United States Patent

Vanderschueren

[15] **3,693,583**

[45] **Sept. 26, 1972**

[54] **VAPOR DEPOSITION APPARATUS**

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[22] Filed: **April 22, 1969**

[21] Appl. No.: **818,270**

[30] **Foreign Application Priority Data**

June 28, 1968 Belgium.....60325

[52] **U.S. Cl.**.....**118/49.5**

[51] **Int. Cl.**.....**C23c 13/12**

[58] **Field of Search**.....118/48–49.5; 117/93.31, 93.3

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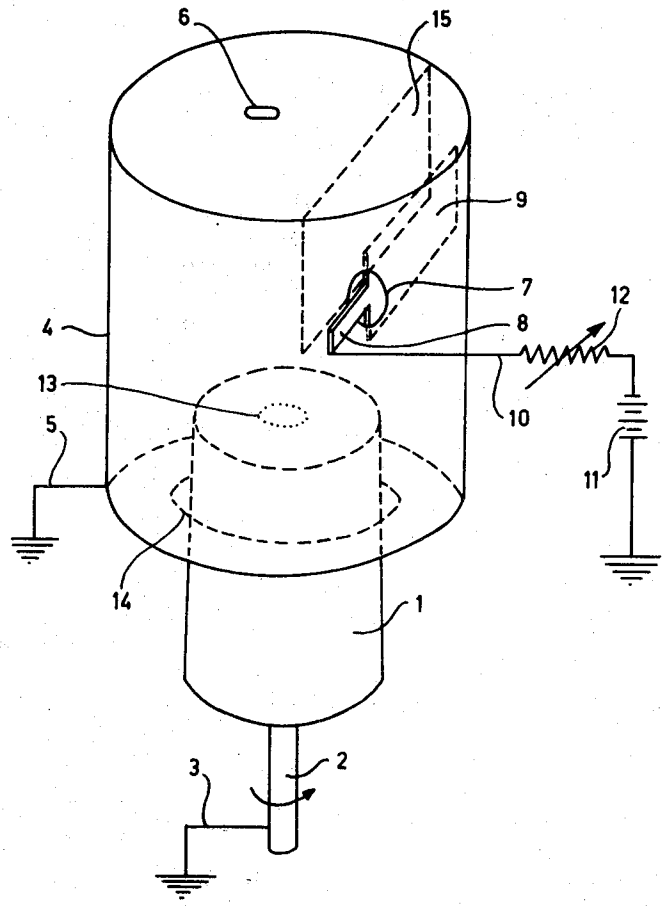
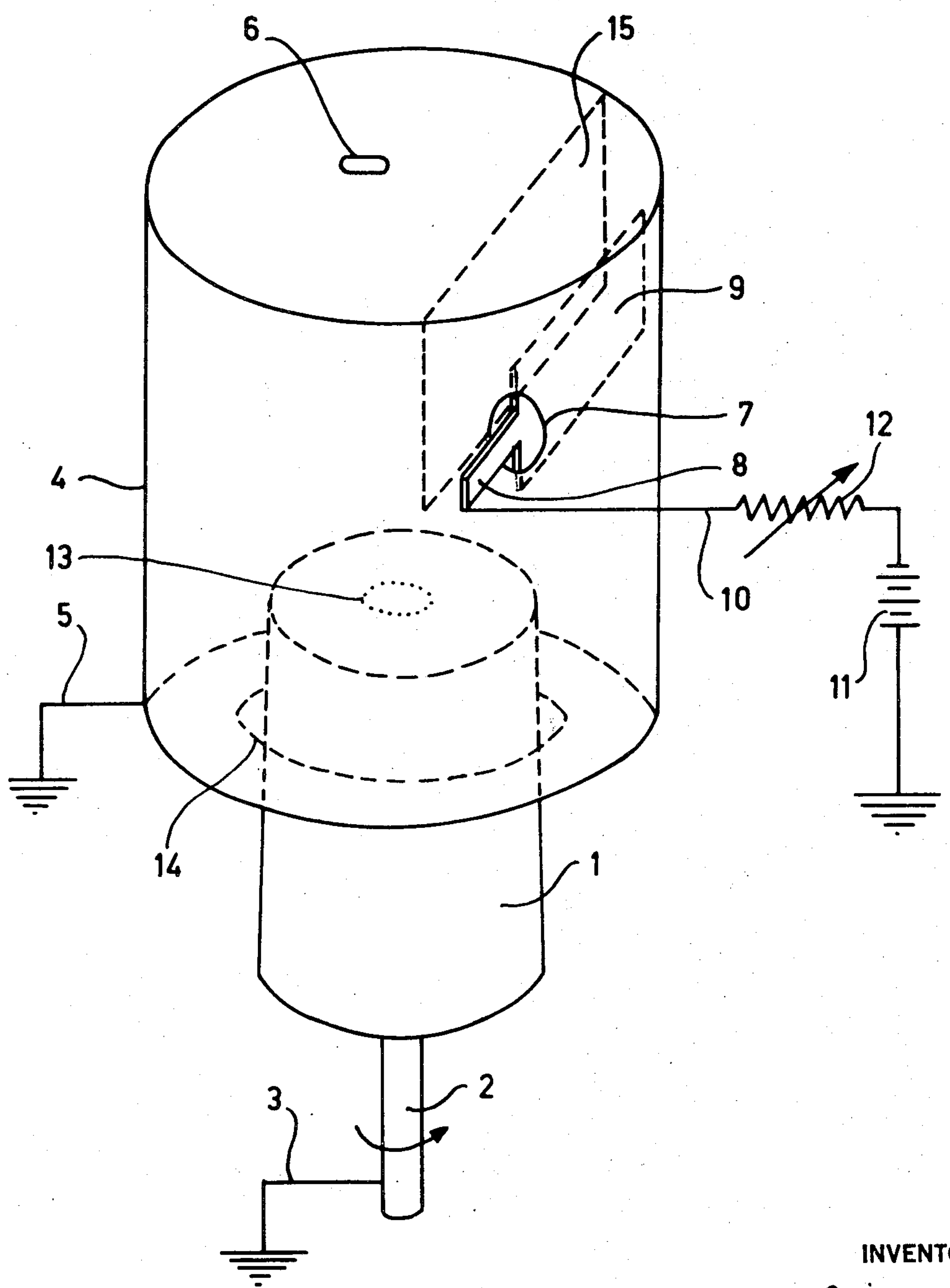
[57] **ABSTRACT**

An apparatus for producing monocrystalline deposits on a substrate by vacuum evaporation. The source of vapor to be deposited is a rotating cylinder which is off center with respect to an electron beam which strikes it and causes vaporization. The chamber walls are grounded and the substrate is held at a low positive potential rather than a high negative potential as is the usual practice.

1 Claim, 1 Drawing Figure





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VAPOR DEPOSITION APPARATUS

The invention concerns apparatus on depositing, by evaporation in a vacuum of at least 10^{-4} Torr, monocrystalline layers of material on substrates of any kind and shape, and a crystallizing vessel or apparatus for carrying out this method. The term "monocrystalline layer" is here used in a broad sense: it means both a true monocrystalline layer, in which the deposit formed consists of a single monocrystal, and a layer consisting of monocrystals all having the same orientation (epitaxy), as opposed to a polycrystalline layer consisting of monocrystals having all possible orientations.

In the present state of the art, there are many methods of producing deposits of material on various substrates in a vacuum. These include the various types of spraying, including high-frequency spraying, and vacuum evaporation. Deposits formed by these methods have variable properties of adhesion, quality and rate of deposition and it is an object of the invention to provide an apparatus which enables the degree of adhesion to be controlled, which provides a high deposition rate and which enables a monocrystalline deposit crystallized along the densest lattice planes to be obtained.

The invention is characterized in that the material which is to be deposited is evaporated in a vacuum of at least 10^{-4} Torr by heating it to its boiling point, the vapor thus produced is concentrated around the substrate and this vapor is ionized and deposited on the substrate to which is applied an electrical potential capable of attracting the ionized vapor but not interfering with ionization, the free surface of the substrate, during a first period necessary for formation of an adhering layer, being at a temperature as near the critical temperature for adhesion of the material evaporated on to the material of the substrate as is desirable for the quality of the adhesion required (which is greatest at the said critical temperature for adhesion) and, for the remainder of the deposition period, at the critical temperature for crystallization of the vapor and surfaces on which no deposition is desired being brought at least to the critical temperature for recoil for the vapor concerned.

The invention is based on the selection of a group of relatively critical operating conditions (temperatures and electric filed). First, it should be noted that the vapor of material to be deposited comes from a source where this material has been heated to its boiling point. In a vacuum, using this vapor, the Applicants have found that certain phenomena take place at definite temperatures already mentioned and which are defined below and at certain electric field values.

a. The critical temperature for crystallization of the vapor coming from a source at is boiling point. The Applicants have found that the atoms or molecules coming from a source in which the material to be deposited is brought to its boiling point are deposited on an existing crystal lattice of this material and continue this lattice or cover it with a monocrystalline layer, provided that at least the layers nearest the free layers of this existing lattice are at a critical temperature which the Applicants call the critical temperature for crystallization. The Applicants have found the value of this critical temperature for various substances. By way of example, the critical temperature for crystallization, in the operating conditions defined above, is about 1000°C for nickel, 1,350°C for alumina, 230°C for cadmium and 1,500°C for molybdenum. As a general rule, and judging from the technical results which have been obtained, this critical temperature for crystallization is between six-tenths and seven-tenths of the melting point for the material.

When the existing crystal lattice (formed either by the original substrate if this is of the same kind as the deposit, or by the vapor already crystallized by the method according to the invention), or at least its free layers, are at the critical temperature for crystallization, the incident atoms or molecules (from a source at boiling point) are deposited on this lattice and rearrange themselves in order to continue it and extend it.

b. The critical temperature for recoil. The atoms or molecules of the vapor to be deposited, come from a source at its boiling point and reaching any surface, recoil from this surface without being deposited on it when it is at a temperature at least equal to the critical temperature for recoil. This critical temperature for recoil is between the critical temperature for substrate, defined above, and the melting point for the material to be evaporated. In apparatus for carrying out the invention, all surfaces where no deposit is desired are brought to this temperature, so that the atoms or molecules of vapor which touch these surfaces are reflected and remain available for deposition on the substrate. In the operating conditions for the invention, the recoil temperature for cadmium is about 290°C and that for alumina about 1,600°C.

c. The critical temperature for adhesion of the crystallized layer to its substrate. Where the substrate is of the same kind as the deposit, the deposit will of course adhere best to the substrate if the latter is at the critical temperature for crystallization. The deposit then continues or extends the structure of the substrate. In the most general case, in which the substrate and deposit are of different kinds, there is for the substrate, or at least for its free surface, a critical temperature for adhesion of the deposit. This temperature is at least equal to the critical temperature for crystallization of the material to be deposited and is less than the recoil temperature.

When the substrate is brought to this adhesion temperature, the atoms of the incident vapor penetrate into the substrate to a depth of a few lattice spacings and arrange themselves along their own lattice, which overlaps or interpenetrates with that of the substrate or, more simply, with the material of the substrate if the latter is not in crystalline form. Adhesion is very good. At this level, one finds a compound of the substances constituting the substrate and the deposit. Going from the substrate towards the deposit, this compound starts by being very poor in atoms of the vapor, but becomes progressively richer in these atoms until it does not contain any of the substrate material.

Deposits obtained in accordance with the invention are formed in a vacuum enclosure (in a vacuum of at least 10^{-4} Torr) by heating the material to be deposited to its boiling point. The free surface of the substrate is brought to its critical temperature for adhesion of the vapor concerned long enough for the adhering layer to form.

If the aim is solely to obtain an adhering layer consisting of a compound of the materials constituting the substrate and the vapor, deposition can stop when there are no longer substrate atoms available to form the compound. Layers of compound several microns thick have been formed in this way, for example in order to make a corrosion-resistant layer.

If, on the other had, it is desirable to obtain a deposit of the evaporated substance when the adhering layer no longer contains anything but the atoms from the vapor, disposed along their own lattice, the free layer of the substrate obtained is brought to the critical temperature for crystallization of the vapor. The vapor is then deposited, forming a monocrystalline layer.

Advantageously, in order to increase the rate and quality of deposition and its adhesion, the density of the vapor around the substrate is increased. To this end, the vapor is concentrated around the substrate by any known means, and all the surfaces on which no deposit is desired are brought at least to the temperature for recoil of the vapor atoms or molecules. These atoms or molecules are then available only for deposition on the substrate, and material losses are greatly reduced. Very simple and very effective means for concentrating the vapor will be described later in this specification.

A spectacular improvement in both the yield and the rate of deposition and in the adhesion and depth of the deposit is obtained by ionizing the vapor particles and applying to the substrate a potential of opposite sign to that of ionization. This potential maintains ionization of the vapor, directs and accelerates the atoms or molecules of the ionized vapor towards the substrate. and carries out an ion pumping action. The latter consists in that the atoms or molecules foreign to the material to be deposited are ejected from the vapor. This potential is effective from low voltages (of the order of some tens of Volts in experimental conditions), and it has an upper limit due to its influence on the stability of the means for heating and ionizing the vapor to be deposited. In practice, during normal operation, it is between 10 and 120 Volts, but it may be higher.

The method is preferably carried out by ionizing the vapor atoms or molecules with an electron beam (coming from a gun or from an emission source) and applying to the substrate a potential higher than that of the surrounding space. The rate of deposition can now be of the order of 1 mm per hour and also — this is important and does not happen without this field — the deposit obtained is crystallized along the densest lattice planes. The density and quality of the deposit are therefore much increased. As regards the adhering layer, the inter-penetration with the material of the substrate is improved, as is its depth, so that the qualities of adhesion of the deposit itself are, of course, also improved.

If, on the other hand, a detachable deposit is desired, it is merely necessary, during a first stage, to avoid bringing the substrate to the critical temperature for adhesion and applying an electrical potential to it. As soon as a monatomic layer has covered the substrate, the latter is subjected to the electric-field and temperature conditions described above with reference to obtaining high-quality monocrystalline deposits. The deposit is is then easily separated from the substrate. The speed at which this deposit forms means that the invention can be used for making sheets or foil of very high quality (being monocrystalline), which can be detached from the substrate by hand.

Some mechanical elements of complex shape can also be made in the form of a monocrystalline layer deposited on a substrate of suitable shape without adhering to this substrate. Elements made in this way are formed of material in a much more perfect state than those obtained by conventional metallurgical means, which cause dislocations in the material.

The invention can also be used very advantageously for making monocrystals of any size or shape.

The method just described also makes it possible to vary the thickness of the deposits locally by placing grounded screens opposite places where no or a decreased deposit is desired. For deposits of complex shape, it is even possible to provide grounded screens containing apertures with the shape desired for the deposit, in the manner of the stencils used in painting.

The present invention can also be used for forming deposits from vapor from a plurality of sources and from different vapors from different sources.

The method just described also makes it possible to form welds of excellent quality between elements which cannot be welded by known methods. In accordance with the invention, the welding material is applied in the form of a vapor from a source in which it has been brought to boiling point. Each of the elements to be welded is, at the level of the connection which is to be made, brought to the critical temperature for adhesion of the vapor for the material constituting it. A grounded screen containing an aperture opposite the place where the weld is required may advantageously be used as described above. As soon as the adhering layers are completed, their free surfaces are brought to the critical temperature for crystallization of the vapor, and a monocrystalline deposit of welding material therefore forms which connects the two elements and adheres strongly to both of them. Metal/ceramic welds of very high quality have been made in this way, although the elements to be welded have been left a at fairly low temperatures.

The apparatus according to the invention is characterized in that it comprises a closed chamber situated inside the vacuum enclosure and containing at least one source of vapor of the material to be deposited, where the latter is brought to its boiling point, and a substrate support, heating means for bringing the walls of the chamber to the temperature for recoil of the atoms of molecules of the vapor from the source, and substrate heating means capable of bringing the free surface of the substrate either to the temperature for adhesion of the vapor from the source or to the temperature for crystallization of this vapor, as required.

A crystallizing vessel according to the invention and for carrying out the method described above and its use will now be described with reference to the accompanying drawing which represents a diagrammatic view of the vessel.

The device shown in this FIGURE is inside a vacuum enclosure (not shown) in which a vacuum of at least 10^{-4} Torr can be produced.

The Figure shows a source of vapor of the material to be deposited, in the form of a cylindrical block 1 having a vertical axis and composed of the material to be

deposited. This block 1 is mounted at the upper end of a vertical shaft 2 coaxial with it. The source is grounded by means of a connection 3. The vertical shaft 2 is rotated by a motor (not shown) at a speed of 2 to 5 revolutions per minute.

The source, or the shaft supporting it, extends into a chamber 4 which is grounded by means of a connection 5. An orifice 6 in the wall of this chamber permits passage of an electron beam from a gun (not shown) situated in the vacuum enclosure outside the chamber 4. The wall of the chamber also has an orifice 7, through which a rod 8 supporting a substrate 9 passes. The rod 8 is fixed or freely movable in respect of rotation and/or translation, and it is electrically connected by a lead 10 to the positive pole of a direct-current generator 11, whose negative pole is grounded. By means of a variable resistor or potentiometer 12, the potential difference between the substrate and the surrounding space can be adjusted as desired between zero and a voltage which does not seriously disturb the electron beam, usually between 10 and 120 Volts. The electron beam passing through the orifice 6 in the chamber wall bombards the flat upper surface of the cylinder 1. It is so directed that its point of impact is at a distance of the order of a few millimeters from the center of this face. Because the shaft 2 is rotating the cylinder 1, the point of impact of the electron beam shifts continuously. Its locus is a circle 13. As a result, the electron beam does not form a deep, narrow hole in the source: the heat is better distributed and melts, on the cylinder 1, a small mass of material to be evaporated, which mass is situated at the center of the upper surface of the cylinder and is shaped like a lens defined approximately by the circumference 13. There is therefore a fairly large and flat surface for evaporation of the liquid, permitting rapid and homogeneous emission of vapor.

The walls of the chamber 4 are brought by any known means to the temperature for recoil of the atoms of vapor from the source or to a temperature as near the recoil temperature as is desired. Other means (also not shown) can bring the free surface of the substrate to the critical temperature for adhesion or to the critical temperature for crystallization of the vapor, or even — if the adhesion of the deposit is to be very poor — to a temperature remote from these temperatures.

Because of the chamber 4, and provided that the apertures in this chamber provide only a small cross-section for the vapor from the source to escape, this vapor cannot disperse into the vacuum enclosure, but recoils from the chamber walls and remains concentrated around the substrate 9.

Also, the peripheral electrons of the beam heating the source ionize the vapor atoms or molecules, so that when the substrate is polarized relative to the space surrounding it these atoms or molecules are concentrated and attracted to the substrate in a preferential manner. The electrons emitted by the source itself, which may be very hot, also take part in this process.

The vapor source described above is extremely clean, in the sense that it does not introduce any impurity due to a crucible. If the vapor must be very pure, the concentrating chamber 4 maybe made of the same material as the cylinder 1. Also, as a result of the phenomenon of ion pumping already mentioned, the vapor is particularly free of foreign atoms or molecules, for example those provided by residual gases.

It should be noted that the substrate is disposed on the side of the chamber away from the electron beam, so that its electric field does not disturb this beam. To prevent drops of liquid from the material of the source from being sprayed on to the substrate, a grounded screen 15 may be inserted between the source and the substrate, to prevent material from following a straight path between the source and the substrate.

This screen, which may be in the form of a grating, also has the great advantage of placing the substrate in a Faraday cage. When the substrate is not conductive, therefore its potential can still be higher than that of the surrounding space, since it is free of the negative potential due to the electron beam.

If the temperatures to be used are very high, a heat shield can be inserted between the chamber and the vacuum enclosure in order to protect the latter. This screen may be in the form of copper sheet cooled by fluid flowing along fluid-tight pipes bearing on it.

The dimensions of the chamber 4 are as small as possible, but they must be compatible with the dimensions and shape of the substrate and the dimensions of the source, so that the potential applied to the substrate does not interfere with the beam. The dimensions of the source depend on the energy available in the beam.

Since the chamber is already at a certain temperature due to radiation form the source and substrate, and since this temperature is fairly near the critical temperature for recoil, it may readily be brought to the latter temperature by additional means. Sometimes it is only necessary to cover or surround the chamber 4 with an additional shielding casing, by means of which the heat losses of the chamber can be reduced cheaply.

It is an advantage of the above method that it can simultaneously give adhesion which is adjustable as desired, from almost zero adhesion of the layer deposited to perfect adhesion corresponding to interpenetration of the crystal lattice of the deposit and the substrate material, a monocrystalline deposit crystallized along the densest lattice planes, and a deposition rate of the order of 1 millimeter per hour.

As regards precious metals, easy recovery — without special chemical treatment — of any material which, in spite of precautions, has been deposited on the walls of the chamber 4 while the latter has not been at the critical temperature for recoil is facilitated if the chamber is made from the material which is to deposited.

The arrangement according to the invention also has the advantage of permitting evaporation of toxic or radioactive substances without special precautions, since the vapor remains confined within the chamber 4.

I claim:

1. Apparatus for producing monocrystalline deposits on a substrate by vacuum evaporation, comprising:

a chamber within a vacuum enclosure, said chamber comprising the same material which is to be deposited, and said chamber containing a substrate and a grounded screen near the substrate, said screen having apertures therein opposite those parts of the substrate where a deposit is desired,

a vertically extending shaft mounted for rotation about its axis,

a cylinder of the source material to be evaporated mounted on the upper end of said shaft, said cylinder projecting only partially into the chamber,

said chamber having an opening therein opposite the cylinder of source material for permitting an electron beam to enter the chamber and hit the cylinder of source material, said cylinder of source material being positioned off center with respect to the opening for an electron beam,

means for heating the walls of the chamber and the substrate,

means for electrically grounding the walls of the chamber and the cylinder of source material, and

means connecting the substrate to the positive terminal of a power source whose other terminal is grounded.

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