United States Patent

[111] 3,603,285

[72] Inventor **William S. Nicol**
Highcliffe, England

[21] Appl. No. **773,530**
[22] Filed **Nov. 5, 1968**
[45] Patented **Sept. 7, 1971**

[73] Assignee **Massachusetts Institute of Technology**
Cambridge, Mass.

---

[54] **VAPOR DEPOSITION APPARATUS**
3 Claims, 1 Drawing Fig.

[52] **U.S. Cl.** **118/48**
[51] **Int. Cl.** **C23c 11/00**
[50] **Field of Search** 118/48–49.5; 117/106–107.2; 148/174, 175

[56] **References Cited**

UNITED STATES PATENTS

2,767,682	10/1956	Smith	118/49
2,768,098	10/1956	Hoppe	118/49 X
2,938,816	5/1960	Gunther	118/49 X
2,945,771	7/1960	Mansfeld	118/49 X
3,446,936	5/1969	Hanson et al.	118/49.1 X

FOREIGN PATENTS

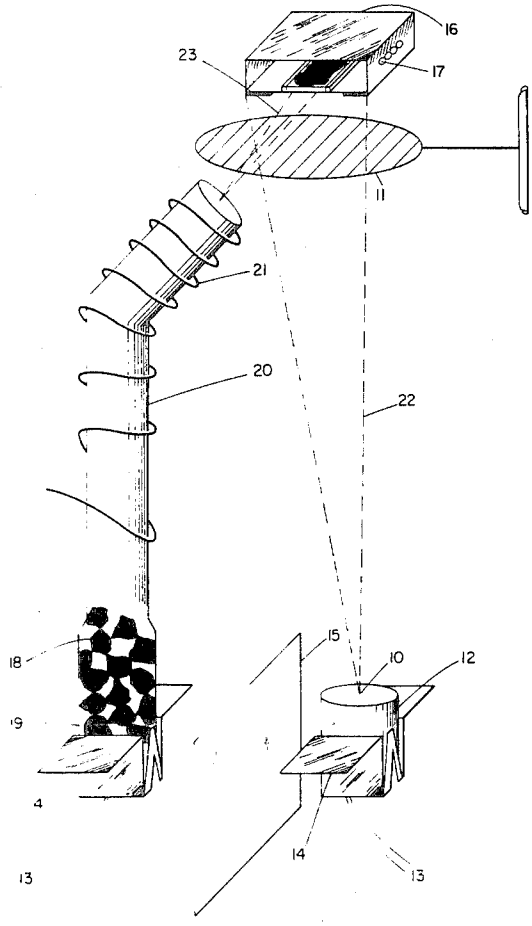
766,119	1/1957	Great Britain	118/49
813,252	5/1959	Great Britain	118/49

OTHER REFERENCES

IBM Technical Disclosure Bulletin, " RF Heated Crucible For Aluminum Evaporation," Ames & Kaplan, Vol. 6 No. 8 Jan. 1964, Copy in 118–49.1

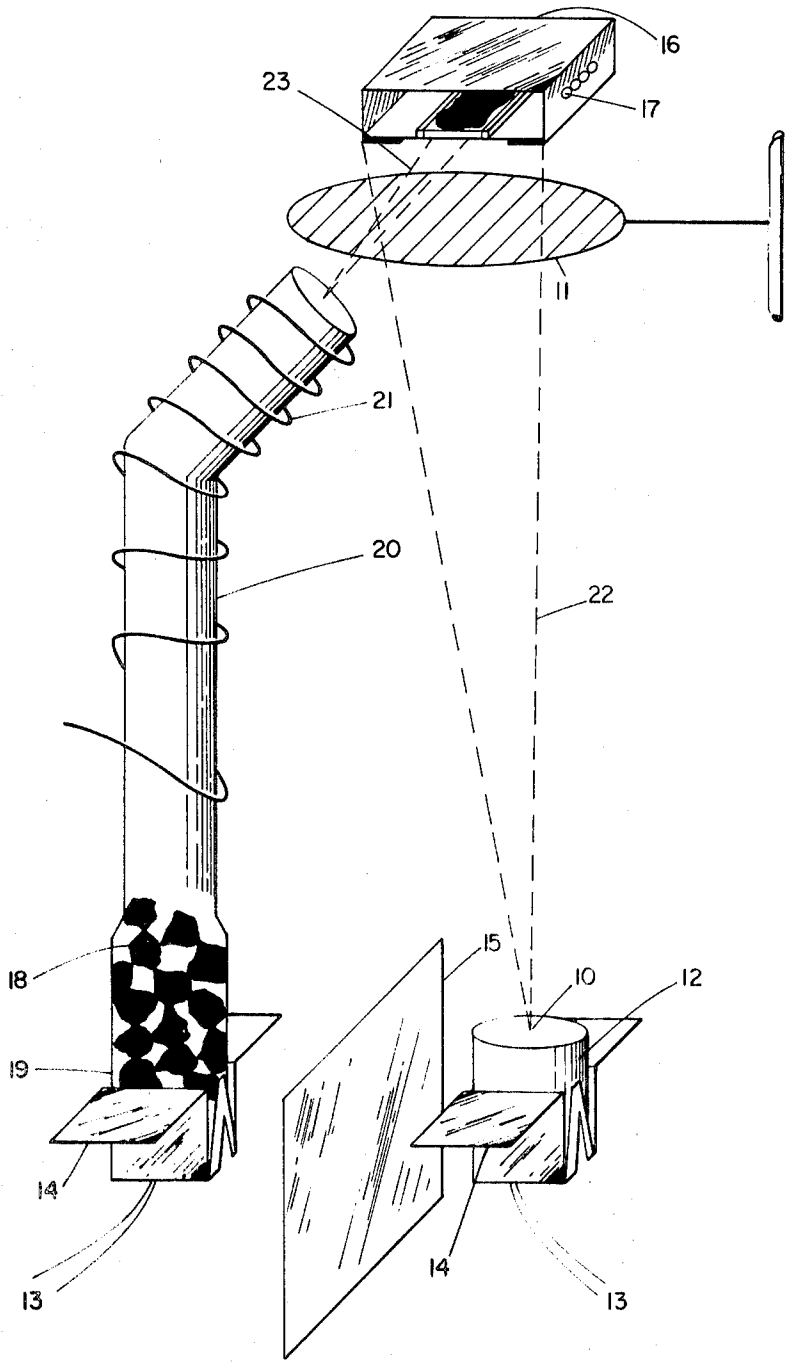
Primary Examiner—Morris Kaplan
Attorneys—Thomas Cooch, Martin M. Santa and Robert Shaw

ABSTRACT: Vapor deposition means include at least two crucibles adapted to contain evaporant materials of different volatilities and which are disposed to each form a vapor stream of uniform density and incident upon a common substrate. A chimney member having an exit disposed in the immediate vicinity of the substrate but outside of the vapor stream of the less volatile material is attached to the crucible containing the material of greater volatility.



PATENTED SEP 7 1971

3,603,285



INVENTOR
WILLIAM S NICOL
BY
ATTORNEY

VAPOR DEPOSITION APPARATUS

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of section 305 of the National Aeronautics and Space Act of 1958, Public Law 85—568 (72 Stat. 435; 42 U.S.C. 2457).

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to the production of thin layers of coatings from semiconducting substances. It particularly relates to apparatus for the coevaporation of binary compound semiconductors, AB, composed of an element, A, and a more volatile element, B, which are evaporated from two sources containing the elements A and B separately.

2. Description of the Prior Art

Former methods of two-source evaporation (also referred to as a "three-temperature" or "three-zone" method—the three temperatures being those of the two sources and the substrate temperature) are generally based on U.S. Pat. No. 2,938,816 by K G. Gunther. Gunther's method uses two separate sources at the same distance from the substrate. Others known to have used a technique of two-source evaporation are:

1. Davey, J. E. and Pankey, T., "Structural and Optical Characteristics of Thin GaAs Films," JOURNAL OF APPLIED PHYSICS, Vol. 35, No. 7, July 1964, p. 2203.

2. Potter, R. F., "Optical Properties of Multisource Thermally Evaporated III–V Semiconductor Compounds," APPLIED OPTICS, Vol. 5, No. 1, Jan. 1966, p. 35.

3. Steinberg, R. F., and Scruggs, D. M., "Preparation of Epitaxial GaAs Films by Vacuum Evaporation of the Elements," JOURNAL OF APPLIED PHYSICS, Vol. 37, No. 12, Nov. 1966, p. 4586.

4. Gunther, K. G., "Vacuum Deposited Lyers of Semiconducting III–V. Compounds," NATURWISS, Vol. 45, (1958) p. 415.

5. Howson, R. P., "Infrared Filters of Evaporated Gallium Arsenide," JOURNAL OF THE OPTICAL SOCIETY OF AMERICA Vol. 55, (1965) p. 271.

The first of these references uses evaporation inside an evacuated closed tube, instead of a conventional vacuum bell jar evaporation system. The others follow Gunther's method.

For deposition of the stoichiometric compound, it is necessary that the more volatile element, B, have a much higher impinging rate at the substrate, since this element generally has a lower condensation coefficient at elevated substrate temperatures. To obtain uniformly thick films over a large area with point or small area evaporation sources, it is necessary to keep a large source-to-substrate distance. However, prolonged evaporation, in which the source crucibles for the two elements are placed at the same distance from the substrate, has the disadvantage of requiring the evaporation of relatively large amounts of the more volatile element. An object of this invention is to overcome this difficulty by providing for vacuum evaporation apparatus that effectively places the source of the more volatile element close to the substrate.

SUMMARY

In the present invention the evaporating beams of elements A and B are kept separate until they reach the vicinity of the substrate. By having a long source tube for element B and heating the wall of this tube to prevent deposition of element B on it, the position of the crucible containing element B is in effect placed close to the substrate. Although the cross-sectional area of the impinging beam of element B is smaller than the substrate area, the method of coevaporation in this arrangement is essentially the evaporation of element A onto a substrate uniformly covered with element B. This is a reasonable assumption since at elevated substrate temperatures (300° C. to 600° C.), element B has an extremely high surface mobility. For a thickness uniformity of gallium arsenide films to within ±5 percent over a distance, d, from the center of a substrate, which is placed at a height, h, above the gallium source, a distance $d=0.1h$ is required assuming a small area source. By arranging a gallium source-to-substrate distance of at least 25 cm., films have been prepared which are uniformly thick to within 5 percent over 7.5 cm.×2.5 cm. substrates.

The method is based on the experimental observation that only the source-to-substrate geometry of the less volatile element, element A, besides uniformity of substrate temperature, is important in determining the thickness distribution over a substrate. The beam direction and cross section of element B are relatively unimportant. These observations have led to the novel feature of placing the element B source tube exit close to the substrate while the element A source remains relatively distant.

It is an object of the invention to evaporate onto the substrate covered by the less volatile element uniformly thick films of binary compounds that are most conveniently evaporated from two sources, the films being fabricated over large area substrates or on arrays of several substrates simultaneously.

It is a further object of the invention to have a much higher impinging rate at the substrate for the element B by directing a restricted beam onto the substrate, the directed beam causing a saving in the amount of the more volatile element evaporated.

It is a further object to coevaporate ternary compounds such as GdGaAs by directing restricted beams for those elements having high surface mobility.

It is a feature of the invention that continuous evaporation of larger amounts of element B can be obtained by storing it in the source tube, element B falling down the source tube to the region where element B is vaporized.

It is a still further feature that the heaters for the elements A and B can be placed relatively distant from the substrate so that radiation heating of the substrate by the crucible heaters is minimized. This is also convenient, in conventional evaporation technique, for allowing the sources to be mounted on a movable source holder, so that sequential depositions of other films can be made.

It is a still further feature that relatively large amounts of element B can be stored for prolonged depositions of the compound AB.

Other objects and a fuller understanding of the invention may be had by referring to the following description and claims, taken in conjunction with the accompanying drawing.

BRIEF DESCRIPTION OF THE DRAWING

The drawing illustrates the crucible arrangements for two-source vacuum evaporation of thin films of uniform thickness..

DESCRIPTION OF PREFERRED EMBODIMENT

In the drawing, element A **10** is evaporated from a crucible source **12**. A thermocouple is inserted into a thermocouple insert **13** provided for the bottom of crucible **12**. Crucible **12** is directly heated by a tantalum ribbon heater **14** surrounded by a tantalum radiation shield **15** to isolate the sources from one another. The substrate is heated to an elevated temperature by placing it in an oven **16** containing an array of heated ceramic tubes **17**. The elevated substrate temperature is required to provide stoichiometry of the final film as specified in U.S. Pat. No. 2,938,816. Element B **18**, used in lump form to minimize oxidation, is evaporated from a source consisting of a crucible **19** and a tube **20** connected to crucible **19**, crucible **19** being wider than tube **20** to allow element B to surround a thermocouple insert in the bottom of crucible **19**. A thermocouple is inserted into the thermocouple insert **13**. The exit part of tube **20** is directed toward the center of the substrate, the exit being as close to the substrate as possible without getting into the path of beam **22**. Crucible **19** directly heated by a tantalum ribbon heater similar to that used to heat element A source. Tube **20** is heated by a helical coil of wire **21**,

preferably tungsten, to a temperature which is below the element B evaporation temperature and above that at which element B will condense on the tube walls or on the element B contained in the tube. Should this occur, condensed element B peels off in flakes which evaporate rapidly thereby spattering the film. Shutter **11** is used to prevent deposition during the time required to stabilize the element A and element B source temperature the element A and element B sources being located within a conventional vacuum bell jar. Element A will evaporate onto the substrate uniformly covered with element B thereby forming a film of the compound AB over that portion of the substrate covered by element A, the film being uniformly thick to a percentage determined by the distance between crucible **12** and the substrate. This is different from the teaching of Gunther wherein the film is shown to be formed only over the areas overlapped by the beams from elements A and B.

It was experimentally observed that the diameter of the exit tube need not be as large as the dimensions of the substrate to produce a uniformly thick layer of film. It was also observed that the incidence angle of the element B beam **23** had no effect on the thickness uniformity of the deposited film. In other words, the thickness uniformity of the final film is calculated from the distance from crucible **12** to the substrate. These observations were advantageously utilized by placing the element B source tube exit close to the substrate while the element A source remains relatively distant. Such an arrangement results in a significant savings in the amount of the more volatile element, element B, that is evaporated. The use of tube **20**, in addition to containing large quantities of material if required, allows element B, used in lump form, to fall continuously into the base of the crucible as evaporation takes place. It is unnecessary to baffle tube **20**, for example, by a quartz wool plug as has been suggested in the prior art. If the source temperatures are increased in an attempt to increase the deposition rate, too great an element B evaporation rate has been found to obstruct the element A deposition. To prevent oxidation of element B when the vacuum system is open to the atmosphere, the exit tube is stoppered.

Uniformity of substrate temperature, also important in the preparation of uniformly thick films, is assured by placing the substrate in an oven preferably containing an array of heated ceramic tubes or in a standard substrate oven.

By placing the two crucible heaters on a rotatable source holder, multiple evaporations of films, metal electrodes and dopant materials may be made. Through having a large source-substrate distance, film doping can be controlled with reasonably large amounts of dopant being evaporated.

The above described apparatus and method may be used to evaporate onto a substrate uniformly thick films of those binary compound semiconductors, AB, composed of elements A and B, which, because of the tendency of the compound AB to dissociate when heated, are most conveniently evaporated from two sources containing the elements A and B separately.

Ternary compounds such as cadmium gallium arsenide can also be coevaporated by using one or more source tubes for those elements having high surface mobility.

EXAMPLE

Gallium arsenide films may be prepared which are uniformly thick to within 5 percent over 7.5 cm.×2.5 cm. substrates as follows:

Gallium, which is placed **26** cm. below the substrate, is evaporated from a boron nitride crucible **12** whose diameter and height is 1.27 cm. The crucible is heated to between 940° C. and 980° C. by a 0.125 mm.-thick tantalum ribbon heater. The substrate is heated to between 300° C. and 500° C. Arsenic, used in lump form or powdered form, is evaporated from a 16 mm. OD quartz source tube **20** having lengths of 17 cm. and 5.5 cm. The base of the arsenic source tube is a 4 cm. length of 20 mm. OD quartz to allow the arsenic to surround a 15 mm. deep thermocouple insert. The exit of the arsenic source tube is 6 cm. from the center of the substrate. The arsenic quartz crucible **19** is heated to approximately 300° C. The arsenic source tube is heated to a temperature of approximately 150° C. which is below the arsenic evaporation temperature and above that at which arsenic will condense on the tube walls or on the arsenic contained in the tube.

Obviously, many modifications and variations of the present invention are possible in the light of the above teachings. It is, therefore, to be understood that within the scope of the appended claims the invention may be practiced other than as specifically described.

What is claimed is:

1. Apparatus for producing a thin layer of a compound semiconductor film on a substrate whose components, in molten condition, have different vapor pressures comprising:

a. an oven including a substrate support therein and capable of maintaining the temperature of said substrate at a uniform selected temperature,

b. a first crucible for containing the less volatile component,

c. means for heating said crucible and maintaining its temperature above that of the melting point of the less volatile component to produce a vapor beam,

d. said first crucible being sufficiently far removed from said substrate support to provide a substantially uniform density of its vapor impinging on said substrate,

e. a second crucible for containing the more volatile component of the compound,

f. means for heating said crucible and maintaining its temperature above that of the melting point of the more volatile component to produce vapor of said component,

g. said second crucible being removed from said substrate support to thermally isolate said second crucible and said substrate support,

h. a tube attached to said second crucible for confining the vapor of the more volatile component,

i. said tube having its exit located in the immediate vicinity of the substrate support to provide a vapor beam incident upon the supported substrate,

j. said tube also being outside the beam of the less volatile component impinging on the supported substrate to eliminate interference therewith.

2. The apparatus of claim **1** wherein said tube is heated to a temperature below that of the more volatile element evaporation temperature and above that at which the element will condense on the tube walls.

3. Apparatus as recited in claim **1**, wherein the exit of the tube has a diameter smaller than the dimensions of the substrate.