Feb. 16, 1971 SHINYA IIDA ET AL 3,563,816

METHOD FOR THE VAPOR GROWTH OF SEMICONDUCTORS

Filed March 31, 1966

FIG. 1a

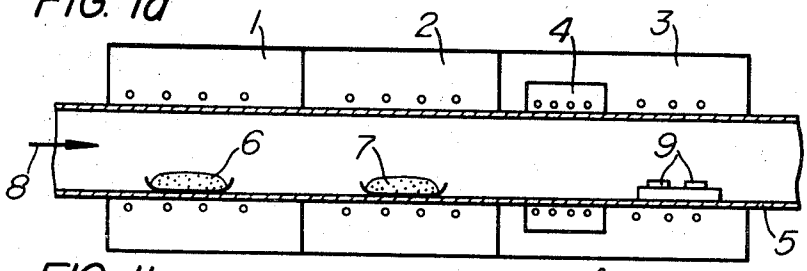


FIG. 1b

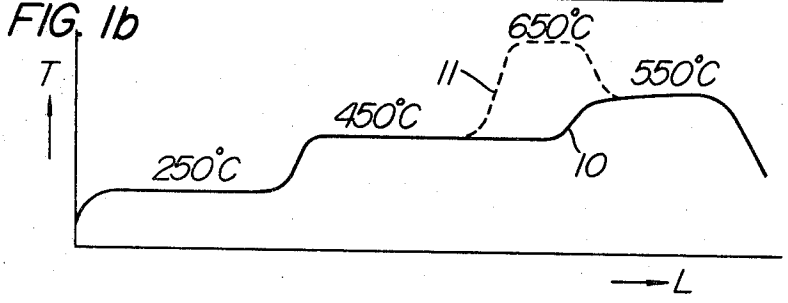


FIG. 2a

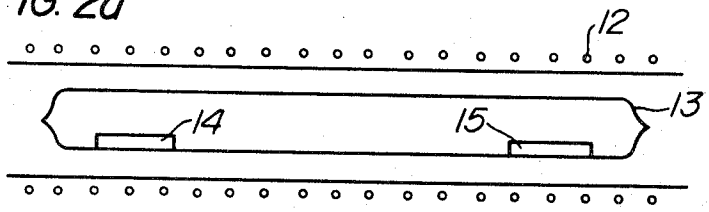
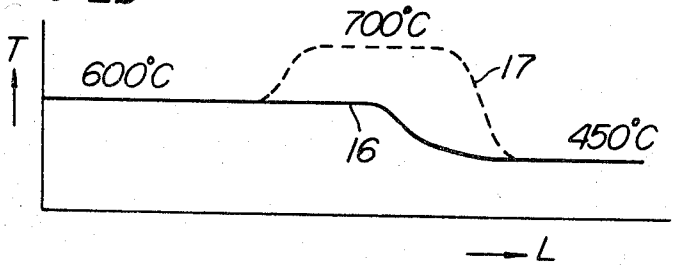


FIG. 2b



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METHOD FOR THE VAPOR GROWTH OF SEMICONDUCTORS

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Int. Cl. H01l 7/36
U.S. Cl. 148—175 2 Claims

ABSTRACT OF THE DISCLOSURE

A layer of semiconductor material is grown on a seed crystal by utilizing a gaseous reaction, wherein a gaseous source material at an initial temperature of T_1 is heated to a higher temperature, T_2, upstream from the seed crystal, and then transported downstream onto the seed crystal which is maintained at a temperature lower than T_2.

This invention relates to a method for the vapor growth of semiconductors and more particularly to a novel and improved method of the type described in which vapor growth of semiconductors is attained by the disproportionation reaction.

Conventional methods commonly employed for the vapor growth of semiconductors include a closed tube method in which a halogen such as iodine, a single crystal seed of semiconductor and a source crystal of semiconductor are enclosed in a closed tube and heat is applied thereto so as to cause the source semiconductor to epitaxially grow on the seed crystal by means of a disproportionation reaction, and an open tube method in which a semiconductor halogenide such as $SiCl_4$ or $GeCl_4$ entrained on a hydrogen stream is supplied in gaseous form onto a single crystal seed of semiconductor so that the semiconductor halogenide is reduced by hydrogen in the vicinity of the seed crystal to thereby cause epitaxial growth of the semiconductor on the seed crystal.

However, this closed tube method, that is, the disproportionation reaction method is not suitable for mass produtcion due to the fact that it relies on the closed tube, and thus its application is still limited to experiments in laboratories due to the fact that the rate of vapor growth is considerably low. The prior closed tube method has also been defective in that the purity of the vapor growth layer of semiconductor so obtained is greatly affected by the purity of the source material and the transport gas such as iodine gas and thus it is considerably difficult to obtain a vapor growth layer of high purity. While the open tube method, that is, the method of reduction of semiconductor halogenides by hydrogen has been satisfactory in respect of the rate of vapor growth, considerably higher temperature of the substrate crystal than in the case of the closed tube method has resulted in disadvantages that impurities from the substrate crystal enter the vapor growth layer by the autodoping effect, or other impurities existing in the system than those impurities described above diffuse into the vapor growth layer, or these impurities are adsorbed on the substrate surface or the vapor growth layer surface so that the perfectness of the vapor growth layer may be lost and the impurity distribution may be degraded. In view of the above problems, the substrate temperature is desirably as low as possible. In an attempt to solve the above difficulties, a method has been proposed according to which infrared rays or ultra-violet rays are directed onto such substrate.

The primary object of the present invention is to

provide a novel and improved method for the vapor growth of semiconductors by which the rate of growth of a vapor growth semiconductor layer can be extremely accelerated in spite of a reaction at low temperatures.

Another object of the present invention is to provide a novel and convenient method for the vapor growth of semiconductors by which the above-described prior problems can be solved without requiring any new additional apparatus.

Basically the present invention contemplates the provision of a method in which, while a source material is being transported onto a seed single crystal by means of a transport gas such as iodine gas, in the case of a closed tube method, or hydrogen gas, in the case of an open tube method, the source material in gaseous form is suitably heated to a state in which it is easily reactable with the seed single crystal.

According to the present invention, there is provided a method for the vapor growth of semiconductors by the utilization of a disproportionation reaction, comprising establishing a high temperature region intermediate between a source material and a seed crystal, said region having a temperature higher than those of said source material and said seed crystal.

The method according to the present invention is quite advantageous in that the rate of growth is remarkably higher than with the prior methods of vapor growth and yet the temperature of a seed crystal need not be made correspondingly higher but can rather be made lower than in the prior methods. This lower temperature of vapor growth layer deposition leads to an advantage of less contamination of the vapor growth layer with impurities. In other words, lower substrate temperature reduces the possibility of occurrence of such phenomena as auto-doping and diffusion of impurities and thus admission of impurities into the vapor growth layer can be avoided. According to results of observation by the inventors, the perfectness, that is, the freedom from defects and the likes, of the vapor growth layer is rather improved owing to the fact that reaction is accelerated in spite of lower substrate temperatures than with the prior methods.

A few preferred embodiments of the present invention will be described hereunder with reference to the drawings so that the invention can more fully be understood.

In the accompanying drawings:

FIG. 1 is a schematic explanatory view showing how a vapor growth layer of semiconductors is obtained according to the invention by a disproportionation reaction by use of an open tube, in which *a* is an enlarged longitudinal sectional view of part of an open-ended reaction tube and *b* is a graphic illustration of temperature distribution across the tube; and

FIG. 2 is a schematic explanatory view showing how a vapor growth layer of semiconductors is obtained according to the invention by a disproportionation reaction by use of a closed tube, in which *a* is an enlarged longitudinal sectional view of a closed reaction tube and *b* is a graphic illustration of temperature distribution across the tube.

Referring first too FIG. 1, there is shown the basic principle for manufacturing a vapor growth layer of GaAs by means of a disproportionation reaction by use of an open tube. In FIG. 1, electric furnaces **1**, **2**, **3** and **4** surrounded a reaction tube **5** of material such as quartz. In the quartz reaction tube **5**, a suitable mass of gallium iodide **6**, a suitable mass of arsenic **7** and seed crystal plates or substrates of GaAs **9** are disposed at positions as shown. When now temperatures in the quartz reaction tube **5** are controlled to have a temperature distribution as shown by a curve **10** in FIG. 1*b* and a stream of hy-

drogen gas **8** is passed through the quartz tube **5**, epitaxial growth of GaAs takes place on the seed crystal substrates **9**. The rate of growth in this case was 2 to 5μ per hours. This rate of growth could however be increased to 10 to 12μ per hour when a high temperature region at 650° C. as shown by a dotted curve **11** was established before the GaAs single crystal substrates **9** in accordance with the present invention.

FIG. 2 shows the basic principle for the vapor growth of a germanium crystal by means of a disproportionation reaction by use of a closed tube. In FIG. 2, a heater **12** surrounds a closed-ended tube **13** of material such as quartz. In this quartz tube **13**, 5 milligrams per cc. of iodine, a source crystal of germanium **14** and a seed crystal of germanium **15** are enclosed. At a temperature distribution in the quartz tube **13** as shown by a curve **16** in FIG. 2*b*, the rate of epitaxial growth of germanium on the surface of the seed crystal **15** was of the order of 5μ per hour. When however a high temperature region at 700° C. as shown by a dotted curve **17** is provided intermediate between the source crystal **14** and the seed crystal **15** in accordance with the present invention, the rate of growth of the epitaxial growth layer could be increased to a value of the order of 8μ per hour. According to the method of the present invention, a single crystalline vapor growth layer could be obtained with a seed crystal temperature of less than 350° C., whereas a polycrystalline vapor growth layer could solely be obtained with a seed crystal temperature of less than 350° C. when the intermediate region at high temperature as described above was not provided.

What is claimed is:

1. A method of producing a vapor growth layer of germanium on a seed crystal by the use of a disproportionation reaction in a closed reaction tube, wherein iodine is employed as the transport gas, which comprises:

spacing a germanium source crystal and a seed crystal near opposing ends of said closed reaction tube; and

heating a portion of said closed tube between said source crystal and said seed crystal to increase the temperature of the germanium laden transport gas within said portion to a temperature higher than the temperature of both said source and said seed crystal.

2. A method of producing a vapor growth layer of germanium according to claim **1**, wherein the temperature of said source crystal is about 600° C. the temperature of said seed crystal is about 450° C. and the temperature of the germanium laden transport gas in said portion of said reaction tube between said source and said seed crystal is about 700° C.

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