219-121 SR
MTR04 XR 2,932,588

April 12, 1960 K. J. FRANK 2,932,588
METHODS OF MANUFACTURING THIN FILMS OF REFRACTORY DIELECTRIC MATERIALS
Filed June 22, 1956

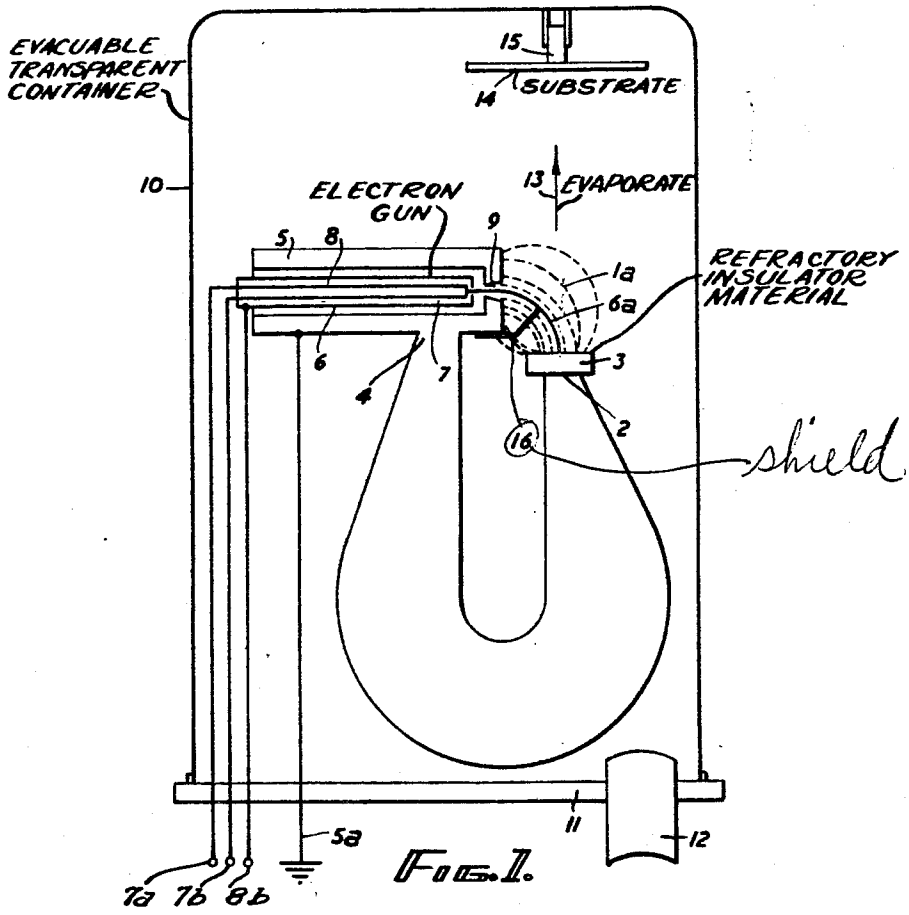


FIG. 1.

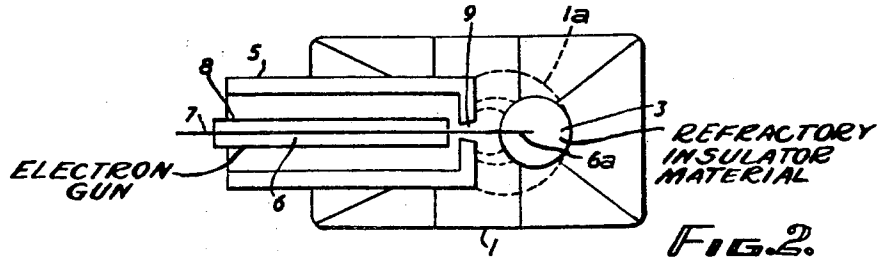


FIG. 2.

INVENTOR:
Kurt Josef Frank
BY: Baldwin & Wight
ATTORNEYS

United States Patent Office 2,932,588
Patented Apr. 12, 1960

2,932,588

METHODS OF MANUFACTURING THIN FILMS OF REFRACTORY DIELECTRIC MATERIALS

Kurt Josef Frank, Darmstadt, Germany, assignor to English Electric Valve Company Limited, London, England, a British company

Application June 22, 1956, Serial No. 593,198

Claims priority, application Great Britain July 6, 1955

2 Claims. (Cl. 117—106)

This invention relates to methods of manufacturing thin films and more particularly though not exclusively to thin films of refractory dielectric materials.

One known method of creating a very thin film of a material is to place said material in, or on, a suitable container or holder and to raise the temperature of the material, in a vacuum, up to or beyond its evaporation temperature. The resultant evaporate is allowed to condense upon a suitable substrate so as to form a thin film deposit. This method is highly suited to certain materials, particularly some metals. Where, however, the material, has a very high evaporating temperature the substance from which the container or holder is made may also evaporate causing, inter alia, contamination of the condensate. Also, some materials, even when at temperature lower than their evaporation temperature, tend chemically to react with the substance from which the container or holder is made, and this effect is also undesirable.

The present invention seeks to provide means whereby materials, which upon being raised to their evaporation temperature as above described, would give rise to the aforementioned undesirable effects, may be satisfactorily evaporated substantially without said undesirable effects.

Although not limited exclusively thereto, the present invention is of great advantage when applied to the evaporation of refractory insulators of which silicon dioxide, alumina, magnesium oxide, and zirconium oxide are well known examples.

According to this invention in its broadest aspect a thin film of material is made by bombarding a specimen of the material in vacuo with an intense electron beam to evaporate material from said specimen and condensing the evaporate as a thin film on a carrier or substrate positioned in the vacuum.

It is, of course, known to make holes in bodies by electronically bombarding said bodies to evaporate the material thereof where the holes are required.

In a preferred way of carrying out the invention a thin film of material is manufactured by producing a magnetic flux path in an evacuated space, said path curving approximately through a right angle over its length, projecting a beam of electrons along said flux path so that the electron trajectory is bent to follow said path and the electrons are focussed on a specimen of material at the end of said path to cause evaporation of said material by electronic bombardment, and condensing the evaporate to form a thin film on a carrier or substrate surface which is positioned clear of the magnetic flux and electron beam path. This preferred method has the great advantage that the electron gun producing the evaporating beam is practically entirely imune from having evaporate condensed thereon.

Preferably, where the material is an insulator, means are provided for regulating the velocity of the bombarding electrons to be substantially equivalent to that corresponding to the second cross-over potential on the secondary emission curve for said material.

A preferred apparatus for carrying out the method of the inventioin comprises, within an evacuable chamber, a magnet of which one pole piece has its end face adapted to support the material to be evaporated and the other pole piece surrounds an electron gun situated so as to fire electrons through an orifice in a face of said other pole piece, said face being substantially at right angles to the end face of said one pole piece, and means situated substantially clear of the magnetic lines of flux between said poles for condensing the evaporate.

The invention is described with reference to the accompanying drawings of which Fig. 1 shows a vertical cross-section of one form of apparatus for carrying out the invention and Fig. 2 is a horizontal cross section of a detail of Fig. 1. Similar references are used for similar parts throughout the figures.

Referring to Fig. 1, a permanent magnet 1 arranged substantially in the shape of a horseshoe and designed so that the magnetic flux across its inter-pole space is of the order of 1,600 gauss or more, has one of its pole-pieces 2 adapted to receive or support a portion of refractory insulator material 3 to be evaporated. The other pole-piece 4 of said magnet comprises a hollow section 5, closed at one end, so that the inter-pole air gap extends from the external face of said closed end to the face of pole-piece 2. Dotted lines 1*a* indicate the general pattern of flux lines in the inter-pole air gap. An electron gun 6, of any well known kind, is centrally situated within section 5 and comprises a cathode 7 surrounded by a control cylinder or grid 8. A small tapered orifice 9, in the closed end of cylindrical section 5, allows electrons emitted by the electron gun to emerge, from the pole-piece.

The whole device, as described, is contained within an evacuable transparent container shown as a bell-jar 10 on a platform 11. Suitable pumping arrangements, not shown, are connected to pipe 12, in platform 11, whereby to control the pressure within the bell-jar. Fig. 2 shows a horizontal cross-section of Fig. 1, taken along a line passing through the center of electron gun 6 substantially on line 6—6 of Fig. 1. For clarity, bell-jar 10, platen 15, screen 16 and platform 11 are not included in this figure.

Magnet 1, and therefore hollow section 5, is maintained through lead 5*a* at earth potential and where the material 3 is an insulator (the case presumed here) a negative potential of approximately 3 kilovolts applied via terminals 7*b* and 8*a* to cathode 7 and control grid 8 respectively. A small voltage, appropriate to the type of cathode used, is applied across terminals 7*a* and 7*b* to heat cathode 7. The actual value of said applied negative potential is preferably such that the velocity of electrons bombarding the material 3 will have an electron velocity substantially corresponding to the so-called second cross-over potential on the secondary emission characteristic for the material to be evaporated. Selection of this velocity has the advantage of enabling a smaller anode potential to be used in the gun than would otherwise be the case. If the material 3 were a metal there would be, in general, no point in restricting the bombarding velocity the upper limit of bombardment velocity being set by practical considerations, principally the necessity of providing adequate insulation in the gun and the difficulty of providing sufficient magnetic flux to maintain a high velocity beam properly focussed on the material. Line 6*a* shows the trajectory of electrons leaving the gun. After passing through orifice 9 the electrons will follow substantially the path of magnetic flux lines 1*a* and impinge upon the material 3 to be evaporated. The point of impingement is made as small as possible in order that

the high current densities necessary to cause evaporation (of the order of 25 amps. per square centimeter) may be obtained.

On bombardment by electrons the material 3 will experience a rapid increase of temperature at the point of electron impingement and evaporation will occur from said point, the evaporate rising through the vacuum in the direction of arrow 13 to condense as a thin film on a major surface 14 (the substrate) of a platen 15, suspended above the material 3. A shield 16, of non-magnetic material, is provided as a further safeguard to prevent any of the evaporate from condensing upon the face of pole-piece 4. Such condensation would form on the wall of orifice 9 a coating which would allow a high electrostatic charge to be set-up on said face, and interfere with the electron beam.

After a sufficient layer of refractory insulator material has been deposited upon substrate 14, the voltages applied to gun 6 are switched off and platen 15 removed. The insulator material on the substrate will be in the form of a thin film and experiment has shown that it is practically uncontaminated and required no further chemical treatment.

Although the hereinbefore described technique is suitable for short evaporation periods, over longer periods the electron beam will gradually drill a hole through the insulator material. It is therefore preferred, in such cases, to arrange for the material 3 to be slowly moved in a plane at right angles to the electron path, so as to continuously bring fresh areas of the material under electronic bombardment.

For evporating glass, or other materials containing several components having different evaporation temperatures, in such a manner that the film condensed on the substrate will contain all these components intimately mixed with each other in the same proportion as in the original material, the following procedure may be employed. A sample of the material is supported on a carriage which can be moved in a plane at right angles to the electron path at the point of impingement, the movement being such that the sample is scanned under the electron beam, at constant speed. This speed and the power density of the beam is so adjusted that the part of the material penetrated by the beam is raised, within the time of bombardment, to a temperature sufficient to evaporate all components, while the temperature of the remainder is not allowed to reach the evaporation point of the most volatile component. In this fashion layer after layer of the material is removed by evaporation.

Free supporting glass films can be made by the method of the present invention using as a substrate an organic film, e.g. collodion, mounted on a ring of a material whose expansion coefficient is matched to that of the glass. After the evaporation process the film is heated in air to a temperature at which the viscosity of the glass is such that the film will tighten by surface tension and the organic film will burn away, leaving the free supporting glass film. A detailed description of the process is not given here as a full description is to be found in applicant's British patent specification No. 709,503.

I claim:

1. Apparatus for making thin films of material comprising within an evacuable chamber, a magnet of which one pole piece has its end face adapted to support the material to be evaporated and other pole piece surrounds an electron gun situated so as to fire electrons through an orifice in the face of said other pole piece, said face extending substantially at right angles to the end face of said first mentioned one pole piece, and means situated substantially clear of the magnetic lines of flux between said poles for condensing the evaporate.

2. A method of making a thin film of material on a substrate consisting in producing a magnetic flux path curving through approximately a right angle along its length in an evacuated space, projecting a beam of electrons along said magnetic flux path so that the electron trajectory is bent to follow said magnetic flux path, supporting a specimen of material at the end of said magnetic flux path, focussing said beam of electrons upon said specimen while simultaneously exposed to said magnetic flux path for effecting evaporation of said material by electronic bombardment and condensing the evaporate in a position external to both the magnetic flux path and the electron trajectory to form a thin film on said substrate.

References Cited in the file of this patent

UNITED STATES PATENTS

2,103,623	Kott	Dec. 28, 1937
2,157,478	Burkhardt et al.	May 9, 1939
2,239,642	Burkhardt et al.	Apr. 22, 1941
2,527,747	Lewis et al.	Oct. 31, 1950
2,754,259	Robinson et al.	July 10, 1956
2,771,568	Steigerwald	Nov. 20, 1956

FOREIGN PATENTS

754,102	Great Britain	Aug. 1, 1956

OTHER REFERENCES

Vacuum Deposition of Films, Holland, 1956, pages 135–140.