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VERIFICATION OF TRANSLATION

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- (2) that he translated the above-identified Application from French to English;
- (3) that the attached English translation is a true and correct translation of the above-identified application to the best of his knowledge and belief; and
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Philip M. Morris

APPARATUS FOR VACUUM DEPOSITION WITH A RECHARGING RESERVOIR AND CORRESPONDING PROCESS FOR VACUUM DEPOSITION

The present invention relates to the area of vacuum deposition. It concerns more particularly the vacuum deposition of thin films of organic material, e.g., for the manufacture of electroluminescent diodes based on organic materials (OLED).

The structure of an elementary cell of an OLED apparatus is constituted by a stack of very fine organic layers sandwiched between a transparent anode and a metallic cathode. The manufacture of these organic layers is carried out by evaporation of the material or materials constituting the layers and by vacuum deposition.

One of the problems posed by this manufacturing process is that of the introduction into an enclosure under a vacuum containing the substrate of the evaporated organic material to be treated.

A known apparatus used to implement this process, described, e.g., in US patent 4,553,022 comprises a thermal effusion cell constituted by a crucible containing the organic material to be evaporated and a furnace that permits the heating of the crucible. This thermal effusion cell can be introduced into the enclosure. The material contained in the crucible is then heated to a given temperature at which the evaporated material escapes via the crucible orifice toward the surface of the substrate, where it is deposited

in order to form a thin film. In order to interrupt the operation of the deposition of the thin film a mask is interposed between the crucible and the substrate that forms an obstacle to the vapor flow. The material is then deposited on the surface of the mask or on the inner walls of the enclosure and can consequently no longer be used.

Moreover, the crucible heating furnace is located facing the substrate in the vacuum enclosure and the heat that it emits risks damaging the thin deposited film.

Finally, it is necessary to open the enclosure in order to recharge the crucible and consequently expose this enclosure to the air again. It is necessary to do the same in order to interact with the furnace, that is located in the enclosure.

There are patents in the technical area of molecular beam epitaxy (MBE) such as US 5, 080, 870 or US 5, 156, 815 that describe an apparatus in which the main enclosure containing the substrate communicates with a secondary enclosure adapted in such a manner as to receive a reservoir containing the material to be evaporated. An injection tube can be open or closed by a valve. The secondary enclosure and the reservoir are each provided with tight covers permitting a hermetic closure. The secondary enclosure and the main enclosure are connected by a tight flange. A heating apparatus surrounds the reservoir as well as the injection tube.

Such an apparatus allows the vapor flow to be controlled by the valve arranged between the reservoir and the main enclosure.

However, here too the reservoir can only be recharged after opening the tight cover of the secondary enclosure, which means that the unit of the secondary enclosure/main enclosure is exposed to the air.

The present invention intends to remedy the disadvantages of the prior art by proposing an apparatus and a process permitting the production of vapors under a vacuum of organic materials in which a product reservoir can be readily recharged.

To this end it proposes a vacuum deposition apparatus comprising an enclosure adapted to receive a substrate to be treated and to be placed under a vacuum and at least one injector for generating a molecular beam of vapor of an organic material, which injector comprises a conduit located inside this enclosure and traversing an injection wall of this enclosure in order to form an outer nozzle adapted in such a manner as to be hermetically connected in a detachable manner to a means for supplying organic material, characterized in that this supply means is a bottle whose neck is adapted in such a manner that it can be introduced into this nozzle and that this deposition apparatus comprises an outer heating apparatus located on both sides of this injection wall and surrounding this bottle and an inner heating apparatus surrounding this conduit, and that a regulatable valve permits the regulation of the conductance of the injector in the enclosure.

This apparatus permits a recharging of organic materials carried out from the outside of the vacuum enclosure and the recharging operation does

not require the vacuum enclosure to be exposed to the air. The capacity of organic materials can be adjusted to whatever the size of the chamber.

According to another aspect of the present invention this conduit of this injector is provided with a heating apparatus adapted in such a manner as to prevent the deposition of the organic material on this conduit.

According to another aspect of the present invention this valve is provided with a heating apparatus adapted in such a manner as to prevent the deposition of the organic material on this valve.

This removable reservoir advantageously has the shape of a bottle with a cylindrical body and a neck whose end is adapted in such a manner as to be introduced into the outer end of this conduit of this injector.

This removable reservoir advantageously comprises a plurality of metallic blades inside its cylindrical body that extend radially between the wall of this reservoir and the central tube extending over the entire length of this cylindrical body.

Such an apparatus allows the transmission of heat to the interior of the reservoir to be improved in such a manner as to avoid the accumulation of the product in the central zone of the reservoir.

According to another embodiment of the present invention this removable reservoir has a cylindrical body with an annular section.

In this way a heating apparatus can be axially introduced through the bottom of this reservoir. This is another manner of avoiding the accumulation of the product in the central zone of the reservoir.

This removable reservoir is advantageously provided with a valve at the level of its neck.

According to another aspect of the present invention this conduit of this injector is vertical and it traverses the bottom of this vacuum enclosure and this substrate extends horizontally in an upper part of this enclosure.

This heating furnace advantageously heats this reservoir with a temperature gradient between the base and the neck of this reservoir, between the neck and the valve and between the valve and the inner mouth of the conduit.

The present invention also relates to a process of vacuum deposition using an apparatus such as defined above, characterized in that it comprises the recharging steps consisting in:

- Closing this valve;
- Detaching this reservoir from this injector;
- Recharging this reservoir;
- Connecting this reservoir to this injector;
- Progressively opening the valve;
- Heating this conduit;
- Heating this valve; and
- Heating this reservoir.

The invention will be better understood with the aid of the description of an embodiment of the invention given in the following in a purely explicative manner and making reference to the attached figures in which:

Figure 1 is a schematic view of a vacuum deposition apparatus with a recharging reservoir in accordance with the invention;

Figure 2 is a schematic view of alternate embodiments of recharging reservoirs for the apparatus of figure 1; and

Figure 3 is a schematic view illustrating the different recharging steps of a vacuum deposition process in accordance with the present invention.

Figure 1 schematically represents an apparatus for the vacuum deposition of thin films. It can concern the deposition of organic materials or of materials under a strong vapor pressure that will be designated in the following by the term of charge. Such an apparatus serves, e.g., for the manufacture of electroluminescent diodes based on organic materials (OLED). The charge is solid under normal conditions of temperature and pressure.

The apparatus comprises an enclosure 1 adapted to receive a substrate 2 extending horizontally in an upper part of enclosure 1. The bottom of the enclosure comprises an injection compartment 5 with a cylindrical form open at the top on the enclosure and closed at the bottom by wall 141.

An injection cell 3 is adapted to inject a charge into enclosure 1 in the form of a vapor beam extending substantially in the form of a cone whose dimensions are such that substrate 2 substantially forms the base of this cone.

Injection cell 3 comprises a cylindrical injector vertically traversing wall 141 of injection compartment 5. The injector can be mounted in a

permanent manner on the enclosure or in a removable manner in order in particular to permit its replacement by another injector, e.g., in order to modify the characteristics of the injection. The injector conduit comprises a main part 10 extending inside this enclosure and comprises a nozzle 120 extending outside of this enclosure.

Injector conduit 110 has a form adapted to the generation of a molecular beam with the desired form. This conduit can terminate in a mouth in the form of a truncated cone, of an extended diffuser of the knob type or of a gas burner or any type of known diffuser.

Outer nozzle 120 is adapted for receiving neck 11 of removable charge reservoir 10. Outer part 120 of the conduit forming a nozzle is designed to be as short as possible as a function of the hooking requirements of reservoir 10.

Valve 20 is arranged on inner part 110 of the injector. This valve is adapted in closed position to hermetically close the conduit.

Valve 20 is slidingly mounted in a transversal housing in such a manner that it can move perpendicularly to the axis of the injector between the position of closing in which it totally plugs the conduit of this injector and between the position of opening. This valve is controlled by shaft 142 extending transversely in injection compartment 5 and can be controlled by a handle located outside of enclosure 1 and the passage of the enclosure is ensured through a tight apparatus 6.

Valve 20 permits the conductance of the injector to be regulated, that is, the delivery of molecules can be made to vary in a continuous manner. The valve is advantageously piloted by a motor acting on shaft 142. This motor can be controlled by a controller that adjusts the position of the valve using a signal coming from a measuring apparatus sensitive to the molecular flow (quartz balance) in order to maintain the molecular flow at a value predetermined by the operator. The piloting of the valve motor permits the user to obtain molecular flow profiles as a function of the time predefined by programming the successive positions of the valve.

Removable charge reservoir 10 has on the whole the shape of a bottle with cylindrical body 12 and neck 11 whose extremity is adapted to be introduced into nozzle 120 of the injector. The neck is connected in a tight manner to the injector nozzle in such a manner that once the reservoir is installed, the injector conduit is isolated from the outer atmosphere.

The neck can advantageously be screwed into the injector conduit.

The tightness between the bottle neck and the injector is ensured by a metallic joint.

This reservoir is manufactured from a material that is chemically inert to the organic material and can tolerate temperatures between -50°C and $+600^{\circ}\text{C}$ without deforming or its qualities of tightness being affected. This reservoir 10 can be made of metal, graphite, glass, quartz, PBN, PG, alumina or several of these materials. The useful volume of this reservoir can advantageously be from 1 cm^3 to several liters.

The inner surface of the reservoir has a very slight rugosity.

The shape of this reservoir is such that it has a maximal surface for the heating.

This reservoir advantageously has a diameter $D > 30$ mm and the ratio of the height to the diameter is greater than two.

The reservoir can be equipped, in addition to a filling orifice, with one or several different entrances permitting, e.g., the introduction of an inert or reactive gas into the recharge and/or permitting the pumping of the inside of the recharge.

When the reservoir is detached from injector 100 and closed by plug 130 it is tight against the outside and can retain a vacuum on the order of $10e^{-8}$ torr without pumping for 1 week.

Figure 3 represents alternate embodiments of reservoir 10. In all these embodiments the shape of the extremity of the neck is identical so that each of these represented reservoirs can be installed on the nozzle of injector 3. Plug 130 permits the closing of the reservoir when it is not mounted on injector 3.

In a first alternate embodiment 10A a plurality of metallic blades 150 extend radially between wall 152 of the reservoir and central tube 151 extending over the entire height of this cylindrical body.

This apparatus permits the transmission of heat to the inside of the reservoir to be improved in such a manner as to avoid an accumulation of the product in the central zone of the reservoir.

In embodiment 10C the reservoir has a cylindrical body with an annular section in such a manner that a housing open toward the bottom 170 extends along its axis. A heating apparatus can be axially introduced through the bottom in order to avoid an accumulation of the product in the central zone of the reservoir.

In an embodiment 10B a valve 160 is installed at the level of the reservoir neck.

Of course, the characteristics of these three embodiments can be combined in one and the same reservoir.

A removable furnace 50 allows reservoir 10 to be heated. This furnace is constituted by a tank closed at the level of its lower part and open at the level of its upper part. The inside diameter of this furnace can receive bottle 10 and fits against outer wall 140 of injection compartment 5 in such a manner as to form a closed cavity enclosing the bottle. Heating elements integrated in the tank walls of furnace 50 are spaced in the tank in such a manner as to heat the walls of reservoir 10 and wall 140 of injection compartment 5. The heating elements are, e.g., lamps or heating resistors. Furnace 50 comprises a temperature measuring apparatus that allows the temperature of the reservoir to be measured (thermocouple or platinum probe). The furnace heating elements are supplied in wattage by an independent feed that can be regulated in its temperature by the temperature measuring apparatus.

Removable furnace 50 has the particular function of bringing the charge to the desired temperature for generating the molecular beam. This temperature is advantageously comprised between 50 and 600 degrees.

Heating system 50 is located entirely outside of enclosure 1 and is independent of the latter.

According to another aspect of the present invention the conduit of lower part 110 of the injector is heated with the aid of inner heating apparatus 30. A heating element, e.g., a heating cable, surrounds the outer surface of inner injector cylinder 110 and also extends (e.g., in a spiral) against the inner surface of lower wall 141 of injection compartment 5. In this manner the injector is heated uniformly from its base to the level of the bulkhead up to its inner mouth. A temperature measuring means at the level of the injector extremity (thermocouple or platinum probe) allows the temperature to be measured at the level of the inner mouth of the injector. The injector heating element is supplied in wattage by an independent feed that can be regulated in its temperature by the temperature measuring apparatus.

According to another aspect of the present invention valve 20 is heated with the aid of a valve heating apparatus 40 located in injection compartment 5. A heating element, e.g., a heating cable, surrounds control shaft 142, and the heat is transmitted to the valve body by conduction. A temperature measuring apparatus is installed on the valve body. The valve

heating element is supplied in wattage by an independent feed that can be regulated in its temperature by the temperature measuring apparatus.

Heating apparatus 30 heats the injector walls in such a manner that the charge is not deposited on these walls, and heating apparatus 40 heats the valve 30 in such a manner that the charge is not deposited on this valve. Heating apparatuses 30, 40 are independent from one another and from heating apparatus 50.

According to an alternative envisioned embodiment the heating apparatuses also allow a cooling of the various injector elements.

According to another aspect of the present invention, heating apparatuses 50, 40 and 30 respectively heat the reservoir, the valve and the injector in such a manner that there is a temperature gradient between the base and the reservoir neck, between the neck and the valve and between the valve and the inner mouth of the injector. In other words, the temperature at the base of the reservoir is lower than the temperature at the level of the neck, itself lower than that of the valve and itself lower than that of the inner mouth of the injector. The control of the gradient is ensured by independent feeds of the three heating means associated with temperature sensors. The heating elements in reservoir 50 are arranged so as to heat the bottom more than the top of the reservoir. Likewise, the spacing of the winding lengths of heating cable 30 is selected with a view to supply a division of power at the height of the injector ensuring this gradient. The fact that the heating of the reservoir allows outer surface 140 of the lower wall of injection

compartment 5 to be heated from the outside and that the heating of the injector allows lower surface 141 of this wall to be heated from the inside allows the continuity of the temperature gradient of the injector conduit to be guaranteed between the outside and the inside.

Figure 3 schematically represents several charge or recharge stages within the scope of a vacuum deposition process. These charge or recharge stages take place when enclosure 1 is under a vacuum and valve 20 is closing the injector orifice.

CLAIMS

1. A vacuum deposition apparatus comprising an enclosure (1) adapted to receive a substrate (2) to be treated and to be placed under a vacuum and at least one injector (110) for generating a molecular beam of vapor of an organic material, which injector (110) comprises a conduit located inside this enclosure and traversing an injection wall of this enclosure in order to form an outer nozzle (120) adapted in such a manner as to be hermetically connected in a detachable manner to a means for supplying organic material, characterized in that this supply means is a bottle whose neck is adapted in such a manner that it can be introduced into this nozzle (120) and that this deposition apparatus comprises an outer heating apparatus (50) located on both sides of this injection wall (141) and surrounding this bottle and an inner heating apparatus (30) surrounding this conduit, and that a regulatable valve (20) permits the regulation of the conductance of the injector in the enclosure.

2. The vacuum deposition apparatus according to Claim 1, characterized in that this valve (20) of this injector (110) is provided with a heating apparatus (40) adapted in such a manner as to prevent the deposition of the organic material on this valve.

3. The vacuum deposition apparatus according to any one of the previous claims, characterized in that this removable reservoir (10) can be filled with solid organic material, placed under a vacuum and closed by a

plug (130) in such a manner as to preserve a vacuum on the order of $10e^{-8}$ torr for one week.

4. The vacuum deposition apparatus according to any one of the previous claims, characterized in that this bottle (10A) comprises a plurality of metallic blades (150) that extend radially between the wall (152) of this reservoir and a central tube (151) extending over the entire length of this cylindrical body.

5. The vacuum deposition apparatus according to any one of the previous claims, characterized in that this bottle (10C) has a cylindrical body with an annular section.

6. The vacuum deposition apparatus according to any one of the previous claims, characterized in that this bottle (10B) is provided with a valve (160) at the level of its neck.

7. The vacuum deposition apparatus according to any one of the previous claims, characterized in that this conduit of this injector (100) is vertical and traverses the bottom of this vacuum enclosure (1) and that this substrate (2) extends horizontally in an upper part of this enclosure.

8. The vacuum deposition apparatus according to any one of the previous claims, characterized in that this heating furnace (50) heats this bottle (10) with a temperature gradient between the base and the neck (11) of this bottle, between this neck (11) and this valve (20) and between this valve (20) and the inner mouth of this injector.

9. A vacuum deposition process using an apparatus according to any one of the previous claims, characterized in that it comprises the recharging steps consisting in:

Closing this valve;

Detaching this bottle from this injector;

Recharging this reservoir;

Connecting another bottle to this injector;

Progressively opening the valve;

Heating this conduit;

Heating this valve; and

Heating this valve [sic – “bottle”, “reservoir”? – cf. p. 5, l. 20 above in the spec.].