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METHOD OF FORMING SINGLE CRYSTAL FILMS BY NONEPITAXIAL GROWTH

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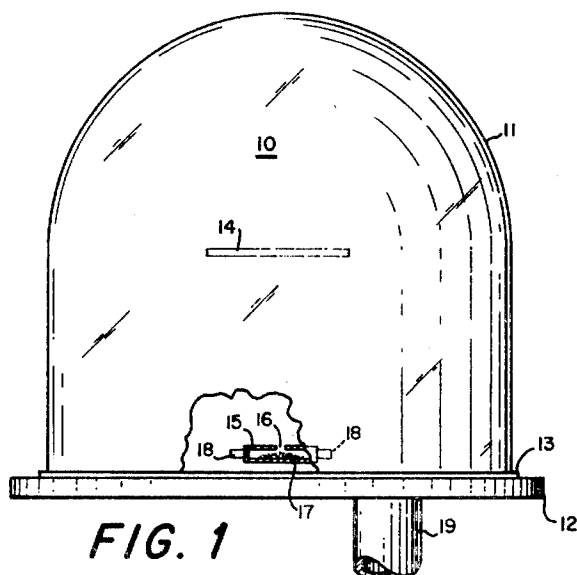


FIG. 1

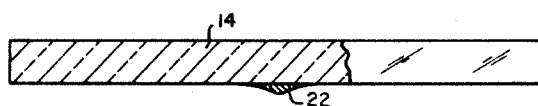


FIG. 2

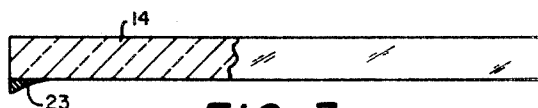


FIG. 3

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**METHOD OF FORMING SINGLE CRYSTAL FILMS
BY NONEPITAXIAL GROWTH**William H. Vaughan, 5209 Manor Drive,
Oxon Hill, Md. 20021Continuation of application Ser. No. 517,863, Dec. 30,
1965. This application Feb. 10, 1969, Ser. No. 800,036

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U.S. Cl. 117-106

8 Claims

ABSTRACT OF THE DISCLOSURE

A single crystal film of a material is grown from a single crystal nucleus on a smooth substrate which is in non-epitaxial relationship with the material. The material is vapor deposited under vacuum onto the substrate having a single crystal nucleus of the material thereon at a rate which promotes growth of a single crystal film on the substrate but below that at which nucleation of the material takes place on the substrate.

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

This application is a continuation of application Ser. No. 517,863, filed Dec. 30, 1965, now abandoned.

This invention relates to a method of forming single crystal films of materials on substrates by nonepitaxial growth of a single crystal nucleus of the film material.

A commonly used method for epitaxial growth of single crystal films of materials involves deposition of the material of the film from the vapor state under vacuum onto a heated substrate. In the practice of this known vapor deposition method, the substrate is selected to have an epitaxial relationship with the material. Without this epitaxial relationship in the method, the films formed will be polycrystalline.

Single crystal films have a number of useful applications: among which are the use of metal or metal oxide films as resistances or conductors in electronic circuitry, of metal oxide films as light sensitive elements in photosensitive devices and of inorganic metal salt films as radiation sensitive elements in dosimeters and nuclear particle counters. Where use of the single crystal film involves flow of an electric current in the film, as in electronic circuitry, the substrate for the film is by necessity, nonconducting. Nonconducting substrates are glass, fused silica, quartz, glazed ceramics and plastics. These substrates, however, are noncrystalline or polycrystalline and therefore cannot form an epitaxial relationship with crystalline film-forming materials for growth of single crystal films by the aforesaid vacuum vapor deposition process.

It is an object of the present invention to provide a method of growing single crystal films of materials from a single crystal nucleus of the material on substrates which are nonepitaxial in respect to the material of the film.

The above and other objects are accomplished by the practice of the method of the invention which is described below and with reference to the accompanying drawings in which like numerals indicate like parts and

FIG. 1 is a schematic showing, partly broken-away and partly in section, of one form of an apparatus for use in forming single crystal films in accordance with the method of the invention,

FIG. 2 is a showing in cross-section of a single crystal nucleus of a material positioned on a substrate for the practice of the method of the invention, and

FIG. 3 is a showing in cross-section of a single crystal nucleus of a material positioned in a different area on a

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substrate for the practice of the method of the invention.

In accordance with the method of the present invention, single crystal films of material are grown from a single crystal nucleus of the material directly on a smooth substrate which is not in epitaxial relationship with the material by a controlled deposition of the material from the vapor state under vacuum onto the substrate having a single crystal nucleus of the material thereon. The deposition of the material from the vapor state onto the substrate is made at a rate which promotes formation of the single crystal film but below that at which nucleation of the material takes place on the substrate. Nucleation will result in formation of polycrystalline films.

In the method of the invention single crystal films are formed on the substrates by virtue of a rapid migration to the single crystal nucleus of particles of the film material which are deposited on the substrate in proximity to the nucleus and in the process of growth to the advancing edge of the growing film. Particles of the deposited material which are not proximate to the nucleus or to the advancing edge of the growing film will evaporate from the substrate.

Heating of the substrate during the deposition of the film material thereon is not necessary to the practice of the method of the invention, although the substrate may be heated if found desirable. The method can be practiced for the formation of single crystal films when the substrates are at ordinary temperatures, i.e. at room temperature (25° C.) or thereabout, during the deposition of the film material thereon. The advantages of operating the method with the substrate at ordinary temperatures during the vapor deposition are the obvious convenience of working at these temperatures and, more, importantly, of avoiding the development of strains between the film and the substrate due to differences in their coefficients of expansion which are to be experienced when heated substrates are subsequently cooled to room temperature.

A further advantage of the method of the invention is that the single crystal films are formed without the usual type of island growth and hence do not have the resultant sharp discontinuities in cross-section.

The method is of general application for the formation of single crystal films of material which may be vaporized under vacuum without dissociation. The material for the single crystal films may be a metal, for example, gold, silver, copper, tin, lead, indium, gallium, silicon, and germanium, or a metal oxide, for example, magnesium oxide, aluminum oxide, boron oxide, nickel oxide and silicon dioxide, or an inorganic metal salt, for example, silver chloride, sodium chloride, potassium chloride, lithium chloride, cesium chloride and rubidium chloride.

The method of the invention may be carried out in the apparatus shown schematically in FIG. 1 which is of the type in general use for forming films by vacuum deposition of the film material from the vapor state onto the substrate. In this apparatus the vacuum chamber 10 is formed by a glass bell jar 11 which is sealed in vacuum-tight relationship to a metal base plate 12 by means of a heat-resistant rubber gasket 13. A tube 19 is provided for pump-down of the chamber 10 to low pressures which may be of the order of 5×10^{-6} mm. of mercury or lower.

An evaporation boat 15 of a suitable electrically-conductive refractory material is supported in the chamber 10 above the base plate for vaporizing the film material 17. As shown, the evaporation boat is a Knudsen type cell having a central circular aperture 16 of small diameter, e.g., 3 mm., in the cover for egress of the vapor developed by evaporation of the film material 17. The cell is provided with a pair of integral metal lugs 18 for connection of leads to a suitable electric power source. The temperature of the boat may be measured by means of a thermo-

couple. To reduce or minimize heat transfer to the substrate by radiation from the heated evaporation boat 15 during formation of the film, a plate (not shown) made of a heat refractory material, e.g., metal, is supported in the vacuum chamber 10 from the base plate 12 a short distance above the boat, e.g., 1-2 mm. to extend over the boat as a heat baffle. This baffle plate has a centrally located aperture of slightly greater diameter than the aperture 16 of the evaporation boat which in the arrangement of the baffle plate is aligned with the aperture 16.

The substrate 14 is supported in the vacuum chamber 10 for vertical and lateral adjustment in respect to the evaporation boat 15. This may be accomplished in any manner found suitable. One means for this purpose (not shown) is a standard supported from the base plate 12, on which a frame is mounted for vertical and lateral movement. The frame may be of a type for gripping the substrate by the edges or upon which it may rest. The standard may also serve for the mounting of a metal shutter (not shown) which is arranged to be swung into position over the evaporation boat 15 to prevent the vapors of the material from reaching the substrate until a desired level of flux of the vapors has been reached in the boat, when it is swung out of position.

The single crystal nucleus of the film material may be formed on the substrate in any suitable manner and be present in any area of the substrate, for example, centrally, as at 22, or at one corner, as at 23, as shown in FIGS. 1 and 2.

Control of the rate of deposition of the vaporized material onto the substrate under vacuum is a matter of geometry and the temperature of the vaporized material. In the method of the invention the rate at which the vaporized material reaches the substrate for deposition involves the distance of the substrate to be coated from the orifice of the vapor source (aperture 16 of the evaporation boat 15), the cross-section of the orifice and the flux level of the vapor at the source. The latter is a function of the temperature of the evaporation boat 15.

A rate of deposition of the film material from the vapor state onto the substrate which is below that at which nucleation of the film material takes place on the substrate may be determined in each instance in the simple, practical manner of trial and error.

Typical of the single crystal films which may be grown by the method of the invention from a single crystal nucleus of the film material on a substrate which is not in epitaxial relationship with the film material are those of gold, silver and copper grown on a glass substrate. Growth of single crystal films of the metals on separate glass substrates was conducted in the apparatus as described above. Evaporation of the metal for the film was made in a Knudsen type cell 15 of tantalum having an aperture 16 of 3 mm. diameter. The arrangement of the glass substrate and evaporation cell in the vacuum chamber 10 was such that the surface of the substrate bearing the single crystal nucleus of the metal faced the evaporation cell and at distance of 15 centimeters above the aperture 16 of the cell. The substrate was at about room temperature during the deposition thereon of the metal from the vapor state, the baffle plate being in position over the evaporation cell 15. The vacuum chamber 10 containing the system for forming the film on the substrate was exhausted to a low pressure of 5×10^{-6} mm. Hg through the tube 19 connected to a vacuum pump (not shown). The evaporation cell 15 containing the metal for the film was heated electrically to a temperature at which the flux level of the developed metal vapor was such, that, on impingement of metal vapor on the substrate, the rate of

deposition of metal particles onto the substrate was below that at which nucleation would take place on the substrate. The vapor shutter was swung out of position to allow impingement of metal vapor on the glass substrate and formation of a single crystal film of the metal thereon.

Once the substrate not in epitaxial relationship with the material of the film is covered with a single crystal film of the material, the rate of deposition of the material on the substrate is no longer critical and may be increased to above the critical rate to form a thicker single crystal film.

A relatively constant thickness of the single crystal film may be obtained in the method of the invention by starting with a single crystal nucleus which is located along an edge or at a corner of the substrate and using a slit-type vapor shutter which is rotated over the substrate surface to be coated at a constant speed.

While the invention has been described herein with reference to certain specific embodiments thereof, the same are intended by way of illustration and not in limitation except as may be defined in the appended claims.

What is claimed and desired to be secured by Letters Patent of the United States is:

1. A method of growing a single crystal film of an inorganic crystalline material from a single crystal nucleus of said material on a smooth substrate which is not in epitaxial relationship with said material, which comprises, under vacuum, vaporizing said inorganic crystalline material, said material being vaporizable in the undissociated state under vacuum, subjecting said substrate and a single crystal nucleus of said material thereon, at about room temperature, to deposition thereon of said inorganic crystalline material from said vapor, and conducting said deposition at a rate which is below that at which nucleation of said inorganic crystalline material takes place on said substrate.

2. The method as defined in claim 1, wherein the inorganic crystalline material is a metal.

3. The method as defined in claim 1, wherein the inorganic crystalline material is a metal oxide.

4. The method as defined in claim 1, wherein the inorganic crystalline material is a metal salt.

5. The method as defined in claim 1, wherein the substrate is a glazed ceramic.

6. The method as defined in claim 1, wherein the substrate is fused silica.

7. The method as defined in claim 1, wherein the substrate is glass.

8. The method as defined in claim 1, wherein the substrate is glass and the inorganic crystalline material is a metal.

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