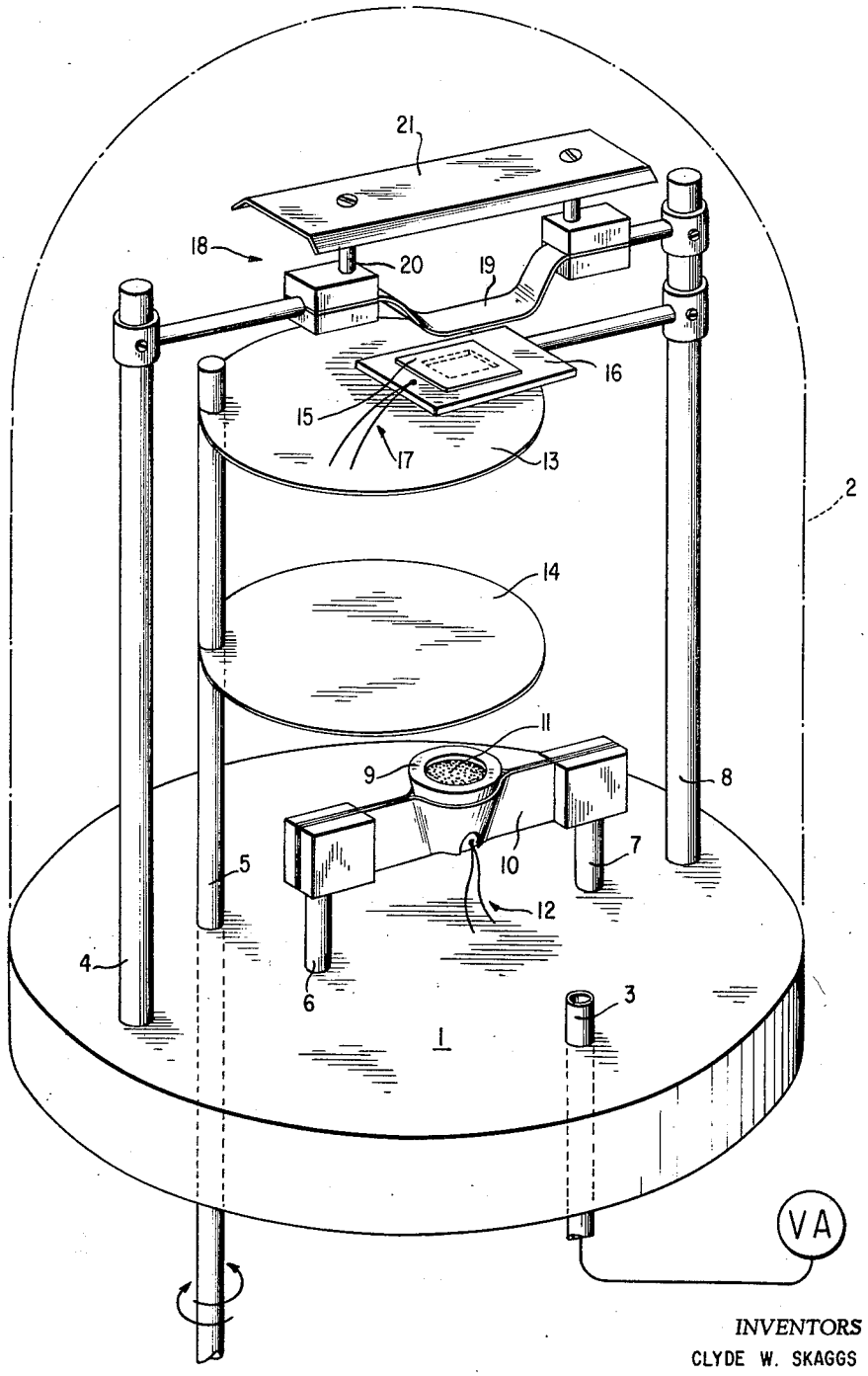
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METHOD OF PRODUCING UNSUPPORTED EPITAXIAL FILMS OF GERMANIUM BY EVAPORATING THE SUBSTIATE

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METHOD OF PRODUCING UNSUPPORTED EPITAXIAL FILMS OF GERMANIUM BY EVAPORATING THE SUBSTRATE

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This invention relates in general to a method of producing unsupported films of semiconductive material and more specifically to a vacuum deposition method for producing unsupported, epitaxial films of semiconductive material of a quality suitable for minority-carrier semiconductor device preparation.

As is well known by those familiar with the art of producing semiconductive devices, one of the most common methods employed to produce thin films or layers of semiconductive material, such as germanium, silicon, selenium, tellurium, cadmium, and the like, is that of vacuum deposition. In carrying out this method, the semiconductive material of which a film is desired to be formed is placed in a crucible which may be controllably heated, as for example by electrical resistance wires surrounding the crucible. A supporting material, or substrate, which is also provided with a controlled heating source, is positioned near the crucible and these elements are placed within an air-tight enclosure such as a bell jar, upon which a vacuum is then drawn. Heat is applied to the crucible to vaporize the semiconductive material, which subsequently condenses on the surface of the heated substrate to form the desired film.

In the past it has been common practice to utilize the resulting bi-layer structure as a unitary assembly rather than attempt to separate the film from the substrate. This restriction has been largely due to the difficulties experienced when attempting to effect a separation. Owing to the extreme thinness of films deposited in this manner, rendering them especially delicate and fragile, and also due to the strong cohesive bond formed between the film and the substrate, the physical separation of the two has most often resulted in the tearing, cracking, breaking, or similar destruction of the film, leaving it wholly unsuitable for use as an electrical element.

In addition difficulty has been experienced in the past with respect to the unassisted wrinkling and cracking of the film upon cooling immediately following the deposition thereof. This has been due to the elevated temperatures at which such vacuum deposition processes are normally carried out, e.g. 400° C.– 600° C., and to the large differences in the coefficients of thermal expansion between the substrates and the deposited materials.

This invention seeks to overcome the above-noted and other disadvantages inherent in the prior art, and has as its primary object the provision of an effective and inexpensive method of producing films of semiconductive material.

Another object of the invention is to provide a method of producing unsupported films of semiconductive material sufficiently thick to have electrical characteristics similar to bulk material.

Yet another object of the invention is to provide a method of producing unsupported epitaxial (and therefore having a mono-crystalline structure) films of semiconductive material suitable for use as substrates for subsequent depositions of other semiconductive materials, thereby making possible the fabrication of active electrical elements whose film properties may be completely utilized without any limitations being imposed by the presence of extraneous substrates or supports.

Briefly, these and other objects that will be readily apparent to one familiar with the art to which this invention pertains, are achieved by selecting a semiconductive material and substrate material having similar crystalline structures (necessary to produce epitaxial layers), forming a film of the semiconductive material on the substrate by a vacuum deposition process, and then slowly raising the temperature of the resulting bi-layer structure to the temperature at which the substrate vaporizes. Upon evaporation of the substrate, what is left is the desired unsupported, epitaxial film of semiconductive material preserved in its deposited structural form.

The invention may be best understood from a consideration of the following preferred embodiment described in conjunction with the single illustration in the drawing.

Referring now to the drawing, there is shown a base or table 1 on which is seated in air tight relationship a glass bell jar 2, indicated by a broken line. Associated with the bell jar and communicating with its interior via the exhaust port 3 is a conventional oil diffusion pump vacuum apparatus (not shown), which is capable of drawing a high vacuum on the bell jar. Also mounted on the base are five supporting rods, 4, 5, 6, 7 and 8, used to support various operative elements of the apparatus, as will later be more fully described. Mounted on supporting rods 6 and 7 is a carbon crucible 9 surrounded by a first tantalum foil heater 10. The crucible is preferably made of carbon since most of the more common metals have a tendency to alloy with molten semiconductive materials. A source of semiconductive material 11 is shown contained in the crucible. The crucible and heater are provided with a first temperature sensing thermocouple 12. The electrical connections to the heater and thermocouple are not shown as they are immaterial to the scope of this invention. They may take any conventional form as long as their communication with the exterior of the vacuum chamber is made through air tight passages. The heater current may be manually controlled and the thermocouple output may be visually monitored, as by observing the needle deflection of a temperature calibrated voltmeter to which the thermocouple leads are connected, or, as another alternative, the thermocouple output may be used to control the magnitude of the heater current in the manner of an automatic thermostat.

Mounted on supporting post 5 are two movable shutters 13 and 14, one being positioned immediately beneath a substrate 15 and the other being positioned over the crucible 9. These shutters may be formed from a thin stainless steel sheet if desired and may be manually swung into or out of the position shown by the rotation of supporting rod 5 which projects through the base 1. The substrate 15 is held in a mask 16 which may be made of spectrographic carbon (a mask of carbon supported by a double mask of stainless steel), and in which a second thermocouple 17 is imbedded. The mask 16 is in turn mounted on supporting rod 8. Positioned directly above the substrate 15 and mounted between supporting rods 4 and 8 is the substrate heater assembly, indicated generally by reference numeral 18. The substrate heater assembly includes a second tantalum foil heater 19 to which are affixed ceramic standoffs 20 which support a stainless steel reflector 21. Once again, the electrical connections to the second heater and thermocouple are not shown, but may be provided in any conventional manner.

The method of this invention will now be described with reference to an exemplary set of parameters that have been found to yield highly satisfactory results. A germanium source is placed in the carbon crucible and a substrate of cleaved sodium chloride (NaCl) is placed in position on the mask 16. Sodium chloride and germanium are two materials that have been found to be especially compatible for use with this invention since both have similar crystalline structures, which is essential

for epitaxial growth, and the vaporization temperature of sodium chloride is only slightly above the temperature at which such epitaxial growth takes place when the germanium is vacuum evaporated and subsequently condensed on the surface of the sodium chloride. The bell jar is fitted in position and a vacuum of between 3×10^{-4} mm. Hg and 5×10^{-5} mm. Hg is drawn. The movable shutters **13** and **14** are rotated to the side presenting a clear path between the germanium source **11** and the sodium chloride substrate **15**, and current is applied to the substrate heater until a temperature of approximately 530° C. is indicated by the thermocouple embedded in the mask. At this point a current is passed through the crucible heater sufficient to heat it to above the melting temperature of germanium (between 1450° and 1500° C.). As the germanium source **11** liquefies it evaporates and subsequently condenses in a thin epitaxial film or layer on the unmasked surface of the sodium chloride substrate. When the film reaches the desired thickness, which may be closely controlled by regulating the vaporization time, the crucible temperature, the distance between the source and substrate, etc., the crucible heater is de-energized and the substrate temperature is slowly raised, at a rate of about 10° C. per minute, to approximately 630° C., at which temperature the sodium chloride substrate begins to vaporize. The movable shutters **13** and **14** are rotated back into the position shown in the drawing, and when the substrate evaporization is complete, the previously deposited film of germanium falls free and is caught intact and undamaged on the upper shutter **13**.

Good quality unsupported, epitaxial germanium films have been produced in this manner ranging in thickness from 4000A to 16000A, as measured from a microscope cover glass monitor with a Zeiss interference microscope. These films have electrical characteristics similar to bulk material and are themselves suitable for use as substrates for the subsequent deposition of other semiconductive materials in the fabrication of active electrical elements.

While the invention has been specifically described with reference to a semiconductor source material of germanium and a substrate of sodium chloride, other compatible materials selected in accordance with the criteria presented herein may be equally amenable to use with the method and apparatus disclosed, and such are to be deemed as being within the spirit and scope of the invention, as well as slight modifications therein which will be apparent to those skilled in the art.

What is therefore claimed and desired to be secured by Letters Patent is:

1. A method of producing an unsupported film of semiconductive material comprising the discrete steps of:

(a) forming a coated substrate by depositing a thin film of vaporized semiconductive material on the surface of a substrate suspended in a vacuum, the vaporization temperature of said substrate being higher than the temperature suitable for vapor deposition and lower than the vaporization temperature of the semiconductive material;

(b) continuously heating said coated substrate above the vaporization temperature of said substrate to vaporize said substrate, thereby leaving an unsupported film of semiconductive material;

(c) cooling said unsupported film of semiconductive material; and

(d) catching intact and undamaged said unsupported film of semiconductive material as it falls free.

2. A method of producing an unsupported film of semiconductive material comprising the discrete steps of:

(a) forming a coated substrate by depositing a thin film of vaporized semiconductive material on the surface of a substrate suspended in a vacuum, the vaporization temperature of said substrate being higher than the temperature suitable for vapor deposition and lower than the vaporization temperature of the semiconductive material;

(b) continuously heating said coated substrate above the vaporization temperature of said substrate to vaporize said substrate, thereby leaving an unsupported film of semiconductive material;

(c) cooling said unsupported film of semiconductive material as it falls free; and

(d) catching intact and undamaged said unsupported film of semiconductive material as it falls free.

3. A method of producing an unsupported, epitaxial film of semiconductive material comprising the discrete steps of:

(a) forming a coated substrate by depositing a thin epitaxial film of vaporized semiconductive material on the surface of a substrate suspended in a vacuum, said semiconductive material and said substrate having substantially similar crystalline structures, and the vaporization temperature of said substrate being higher than the temperature suitable for epitaxial growth of said semiconductive material thereon and being lower than the vaporization temperature of said semiconductive material;

(b) continuously heating said coated substrate above the vaporization temperature of said substrate to vaporize said substrate, thereby leaving an unsupported epitaxial film of semiconductive material;

(c) cooling said unsupported, epitaxial film of semiconductive material; and

(d) catching intact and undamaged said unsupported, epitaxial film of semiconductive material as it falls free.

4. A method of producing an unsupported, epitaxial film of germanium comprising the discrete steps of:

(a) forming a coated substrate by depositing a thin epitaxial film of vaporized germanium on the surface of a cleaved sodium chloride substrate suspended in a vacuum;

(b) continuously heating said cleaved sodium chloride substrate above the vaporization temperature of said substrate to vaporize said substrate, thereby leaving an unsupported, epitaxial film of germanium;

(c) cooling said unsupported, epitaxial film of germanium; and

(d) catching intact and undamaged said unsupported, epitaxial film of germanium as it falls free.

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