurity molecules in adjacent devices having a different structure, and usually emitting a different color of light. Where an impurity molecule is emissive in the device where it is considered an impurity, it is reasonably easy to quantify the amount of impurity present by measuring the emission of the device. The experiment of FIG. 5 shows that modest amounts of blanket gas can readily reduce the amount of impurity relative to a situation where the blanket gas is not present, but the same total pressure is the same (and resultant from the presence of carrier gas). In general, a nozzle used for OVJP will have a “smallest dimension,” described with respect to FIG. 3. One way to quantify whether the blanket gas has a partial pressure sufficient to have the desired effect is to perform a simple experiment, comparing OVJP performed with the use of a blanket gas to OVJP performed where only carrier gas is present, with the same total pressure. This may be accomplished as described with respect to FIG. 5. The effect of the overspray may be measured at a distance of one smallest dimension from an edge of a patterned feature. When the partial pressure of the second gas in the chamber during the depositing of the organic material is sufficient to reduce by a factor of 2 the amount of organic material deposited at a distance of one smallest dimension from the edge of the patterned feature, relative to an otherwise identical deposition performed without the second gas, it can be said that the blanket gas is having a significant effect. As illustrated with respect to FIG. 5, this effect is reasonably easy to achieve with a modest amount of blanket gas.

[0049] Preferably OVJP takes place at relatively poor vacuum, typically from 1 mTorr to 1 Torr, although embodiments from higher vacuum levels all the way to atmospheric pressure or higher are possible. There may be, therefore, an appreciable partial pressure of residual gas in the vacuum chamber seen by the organic molecules after they have been carried through the nozzle by the carrier gas. Within this limitation, some combinations of pressure and carrier gas flow rate will lead to a minimum amount of overspray.

[0050] Embodiments of the present invention involve further reducing overspray by intentionally introducing into the deposition chamber a partial pressure of a gas heavier than the carrier gas. This heavier gas may be referred to as a “blanket” gas. The heavier gas restricts the expansion of the carrier gas and organic vapor exiting from the nozzle better than carrier gas. In a specific illustrative example, the carrier gas is nitrogen and the chamber is filled with a partial pressure of argon. The overspray in the case where the chamber contains argon is measurably less than the overspray when the chamber contains only nitrogen introduced by the carrier gas.

[0051] There may be an optimal total pressure for the Ar blanket which may be different from the optimal pressure using just N<sub>2</sub>, and it may be desirable to determine this optimal total pressure. Optimal total pressure may be readily determined by performing a series of depositions at different total pressures and measuring the results. This is routinely done for regular OVJP without blanket gas, and should be equally routine for OVJP with blanket gas.

[0052] If reducing overspray is the only consideration, using the heaviest possible blanket gas is desirable. However, other factors should be considered in selecting the blanket gas, such as cost, toxicity and environmental effects should also be considered. The blanket gas should also be inert, i.e., it should not detrimentally interact with any parts of the organic device. In terms of gases desirable for use as a blanket gas due to high molecular weight, preferred choices include Kr, complex gas molecules such as CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub> and higher order freons, Xe, CO<sub>2</sub>, and WF<sub>6</sub>. It is expected that overspray will be desirably reduced when a heavy blanket gas is present as compared to the same total pressure when only carrier gas is present. However, it is expected that each blanket / carrier gas combination may have a different partial pressure at which overspray is minimized, which can be determined by a relatively simple experiment.

[0053] One consideration of using an exotic gas to blanket OVJP deposition is potentially cost. Fresh blanket gas is preferably continually introduced in order to offset the carrier gas coming out of the nozzle, otherwise the deposition chamber will eventually just fill with carrier gas. This means that, over time, a significant volume of blanket gas may be used, and cost and / or disposal could be a consideration.

[0054] Embodiments of the invention may be practiced across a wide variety of dimensions. The use of a heavy ambient gas may be used advantageously at any dimensions that are desired for an OVJP system.

[0055] A simple, single nozzle implementation of an embodiment of the invention is shown in FIG. 4. Figure 4 shows systems 410 and 450. System 410 includes a chamber 420 having an OVJP nozzle 422, an aperture 424 for the introduction of blanket gas, and an aperture 426 for the removal of gas from chamber 420. A vacuum system may be attached to aperture 426. Nozzle 422 is illustrated abstractly as introducing a jet of gas 430 where the gas is from sources outside the chamber. It should be understood any of the various known systems including nozzles for OVJP may be used. System 410 illustrates a wider jet spread when a light ambient gas is present.

[0056] System 450 includes a chamber 460 having an OVJP nozzle 462, an aperture 464 for the introduction of blanket gas, and an aperture 466 for the removal of gas from chamber 460. A vacuum system may be attached to aperture 466. Nozzle 462 is illustrated abstractly as introducing a jet of gas 470 where the gas is from sources outside the chamber. It should be understood any of the various known systems including nozzles for OVJP may be used. System 450 illustrates a narrower jet spread when a heavy ambient gas is present.

[0057] A one dimensional array of nozzles (i.e., a line of nozzles) is a preferred embodiment for a nozzle block. Such an array allows for high throughput patterning by moving the nozzle relative to the substrate or vice versa in the direction perpendicular to the line of the nozzles. Other arrangements of multiple nozzles, such as a two dimensional array, may also be used. A variety of nozzle shapes may be used. For example, the nozzles may be elongated, e.g. rectangular, preferably with the long axis in the direction of translation of the array relative to the substrate.

[0058] Embodiments of the invention may generally be practiced in conjunction with other techniques for OVJP or improving OVJP. For example, embodiments of the invention may be practiced in connection with an exhaust disposed in a nozzle block that creates a localized vacuum, such as disclosed in U.S. Patent Application No. 11/643,795, which is incorporated by reference.

[0059] FIG. 5 shows plots of emission ratios vs. distance from a deposition edge, which provides a measure of how much overspray occurred during deposition. The different deposition conditions illustrate the effect of a heavy blanket gas on deposition via OVJP, and specifically the reduction of overspray through the use of a heavy blanket gas. An NPD/TPBi bilayer device was grown via vacuum thermal deposition (VTE) across a 6" glass substrate patterned with 1mm wide ITO anodes, with a 0.5 mm separation between lines. This device

is highly asymmetric in charge injection and transport characteristics so that all the excitons generated are tightly confined at the NPD/TPBi interface. In the absence of contamination, the resulting devices show blue EL from NPD. A thin line of red dopant is deposited using OVJP along one of the ITO lines between the blanket VTE deposition of the NPD and TPBi.

5 The deposited line shows red electroluminescence because of efficient exciton transfer to the red dye. Any overspray of red dye beyond the deposited ITO stripe will also show some level of red emission depending on the amount of red dye deposited at that location. Peaks in the electroluminescence spectrum due to the red dye and the default NPD emission are clearly separable and the ratio of the red and blue peaks quantitatively defines the amount of  
10 red dye present; which was be calibrated using controlled VTE depositions of test structures. Because of the efficient confinement of excitons at the organic heterointerface and the high efficiency of downhill energy transfer, the structures are very sensitive to the presence of overspray, having been used to detect  $< 0.25 \text{ \AA}$  of material, or about 1/10 of a monolayer.

[0060] The experimental setup was somewhat limited. Schematically, the OVJP part of  
15 device fabrication was performed in a chamber such as that illustrated in FIG. 4. The chamber was a vacuum chamber, but the vacuum did not have a variable valve – i.e., the vacuum is either on or off without settings in between. Given that the vacuum is on, the total pressure in the chamber is determined by the flow rate of carrier gas and blanket gas. The chamber had a single pressure measuring device, able to measure total pressure in the  
20 chamber.

[0061] The different plots of FIG. 5 represent the following:  $\text{N}_2$  at 0.1 Torr represents a calibration run, to determine the total pressure (0.1 Torr) when the carrier gas flow rate is set to a particular amount, and the only gas let into the chamber is carrier gas through the nozzle. This plot shows less overspray because the total pressure is less, and is not comparable to the  
25 other plots for purposes of measuring the effect of whether the ambient gas is the same as the carrier gas, or includes a heavier blanket gas. The two plots for  $\text{N}_2$  at 0.3 Torr, Ar blanket were identical experiments, where the flow rate of  $\text{N}_2$  carrier gas was the same as that for  $\text{N}_2$  at 0.1 Torr, but Ar gas was also let into the chamber through an aperture remote from the nozzle. The flow rate of Ar was sufficient to reach a total pressure of 0.3 Torr. The two plots  
30 for  $\text{N}_2$  at 0.3 Torr,  $\text{N}_2$  blanket were identical experiments, performed in the same way as the Ar blanket experiment, except that  $\text{N}_2$  gas instead of Ar gas was let into the chamber through an aperture remote from the nozzle to bring the total pressure up to 0.3 Torr. The data shows

less overspray using an Ar blanket at 0.3 Torr than using the default N<sub>2</sub> blanket at the same pressure.

[0062] The smallest amount of overspray shown in FIG. 5 is for the calibration run with no blanket gas. Both results with blanket gas show more overspray than deposition at 0.1 Torr using the default N<sub>2</sub> blanket. However, due to the limited nature of the experimental apparatus, 0.1 Torr is the minimum achievable pressure with flow through the nozzle and any blanket gas adds pressure, so it was not possible with the limited apparatus to test with an Ar blanket at a total pressure of 0.1 Torr. The relevant comparison is N<sub>2</sub> at 0.3 Torr, N<sub>2</sub> blanket compared with N<sub>2</sub> at 0.3 Torr, Ar blanket, which shows that a heavier ambient gas (or more accurately, an ambient gas where at least a significant partial pressure is due to a heavy gas) reduces overspray relative to a lighter ambient gas at the same pressure. This is true even where the presence of a heavy gas is achieved via introduction into the chamber through an aperture remote from the nozzle.

[0063] It is understood that the various embodiments described herein are by way of example only, and are not intended to limit the scope of the invention. For example, many of the materials and structures described herein may be substituted with other materials and structures without deviating from the spirit of the invention. The present invention as claimed may therefore include variations from the particular examples and preferred embodiments described herein, as will be apparent to one of skill in the art. It is understood that various theories as to why the invention works are not intended to be limiting.



## CLAIMS

1. A method, comprising:  
providing a chamber having a substrate disposed therein;  
depositing an organic material over the substrate by ejecting from a nozzle directed at  
5 the substrate:  
a first gas; and  
a vapor of the organic material carried by the first gas;  
providing in the chamber, during the depositing an organic material, a second gas;  
wherein  
10 the flow rate of the second gas is at least 5% of the sum of the flow rates of all  
gases flowing into the vacuum chamber;  
the second gas has a molecular weight at least 20% greater than the molecular  
weight of the first gas; and  
the second gas is provided in the chamber via an aperture remote from the  
15 nozzle.
2. The method of claim 1, wherein the flow rate of the second gas is at least 30% of  
the sum of the flow rates of all gases flowing into the vacuum chamber.
- 20 3. The method of claim 1, wherein the flow rate of the second gas is at least 60% of  
the sum of the flow rates of all gases flowing into the vacuum chamber.
4. The method of claim 1, wherein, during the depositing of an organic material, the  
total pressure in the vacuum chamber is between 1 mTorr and 1 Torr.
- 25 5. The method of claim 1, wherein the first gas is N<sub>2</sub>.
6. The method of claim 1, wherein the second gas is selected from the group  
consisting of Ar, Kr, freons, Xe, CO<sub>2</sub> and WF<sub>6</sub>.
- 30 7. The method of claim 1 wherein the second gas is a single material.

8. The method of claim 1, wherein the second gas has a molecular weight at least 100% greater than the molecular weight of the first gas.
9. The method of claim 1, wherein the second gas is a mixture of materials each having a molecular weight at least 20% greater than the molecular weight of the first gas.
10. The method of claim 1, wherein the second gas is a mixture of materials each having a molecular weight at least 100% greater than the molecular weight of the first gas.
11. The method of claim 1, wherein the chamber is a vacuum chamber.
12. . A method, comprising:  
providing a chamber having a substrate disposed therein;  
depositing an organic material over the substrate by ejecting from a nozzle directed at the substrate:  
a first gas; and  
a vapor of the organic material carried by the first gas;  
providing in the chamber, during the depositing an organic material, a second gas;  
wherein  
the second gas has a molecular weight at least 20% greater than the molecular weight of the first gas.  
the nozzle has an aperture having a smallest dimension;  
the organic material is deposited over the substrate as a patterned feature having a shape defined by the shape of the aperture;  
the partial pressure of the second gas in the chamber during the depositing of the organic material is sufficient to reduce by a factor of 2 the amount of organic material deposited at a distance of one smallest dimension from the edge of the patterned feature, relative to an otherwise identical deposition performed without the second gas.

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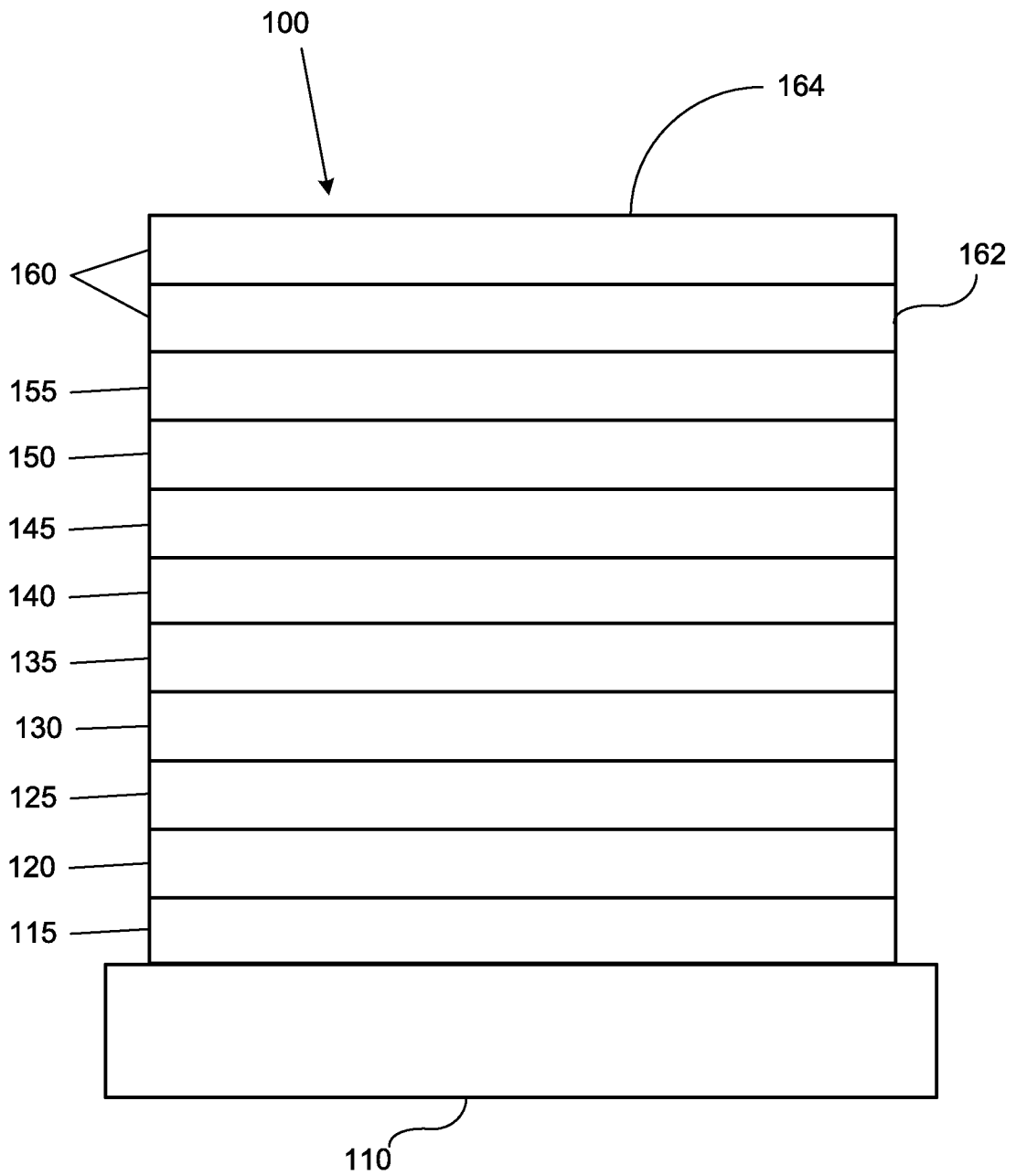


FIGURE 1

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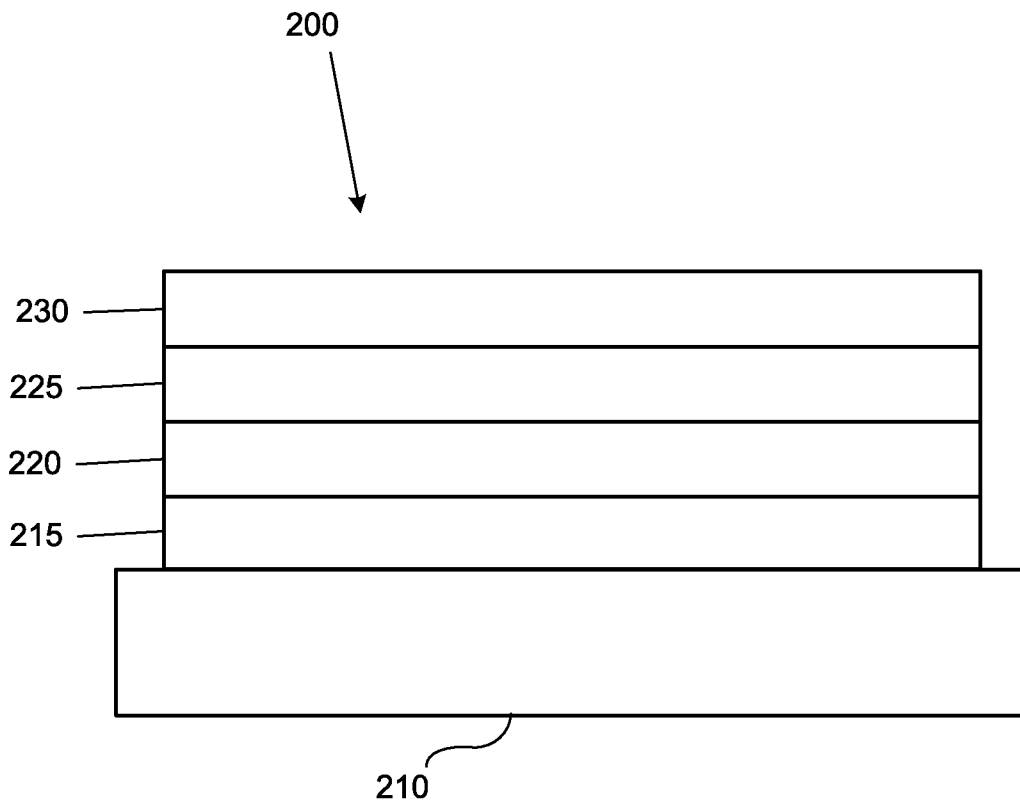


FIGURE 2

3 / 5

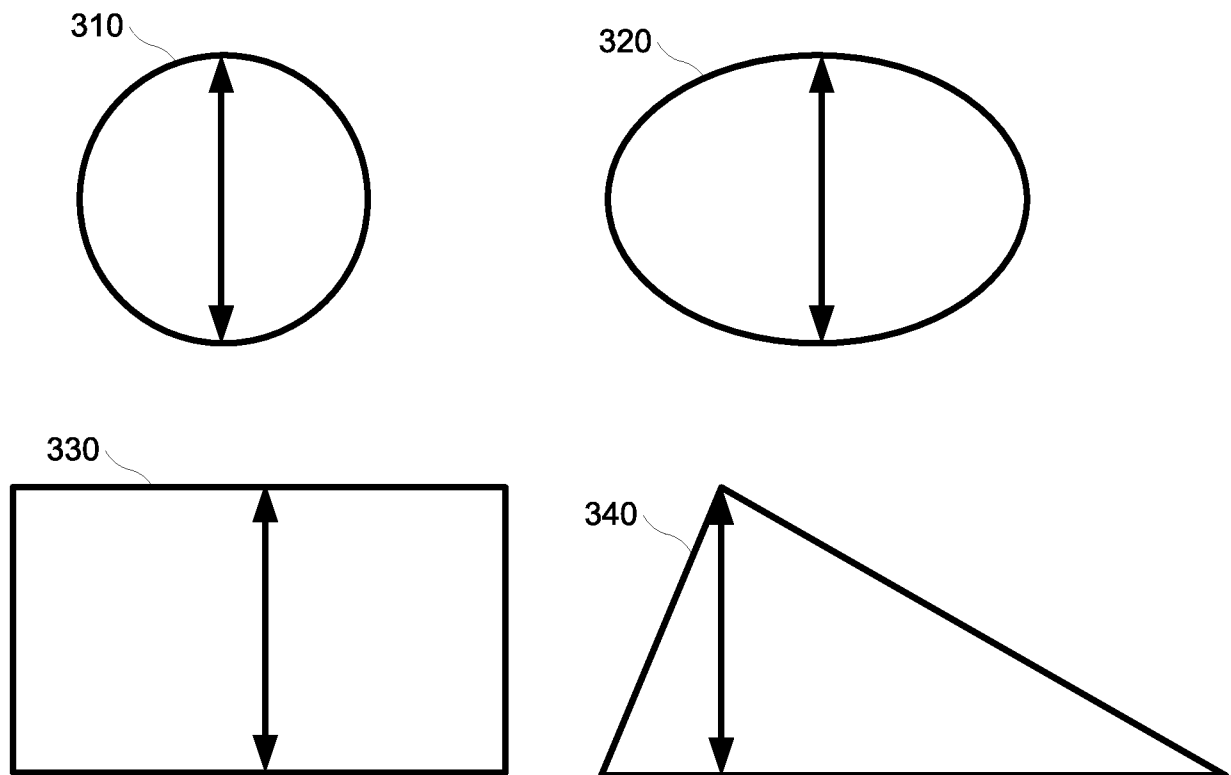
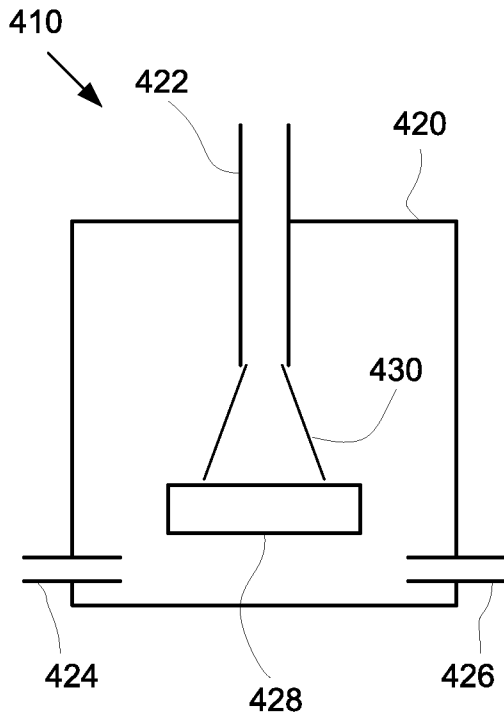
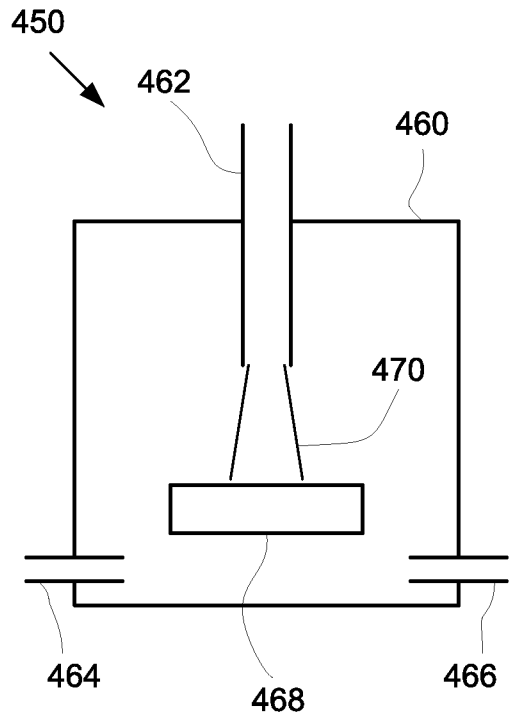


FIGURE 3



Light Ambient Gas  
Wider Jet Spread



Heavy Ambient Gas  
Narrower Jet Spread

FIGURE 4

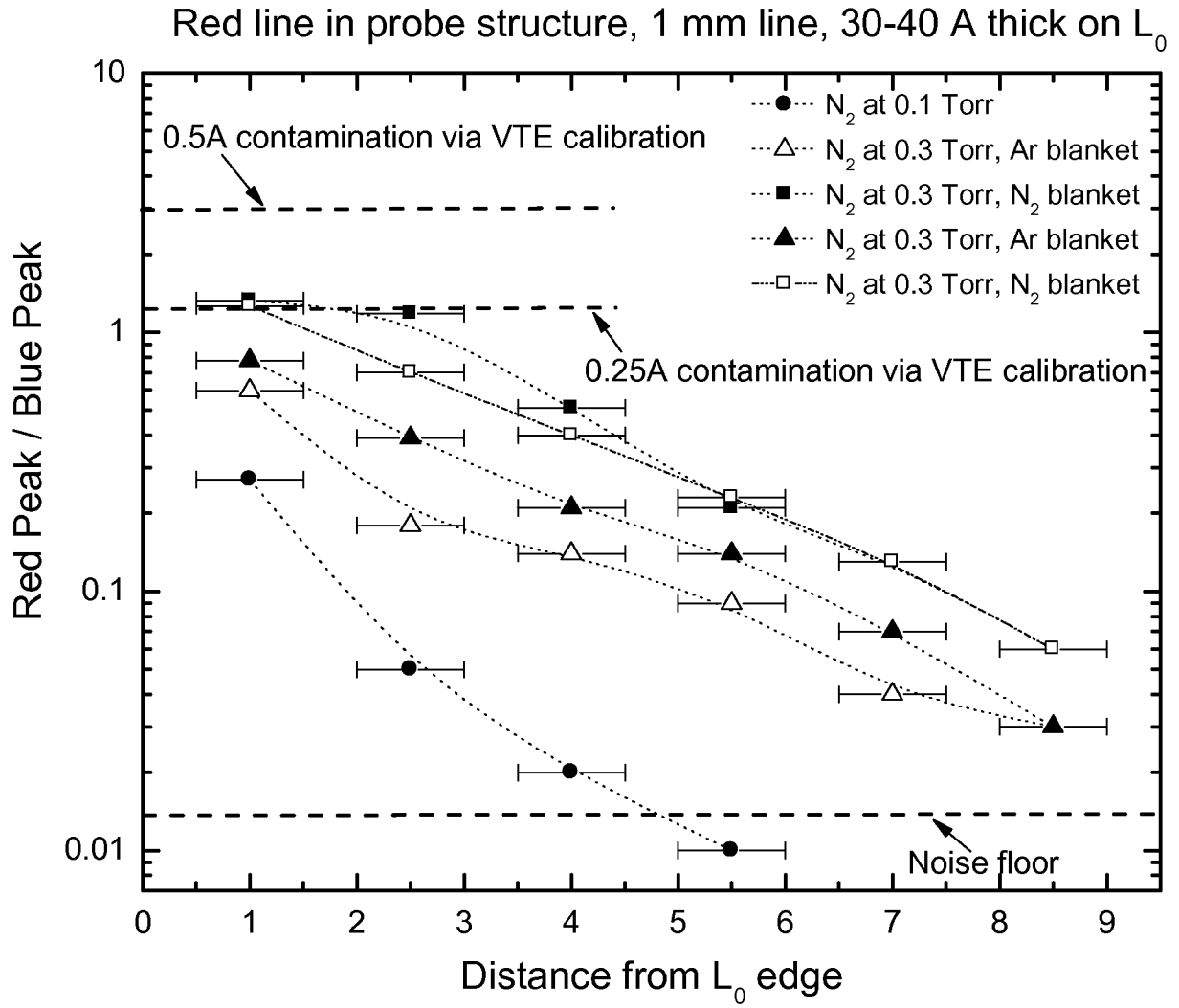


FIGURE 5

INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2010/042923

A. CLASSIFICATION OF SUBJECT MATTER  
INV. C23C14/04 C23C14/12  
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

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

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2005/087131 A1 (SHTEIN MAX [US] ET AL FORREST STEPHEN R [US] ET AL) 28 April 2005 (2005-04-28) cited in the application paragraphs [0031] - [0033], [0 49]	1-12
A	WO 2008/035818 A1 (FUJIREBIO KK [JP]; HIMMELHAUS MICHAEL [JP]; WORSFOLD OLIVER [JP]; WHIT) 27 March 2008 (2008-03-27) page 26, line 11 - page 27, line 5	1-12

Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search  24 March 2011	Date of mailing of the international search report  31/03/2011
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  Ekhuylt, Hans
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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2010/042923

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