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Van Cakenberghe

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[54] **PLASMA DEPOSITION OF THIN LAYERS OF SUBSTRATED OR THE LIKE**

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[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.**..... **118/49.1;** 117/93.1 PF; 219/10.49; 313/231.3

[51] **Int. Cl.²**..... **C23C 13/12**

[58] **Field of Search**..... 118/49.1, 49.5; 117/93.1 R, 93.1 GD, 93.1 PF; 219/10.49, 121 P; 313/231.3, 362

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[57] **ABSTRACT**

Device for producing thin layers of mineral substances comprising a vacuum container and a cavity whose walls consist of the substance to be deposited, and having an opening in one of its faces. An electromagnetic field is generated in the cavity to form a plasma.

5 Claims, 3 Drawing Figures

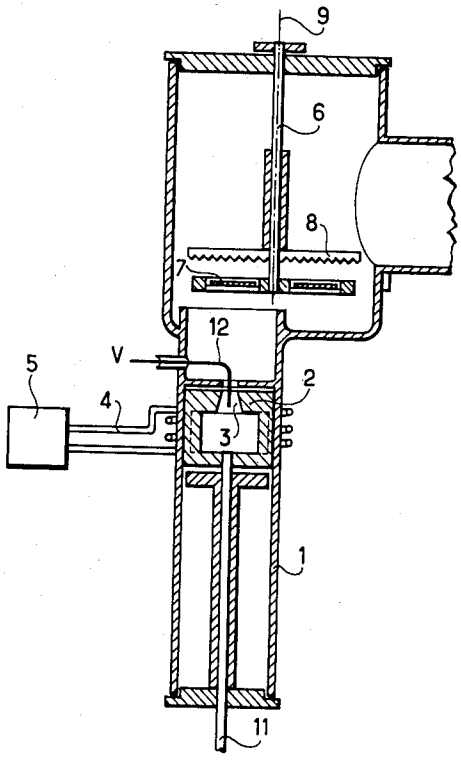


FIG. 1

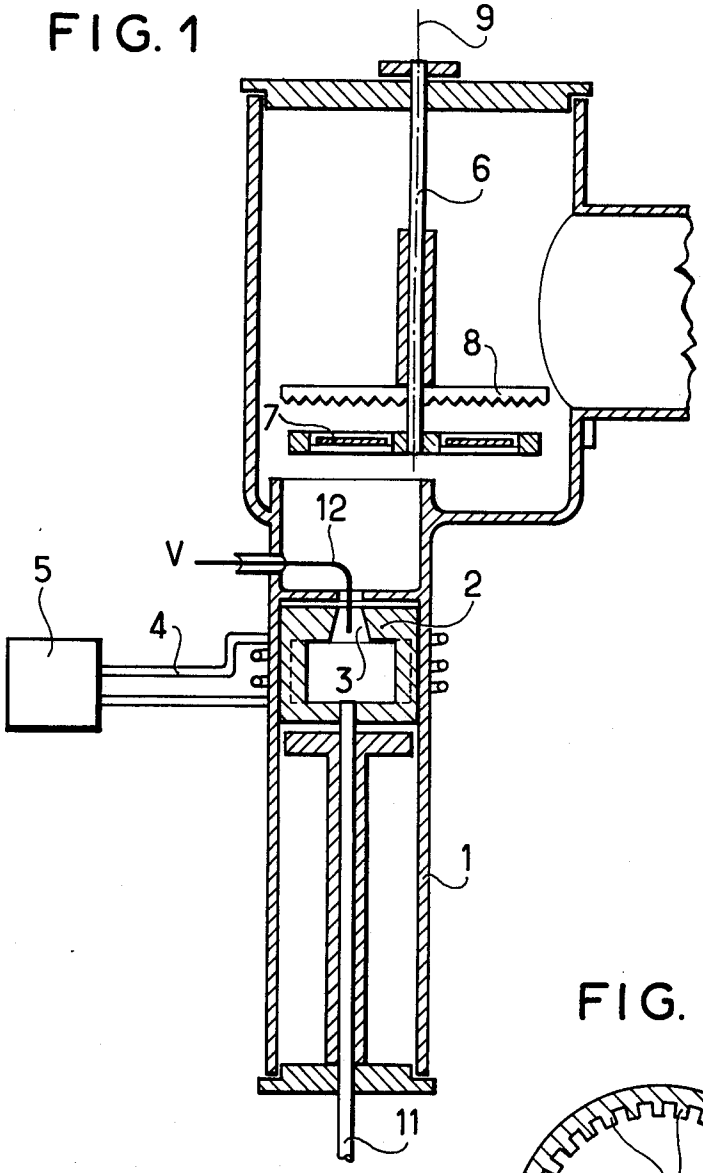


FIG. 2

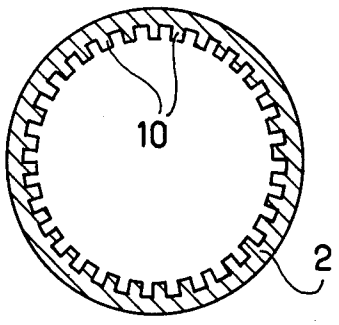
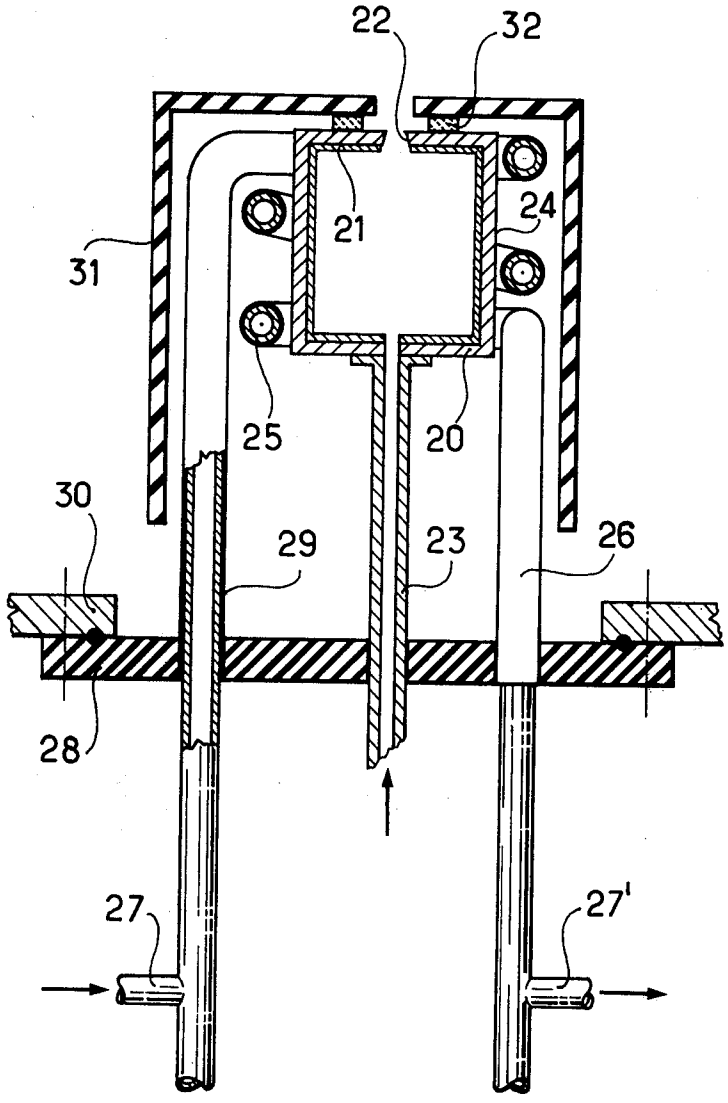


FIG. 3



PLASMA DEPOSITION OF THIN LAYERS OF SUBSTRATED OR THE LIKE

This is a division of application Ser. No. **246,019**, filed Apr. **20, 1972** now U.S. Pat. No. **3,801,355.**

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention concerns a method enabling thin layers of mineral substances to be deposited, as well as the device for implementing the method.

2. Description of the Prior Art

Thin layers are usually produced by evaporation in a vacuum or by a method called reactive projection. The first method can be used only in cases where the substance to be deposited decomposes when it is brought to a high temperature in a vacuum, into elements having very different vapor pressures and the most volatile of which can have a vapor pressure which can be measured at the depositing temperature. Such is the case, more particularly, with the majority of oxides, certain sulphides as well as of gallum arsenide and gallium phosphide.

The second method mentioned above consists in causing the evaporation of the material to be deposited in an electrical discharge at low pressure, between two electrodes one of which consists of the material to be deposited or the metallic component of that material, the other component then being contained in gaseous phase. The material to be deposited is deposited in the form of a thin layer on a substrate, arranged at a few centimeters from that electrode, which can be in contact or otherwise with the second electrode. In the case where a thin layer of zinc oxide, for example, is to be deposited, the first electrode can consist either of zinc oxide or of metallic zinc with a pure gaseous oxygen atmosphere or an atmosphere consisting of oxygen mixed with a neutral gas such as argon.

This second method can certainly be used for the above-mentioned substances, but it is unsuitable for semi-conductor materials, for the thin layers thus obtained consist of very small micro-crystals so that certain electrical properties such as the mobility and service life of the charge carriers are subjected to detrimental influence. Moreover, this second method is characterized by a relatively considerable dissipation of energy and a relatively low depositing speed which can, moreover, vary within wide limits.

The object of the invention is therefore a method for depositing thin layers which does not have the above-metnioned disadvantages.

It also provides a device for producing thin layers, either on insulating supports or on electrically conductive or semi-conductive supports.

Lastly, it provides a device enabling thin layers of material having electrical, semi-conductive, piezo-electrical, magnetic and/or optical properties, as well as thin layers of material having a high melting point such as refractory materials to be produced.

SUMMARY OF THE INVENTION

The method enabling thin layers to be deposited in a vacuum on the surface of a substrate arranged adjacent to the opening of a cavity in which a gas is injected at a pre-determined pressure is characterized in that a plasma is formed inside the cavity previously lined on the inside with the substance to be deposited.

The method also enables layers to be deposited on the surface of a substrate when the cavity consists directly of the substance to be deposited.

The device implementing the method according to the invention is characterized in that it comprises, on the one hand, a high-frequency excitation means generating an electromagnetic field, and, on the other hand, inside a vacuum container, at least a substrate support, a substrate, a cavity lined on the inside with the substance to be deposited and having an opening adjacent to the substrate and a means for injecting a gas at a predetermined pressure into said cavity, promoting the forming of a plasma within said cavity where there is the electromagnetic field.

The device implementing the method according to the invention is also characterized in that the support for the substrate comprises an electrical heating means enabling the substrate to be brought to a predetermined temperature.

In a particular embodiment, the device according to the invention is characterized in that it comprises, moreover, an electrode in the cavity, this electrode being connected to an appropriate electrical potential so as to produce a spark suitable for causing the starting up of the plasma.

The cavity has, to great advantage, a cylindrical shape, the cylindrical wall being provided, on its inside, with longitudinal ribs. Moreover, the insulating container may, to great advantage, be cooled.

The invention will be described herebelow with reference to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a longitudinal sectional view of an embodiment of the device according to the invention.

FIG. **2** is a transversal sectional view of an embodiment of the cavity having a great advantage, used in the device according to the invention.

FIG. **3** is a longitudinal sectional view of another embodiment of the device according to the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

According to FIG. **1,** a cylindrical cavity **2,** whose wall consists of, or is lined on the inside with the substance to be deposited, is arranged inside the tube **1,** made of quartz or ceramic material, for example. One of the transversal faces of the cavity is provided with an opening **3.** The high-frequency excitation device consists, here, of an induction winding **4** surrounding the tube **1** at the level of the cavity **2.** This winding is connected to a high frequency voltage supply **5.** A substrate support **6** is placed so as to have a substrate **7** adjacent to the opening **3** in the cavity **2.** The electrical heating device **8** enables the substrate **7** to be brought to a required temperature. In the embodiment shown by way of an example, the substrate support **6** is arranged so as to be able to pivot about an axis **9** in order to bring several substrates successively before the opening **3.**

As shown in FIG. **2,** the cylindrical wall of the cavity comprises, on the inside, longitudinal ribs **10** so as to reduce the transmission of heat through the wall.

The operation of this device is as follows:

A gas is injected into the cavity **2** through the duct **11** so as to produce an atmosphere at a pre-determined pressure therein. When a high frequency current

through the induction winding **4,** the electromagnetic field it induces inside the cavity forms a plasma thereon. The discharge which takes place in the plasma causes a great increase in the temperature of the inside wall of the cavity, this producing a distilling of the inner wall and the establishing of a vapor pressure of the substance to be deposited. This distilled substance escapes through the opening **3** and is deposited on the substrate **7.** In the arrangement according to the invention, the plasma is confined inside the cavity.

It has been noted that the thin layers thus obtained consist of crystals which are appreciably larger and better formed than those obtained by reactive projection. It has also been noted that the crystalline direction of the thin layers is perfect.

In this device according to the invention, the walls of the cavity constitute a thermal screen. In certain embodiments, the latter have been reinforced by arranging a second cavity round the first. This screen effect enables the energy dissipated in the plasma to be increased so as to bring the inside surface of the cavity to a very high temperature in the order of several thousands of degrees without danger for the insulating tube **1.**

In the particular embodiment shown in FIG. **1,** the device comprises, moreover, an electrode **12** in the opening **3** formed in the cavity **2.** This electrode **12** is connected to an appropriate electrical potential supply V so as to produce a spark suitable for promoting the starting up of the plasma.

In a varied version of an embodiment, the tube **1** is surrounded by a cooling funnel. It is thus possible to obtain high evaporating speeds and relatively high vapor pressures inside the cavity, this promoting molecular combination.

In a particular example of an embodiment, a cylindrical cavity consisting of zinc oxide, **50** mm in diameter and **60** mm in height, has been placed in a quartz tube. An induction winding consisting of three turns made of copper tubing **6** mm in diameter, connected to a high-frequency power generator, has been arranged about the tube, on the level of the cavity.

After having produced a vacuum in the order of 10^{-5} mm Hg in the tube **1,** and after having heated the substrate to a temperature of **200**℃, oxygen has been injected in the cavity in order to produce a pressure in the order of 5.10^{-2} mm Hg therein. The pressure in the container in which the substrate is placed is appreciably lower subsequent to the loss of head at the outlet of the cavity.

After having started up the high-frequency generator so that it supplies a power of **4** kw at **3** mc/s, the rated power is reached after barely a few minutes, and the zinc oxide is then deposited on the substrate in the form of a thin layer which has reached a thickness of **0.5** micron in one minute.

According to another form of the invention, the induction means implemented to generate the plasma inside the cavity is placed in the vacuum about the cavity. Various precautions are taken in that case to avoid the pollution of the substrate. This embodiment, shown in FIG. **3,** comprises a cylindrical cavity **20** placed in a vacuum container shown in the figure only by its base **30.** This cavity **20** is lined inside with the material **21** to be sprayed, it comprises, at its upper part, a central opening **22,** and at its lower part, a gas inlet **23.** The lateral face **24** of that cylindrical cavity **20** is surrounded by the turns **25** of an induction circuit **26,** fed by a HF supply, not shown, arranged outside the container. This induction circuit **26** consists of a hollow conductor internally cooled by a water circuit **27, 27'.** The induction circuit is held in position by an insulating base **28** fixed to the base **30** of the container. The conductor forming the induction circuit is itself lined with a layer of protective insulating material **29,** made of teflon, in a series of experiments, and of glass in another series of measurements. A protective screen **31** made of insulating material completes the protection of the substrate with respect to any pollution caused by the metal forming the induction circuit. A seal ring **32** made of refractory material which is a bad heat conductor arranged round the opening **22** of the cavity **20** provides a poor heat contact between the cavity **20** and the insulating screen **31** while providing satisfactory sealing.

The embodiments described obviously have no limiting character, and, needless to say, varied versions may easily be conceived by the man in the art. The excitation of the plasma in the cavity has, for example, also been obtained by means of a wave guide device. The cavity has also been divided into fragments in certain cases, so as to enable a penetration of the electromagnetic field in the case of very conductive or refractory substances.

The applicant has also produced a device in which the cavity is drilled with several openings so that several substrates are covered simultaneously.

Moreover, the cavity has been divided into several compartments without an appreciable reduction in the depositing speed having been noticed.

It must be understood that the devices according to the invention may be used to great advantage, for producing thin layers of various substances: piezo-electric, semi-conductive, optical, magnetic, insulating substances, materials having great dielectric constancy, refractory materials or compounds thereof having a high metling point.

What is claimed is:

1. A plasma deposition device comprising:
a vacuum container formed of an insulating material,
means for maintaining said container at high vacuum,
a substrate support within said container,
a substrate carried thereby,
means defining a cavity lined on its inside with the substance to be deposited and having an opening therein adjacent to the substrate, the wall of said cavity being formed of an insulating material,
a high-frequency excitation means for generating an electromagnetic field within said cavity, and
means for injecting into said cavity a gas at a predetermined pressure for promoting the formation of a plasma in the cavity in the presence of the electromagnetic field.

2. The device according to claim **1,** wherein: said cavity is of generally cylindrical shape and defined by the cylindrical wall provided on its inside with longitudinal ribs.

3. The device according to claim **1,** further comprising: an electrode in the cavity; said electrode being connected to an electrical potential supply producing a spark to promote the starting up of the plasma.

4. The device according to claim **2,** wherein: said high-frequency excitation means comprises an induction winding surrounding the insulating container at the

level of the cavity and means connecting said induction winding to a high-frequency voltage supply.

5. The device according to claim 3 wherein: said high-frequency excitation means comprises an induction winding within the vacuum container and surrounding said cavity which is lined on its inside with the substance to be deposited.

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