

United States Patent

[11] 3,607,135

[72] Inventors **Reinhard K. Gereth**
Heilbronn, Germany;
Edward M. Hull, Lagrangeville; Thomas B.
Light, Chappaqua, N.Y.
 [21] Appl. No. **674,867**
 [22] Filed **Oct. 12, 1967**
 [45] Patented **Sept. 21, 1971**
 [73] Assignee **International Business Machines**
Corporation
Armonk, N.Y.

3,152,933 10/1964 Reuschel 117/106 A
 3,178,313 4/1965 Moest 117/106
 3,249,473 5/1966 Holonyak 23/294

Primary Examiner—Norman Yudkoff
Assistant Examiner—Arthur F. Purcell
Attorneys—Hanifin and Jancin and Thomas J. Kilgannon

[54] **FLASH EVAPORATING GALLIUM ARSENIDE**
 2 Claims, 3 Drawing Figs.

[52] U.S. Cl. **23/294,**
 23/300, 117/106
 [51] Int. Cl. **B01d 7/00,**
 C01b 29/00
 [50] Field of Search 23/293,
 294, 300; 117/106, 106 A, 107

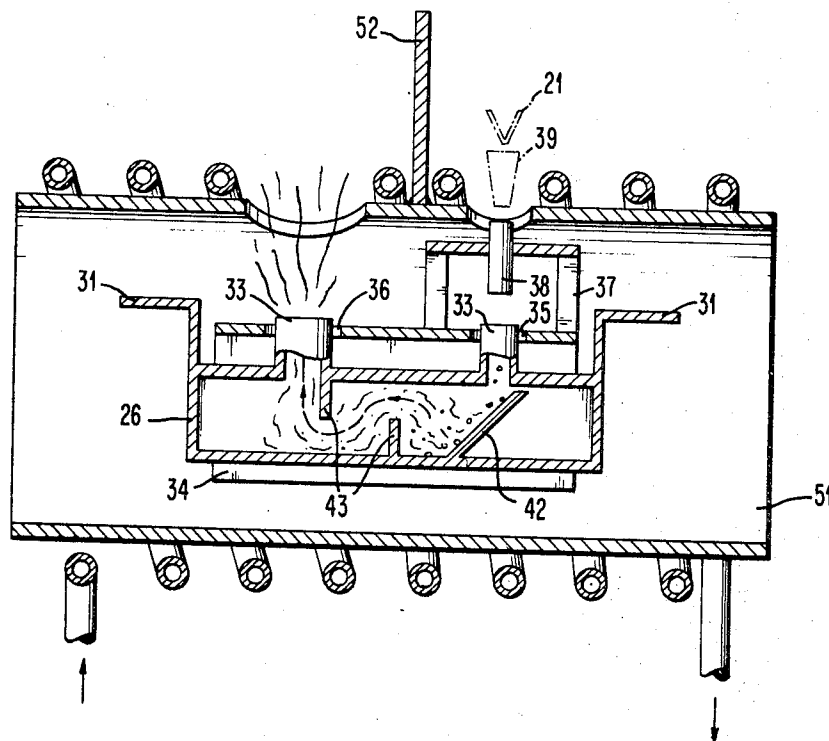
[56] References Cited

UNITED STATES PATENTS

1,518,126	12/1924	Reed	23/294
2,368,319	1/1945	Muskat	23/294
2,376,045	5/1945	Gaither	23/294
2,419,310	4/1947	Belchetz	23/294
2,582,794	1/1952	Porter	23/294
2,947,613	8/1960	Reynolds	23/294
3,042,501	7/1962	Noblitt	23/294

ABSTRACT: A process and apparatus for producing thick films of a material, containing a number of constituents such as compounds, physical mixtures and alloys of material, by flash evaporation is described. Specifically, high feed rates of the material, gallium arsenide, for example, to be flash evaporated are required for depositing uniform, thick films on a substrate and such high feed rates are made possible by preventing clogging of the feed apparatus by the feed materials.

Clogging is prevented by the use of a guide funnel and guide tube arrangement which are disposed one above the other in coaxial vertical alignment with an aperture in a box source heater, the lower extremity of the guide tube is vertically displaced from the aperture a distance sufficient to maintain the temperature of the guide tube below the decomposition or melting temperature of the material but at a temperature in excess of the condensation temperature of the more volatile constituent of the material being evaporated; arsenic in the instance where gallium arsenide is being evaporated.



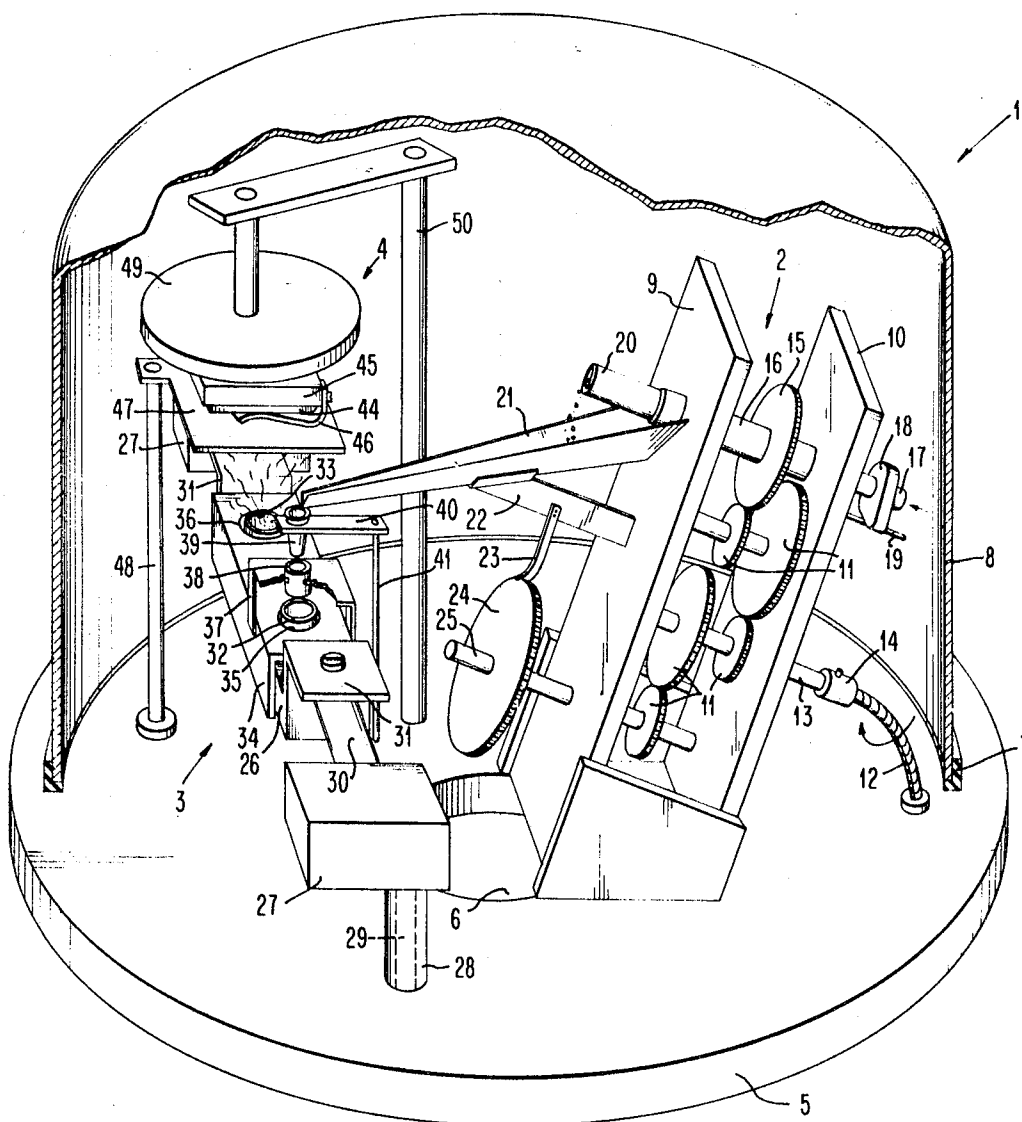


FIG. 1

INVENTORS

REINHARD K. GERETH
EDWARD M. HULL
THOMAS B. LIGHT

BY

Thomas B. Light
ATTORNEY

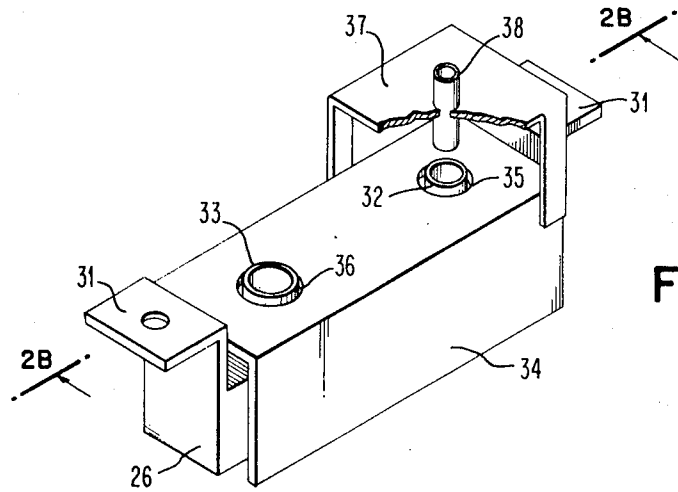


FIG. 2A

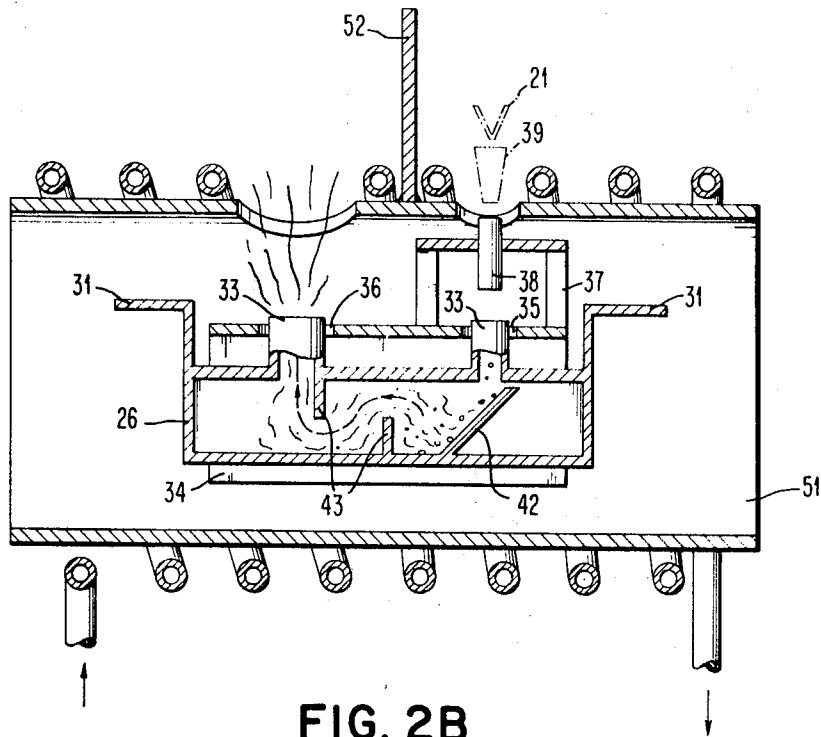


FIG. 2B

FLASH EVAPORATING GALLIUM ARSENIDE

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates generally to the vacuum evaporation of materials containing a number of constituents. More specifically, it relates to a method and apparatus for flash evaporating compounds physical mixtures and alloys for relatively long periods of time, at high feed rates, to provide thick, uniform films of the evaporated materials. The method and apparatus of the invention are utilized and designed to permit relatively long term evaporation without the formation of undesired deposits which can and often do clog the apparatus which feeds and collimates the evaporant material.

2. Description of the Prior Art

In the past, flash evaporation of materials such as compounds and chemical mixtures and alloys of materials has been accomplished quite successfully, but only where low feed rates, low evaporation times, and relatively thin films of the materials were required. Where thick films of such materials were desired, high feed rates of pelletized or powdered materials were required to accomplish deposition in a reasonable time. The use of high feed rates, though, led to the condensation of a constituent of the material or the collection of another constituent in certain regions of the feed tube causing clogging of the tube. To clear the tube, evaporation had to be halted and high temperatures generated in the region of the tube to cause vaporization of the clogged constituents thereby clearing the feed tube. This technique is unsatisfactory because it lengthens the time required for deposition, affects the uniformity of the resulting film, and subjects the apparatus to repeated temperature cycling which, in turn, affects the overall life of the evaporation apparatus.

In known instances, where flash evaporation is carried out at high feed rates, a box source heater is utilized in conjunction with a feed tube which is attached at its lower extremity to an aperture in the box source heater. The feed tube which may have a funnel portion is meant to collimate the feed material so that it enters the box source heater directly to ensure rapid film growth and lessen loss of material due to scattering. However, because the decomposition temperature or the melting temperature of at least one of the constituents is reached prior to entering the box source heater and within the feed tube, deposition of the melted constituent or the less volatile constituent, in the case of a compound like gallium arsenide, takes place on the walls of the tube. This deposited material acts as a constriction or a glue for incoming particles, catching them and, in a short time, causing a buildup of material which clogs the feed tube. Under conditions where the materials are made up of constituents which have substantially different vapor pressures, an additional source of clogging is present. Because the temperature gradient from the surface of the box source to the top of the feed tube is rather steep, temperatures lower than the condensation temperature of the more volatile constituent of the material are present. Upon evaporation in the box source heater, the more volatile constituent is able to pass upwardly through the feed tube and, at a point where the temperature gradient is below the condensation temperature, the more volatile constituent of the materials being evaporated condenses. Again, the condensed constituent acts as a constriction or a glue for the incoming material, and in a relatively short time, the feed tube is clogged. At this point, evaporation is halted and a temperature sufficient to vaporize the clogging materials must be applied to remove them from the feed tube.

In the instance where a single feed tube connected to the aperture of the box source heater is used, another effect is present which affects the flow of material into the box source heater. Upon vaporization of the material in the box source heater, a considerable back pressure is generated by the vaporized material which is partially relieved by the vaporized material (principally the more volatile constituent of the material) passing at considerable velocity back through the feed tube. The feed tube, in other words, acts as a chimney

having an up draft which impedes the downward flow of the particles being fed to the heater. This "chimney" effect, in conjunction with the other effects mentioned, contribute to the clogging problem. As indicated, hereinabove, the prior art approach extends the time of evaporation, adversely affects the composition of the ultimately deposited material, and subjects the total apparatus to temperature cycling which affects its overall life.

SUMMARY OF THE INVENTION

In its broadest aspect, the method of the present invention consists of positioning the material feed apparatus of a flash evaporation system within a temperature gradient which decreases with increasing distance from a box source heater such that at least the portion of the feed apparatus which is spaced from but closest to the heater is held at a temperature below the decomposition or melting temperature of the material or its constituents, but above the condensation temperature of the more volatile constituent of the material being evaporated.

In its broadest aspect, the apparatus of the present invention includes a material feed apparatus positioned within a temperature gradient which comprises at least two hollow members one of which is disposed within a higher temperature portion of the gradient and the other of which is disposed within a lower temperature portion of the gradient. The hollow members have at least facing portions which are in alignment are spaced from each other. The member disposed within the higher temperature gradient has a portion which is in alignment with an aperture in a box source heater and is spaced from said aperture to maintain the aligned portion at a temperature lower than that at the aperture.

In accordance with a more particular aspect of the invention, a process for flash evaporating thick films of a III-V compound, such as gallium arsenide is contemplated. A hollow tube is positioned within a temperature gradient provided by energizing a box source heater and spaced from the heater such that the temperature encountered by the tube is less than the decomposition temperature of the gallium arsenide (800° C.) but is greater than the condensation temperature of arsenic along the length of the tube. In addition, a coaxially disposed hollow tube is positioned vertically above and spaced from the tube disposed adjacent to the heater and in a temperature gradient which is below the condensation temperature of the arsenic. In addition to providing discrete members of a feed apparatus where desired temperature gradients can be maintained, the spacing of the various portions of the material feed apparatus act as diffusers or vents for the up-draft from box source heater thereby minimizing the effect of any up-draft on the feed material.

It is therefore an object of this invention to provide a process and apparatus which provides thick films of materials without clogging of the apparatus involved.

Another object is to provide a flash evaporation process and apparatus which is capable of depositing thick films of high resistivity.

Still another object is to provide a process and apparatus whereby material to be flash evaporated can be continuously fed at high rates to a heating element for extended times.

Yet another object is to provide a flash evaporation process and apparatus which is capable of producing thick monocrystalline films in addition to highly oriented polycrystalline films. Both the polycrystalline and monocrystalline films may be doped or undoped.

The foregoing and other objects, features and advantages of the invention will be apparent from the following more particular description of a preferred embodiment of the invention as illustrated in the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a partially cutaway perspective view of flash evaporation apparatus containing the novel material feed ap-

paratus with which the process of the present invention is practiced. FIG. 2A is a partially cutaway perspective view of a source box heater. The drawing shows the relative positions of the heater and the feed apparatus of the invention.

FIG. 2B is a cross-sectional view of the source box heater and feed apparatus taken along line 2B—2B of FIG. 2A which shows the internal arrangement of the box source heater and the relationship of a water jacket to the heater.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In accordance with the invention, FIG. 1 shows a partially cutaway perspective view of flash evaporation apparatus including material feed apparatus used to practice the method of this invention.

The flash evaporation apparatus of FIG. 1 may be utilized to flash evaporate any substance limited only by extremely high-temperature considerations. The present invention contemplates a somewhat more limited application in that the method and apparatus are adapted to optimally flash evaporate material such as physical or chemical mixtures and alloys. It should be understood, therefore, that hereinafter when the word material is used, it is intended to cover compounds and physical mixtures and alloys and that any specific material referred to is by way of example and is not to be construed as limiting the scope or application of the invention. In exemplifying this invention, gallium arsenide, a compound selected from the group known as III-V compounds, will be used to show the use of the apparatus and the method of practicing the invention.

Referring again to FIG. 1, a flash evaporation system 1 is shown. Flash evaporation system 1 consists of a material feed apparatus 2, heat generating apparatus 3 and substrate mounting and heating apparatus 4. These apparatuses are mounted on a baseplate 5 which contains an aperture 6 to which vacuum apparatus (not shown) is connected. A gasket 7 is fitted onto a bell jar 8 to maintain a low vacuum environment for system 1.

Considering now material feed apparatus 2, it consists of support members 9, 10 between which are supported a number of gears 11 which are arranged in the form of a train and driven by a flexible shaft 12 which extends through baseplate 5 to a variable speed motor (not shown). Shaft 12 is connected to a rigid shaft 13 by connector 14. Shaft 13 extends through support member 10 providing rotary motion to gears 11 of the gear train. Gear 15 is mounted on a tubular shaft 16 into which shaft 17 extends. The interior surface of shaft 16 and the exterior surface of shaft 17 are threaded such that the rotation of gear 15, causing the rotation of tubular shaft 16, causes shaft 17 to advance within shaft 16. Shaft 17 is prevented from rotation by a CAM 18 affixed to shaft 17 and a stop 19 which permits only translation of one shaft within the other. Shaft 16, which extends through support 19, has an extension 20 into which material to be flash evaporated is placed. As shaft 17 advances within hollow shaft 16, the material, in addition to being pushed out extension 20, in metered fashion, is tumbled to achieve good mixing and separation of the material. The material dropping from extension 20 is carried down trough 21 by gravity and by vibration of the trough 21. Vibration of trough 21 is accomplished by member 22 which extends cantilever fashion from the bottom of trough 21. A flexible element 23 is in turn affixed at one end to member 22 while the other end is disposed between the teeth of a gear 24 which is mounted on a shaft 25 to which is affixed another gear 11 and driven by the aforementioned gear train. Gear 25, when rotated, vibrates element 23 which in turn vibrates member 22 and trough 21.

Considering now, heat generating apparatus shown generally in FIG. 1 and in more detail in FIGS. 2A, 2B, a box source heater 26 is shown disposed between heat conducting copper blocks 27. Blocks 27 are supported by insulating bushing 28 through which pass conductors 29, the upper portions of which are screwed in blocks 27. Bushings 28 and conduc-

tors 29 pass through baseplate 5 to a source of power (not shown). Conductive rods 30 interconnect blocks 27 and tabs 31 on box source heater 26. Box source heater 26 has input and output tubulation, 32,33, respectively, attached to the upper surface thereof. Heat shield 34, containing apertures 35,36 which register with tubulation 32,33 respectively, surrounds box source heater 26. A bracket 37 containing an aperture into which guide tube 38 is inserted is mounted on heat shield 34 such that guide tube 38 is in registration with input tubulation 32. A guide funnel 39 moveably mounted in arm 40 which extends from vertical rod 41 is disposed coaxially with and spaced vertically from guide tube 38 such that particles of material from trough 21 pass into guide funnel 39 through guide tube 38 into box source heater 26. The particles of material to be evaporated, as shown clearly in FIG. 2B, enter box source heater from guide tube 38, pass through input tubulation 32 and strike a plate 42, disposed at a 45° angle, from which the particles bounce and vaporize. The vaporized material passes baffles 43 and exits from heater 26 through output tubulation 33 to substrate mounting and heating apparatus 4 which includes a substrate 44, which is mounted on a tantalum plate 45 by means of molybdenum clips 46, (see FIG. 1). A shutter 47 is shown in FIG. 1, mounted on a rotatable rod 48 which extends through baseplate 5 and is actuatable externally of system 1 to cut off deposition on substrate 44 at a desired thickness. Tantalum plate 45 is heated by radiation from tantalum coils (not shown) wound on fused quartz rods and is supported in position over output aperture 33 by radiation shield 49 which, in turn, is positioned by support structure 50.

In operation, system 1 is enclosed in bell jar 8 and evacuated through aperture 6 by a 6-inch oil diffusion pump (not shown). A liquid nitrogen cooled baffle prevents back streaming of pump oil and provides pressures around 10^{-10} torr in about an hour of pumping. Pressure in system 1 during evaporation rises to about 1×10^{-5} torr because of the large volume of gases released by heating of the finely divided evaporant material and, as a result, a pump of large capacity is required. Prior to evacuation, the material to be evaporated is loaded into tubular shaft 16 from which it is pushed by the actuation of threaded shaft 17. When gallium arsenide is to be evaporated to produce a thick film of semi-insulating gallium arsenide, powdered chromium doped gallium arsenide of 40–60 mesh size is placed in tubular shaft 16 and dropped from extension 20 in metered amounts into vibrating trough 21. To obtain gallium arsenide of stoichiometric composition, arsenic is added to the chromium doped gallium arsenide in a volumetric ratio of 1:1. To evaporate the gallium arsenide particles, sufficient power is applied to conductors 28 to raise the temperature of box source heater 26 to a temperature of 1325° C., a temperature above the gallium arsenide congruent melting point. Heat shield 34 acts to maintain the temperature substantially constant within box source heater 26. Also, excessive heating of the other portions of system 1 is prevented by the use of a water jacket 51 disposed as shown in FIG. 2B about heater 26. In spite of these efforts to minimize heating of other portions of system 1, a temperature gradient is established which extends from the surface of heat shield 34 in the region of input tubulation 32, and decreases with increasing distance from the surface of heat shield 34. Thus, from the point of view of an incoming particle, the particle encounters a first temperature zone in the region of guide funnel 39. This zone is not particularly critical except that in practice the lower extremity of funnel 39 does not exceed the condensation temperature of arsenic. The function of funnel 39 is to collimate the incoming particles of gallium arsenide and is preferably of smaller diameter than guide tube 38. Since the funnel 39 is spaced from guide tube 38 to electrically isolate it from the electrically energized heater 26, it is the first portion of the system which arsenic in vapor form encounters when vaporized arsenic, after evaporation of gallium arsenide and arsenic on plate 42, passes from heater 26 through tubulation 32, and guide tube 38. The spacing of funnel 39 from guide

tube 38 also serves to diffuse the updraft of arsenic vapor from heater 26. Because the lower extremity of funnel 39 is at a temperature lower than the condensation temperature, the arsenic tends to condense and build up at the lower extremity of funnel 39 without clogging during an evaporation cycle. Such deposits should be removed between evaporation cycles and removal of funnel 39 is facilitated by the slip-fit arrangement of funnel 39 in arm 40.

From the foregoing, it should be clear that the particles of gallium arsenide and arsenic are substantially unaffected in their passage through guide funnel 39 by the temperature gradient across funnel 39 or by any updraft. Arsenic vapor is, however, present and a temperature condition is created so that condensation can occur without interfering with the passage of the particles. Because arsenic is present in funnel 39, it follows that it is also present in guide tube 38. Since condensation of arsenic would occur within guide tube 38 and cause clogging if the temperature were low enough, the lowest permissible temperature encountered in guide tube 38 must be in excess of the condensation temperature of arsenic. Another condition obtains, however, which limits the highest acceptable temperature in guide tube 38. If the temperature anywhere within guide tube 38 were to exceed the decomposition temperature ($\sim 800^\circ\text{C}$.) of gallium arsenide, the gallium arsenide would decompose giving off arsenic vapor and leaving liquid gallium on the interior wall of guide tube 38. The liquid gallium would then act as a glue for incoming particles and clog tube 38 in a short time. Guide tube 38, therefore, must be held at a temperature which does not exceed the decomposition temperature of gallium arsenide. Thus, the temperature criteria for guide tube 38 are that the temperatures encountered must be greater than the condensation temperature of arsenic but less than the decomposition temperature of gallium arsenide. These conditions can be obtained by positioning guide tube 38 within the temperature gradient a small distance from the extremity of input tubulation 32 such that the first temperature encountered by the particles on passing through tube 38 is the temperature at input tubulation 32. This latter temperature is approximately $1,325^\circ\text{C}$. or above the congruent melting temperature of gallium arsenide. Again, the spacing between the extremity of tube 38 and input tubulation diffuses the updraft from heater 26 and minimizes its effect on the incoming particles.

In addition to arsenic vapor, gallium vapor can pass from heater 26, into guide tube 38, but the flux is insufficient to exceed nucleation conditions at guide tube 38, and a very thin layer of gallium arsenide which does not affect the operation of system 1 may build up. Guide tube 38 is preferably of smaller diameter than input tubulation 32 to ensure that the particles enter tubulation 32 and do not vaporize on heat shield 34.

The gallium arsenide particles upon touching plate 42, vaporize. The vapor passes baffles 43 and exits from heater 26 via output tubulation 33. The vapor then passes to substrate 44 which is maintained at a temperature below the decomposition temperature of gallium arsenide and deposits as a layer on substrate 44. In FIG. 2B, a shield 52 is shown mounted on water jacket 52, to prevent vapor exiting from output tubulation 33 from depositing on material feed apparatus 3. Depending on the thickness desired, evaporation may be carried on for various durations.

The following conditions are typical for flash evaporating gallium arsenide. Substrate 44 is either germanium or gallium arsenide.

Box source heater temperature	$1,325^\circ\text{C}$.
Substrate temperature	$525^\circ\text{--}600^\circ\text{C}$.
Rate of deposition	$0.05\text{--}0.15\mu\text{m}/\text{min}$.
Pressure during evaporation	$10^{15}\text{--}4\times 10^{16}$ torr
Source to substrate distance	10 cm.
Deposition time	90 minutes

The gallium arsenide deposition may have thicknesses which range from 5–50 microns. The resulting gallium arsenide layers may be highly oriented and semi-insulating (high resistivity) and may be either monocrystalline or polycrystalline. Flash evaporated layers having such characteristics are useful in the semiconductor art for isolating active devices while at the same time matching crystal lattices and coefficients of thermal expansion to a high degree. Various substrates such as chromium doped semi-insulating gallium arsenide having a (110) orientation, gallium arsenide having a (111) orientation and germanium having a (110) orientation have been successfully used in the practice of this invention. It should, however, be appreciated that any appropriate substrate may be used provide the material being evaporated is not incompatible with the substrate.

In the foregoing, no specific temperatures have been mentioned as the condensation temperature of arsenic during the flash evaporation of gallium arsenide because this temperature is dependent on a number of factors. The condensation temperature is dependent on: the condition of the surface within the guide tube and the amount of flux necessary to achieve nucleation conditions. In the example given above, a temperature of approximately 350°C . was sufficient to prevent condensation on guide tube 38 but, it should be appreciated that in other systems and under different circumstances this temperature may vary widely.

From the foregoing, it should be apparent that the method and apparatus of the present invention are not limited to use with gallium arsenide or to other III–V compounds, but are broadly applicable for use with any compound, physical mixture or alloy. Thus, where a physical mixture is used and it is desired to flash evaporate the constituents thereof, the criteria to be observed are that guide tube 38 be held below the melting temperature of all the constituents of the mixture but in excess of the condensation temperature of the more volatile of the constituents.

Thus, depending on the temperature of the box source heater, the position of guide tube 38 may be spaced from the box source heater so that melting temperatures of the constituents occur in the space between the box source heater and guide tube 38.

All the parts of the apparatus shown are fabricated from refractory metals or other refractory materials which are heat resistant.

The present apparatus and method find preferential application where the vapor pressures of the constituents of the material being evaporated are substantially different.

While the invention has been particularly shown and described with reference to a preferred embodiment thereof, it will be understood by those skilled in the art that the foregoing and other changes in form and details may be made therein without departing from the spirit of the invention.

What is claimed is:

1 A method for flash evaporating gallium arsenide in evaporation apparatus having a box source heater comprising the step of:

providing gallium arsenide and arsenic in particulated form, introducing said gallium arsenide and arsenic into a guide funnel and guide tube the latter being disposed within a temperature gradient such that it has a minimum temperature in excess of the condensation temperature of arsenic and a maximum temperature which is less than the decomposition temperature of gallium arsenide, evaporating said gallium arsenide and arsenic in said box source heater at at least the melting temperature of gallium arsenide to form a vapor of gallium arsenide and arsenic,

depositing said vapor on a substrate said substrate being at a temperature below the melting temperature of gallium arsenide to form a layer of gallium arsenide having a stoichiometric composition.

2. A method according to claim 1 wherein said minimum temperature is approximately 350°C . and said maximum temperature is approximately 800°C .