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[54] **VAPOUR-PHASE DEPOSITION METHOD**

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[51] **Int. Cl.**[2] **C23C 11/00**

[58] **Field of Search** ..... 117/106 R, 106 A, 107.2 R, 117/201; 118/48, 49, 49.1, 49.5, 500

[56] **References Cited**

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3,409,483	11/1968	Watson	148/175
3,678,893	7/1972	Bell	118/500
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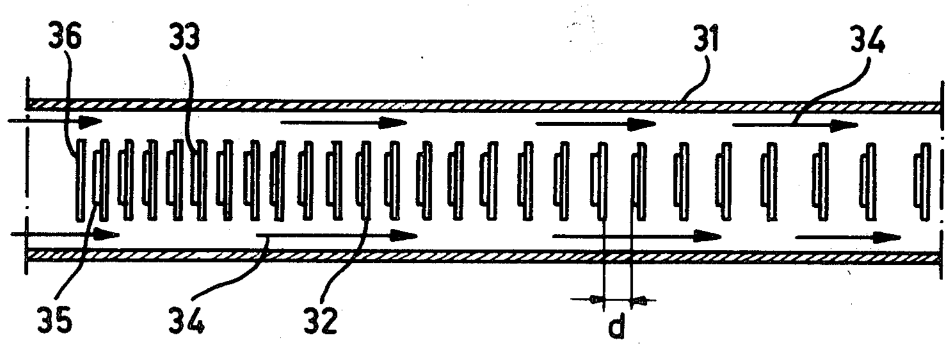
[57] **ABSTRACT**

A method of forming a deposit from a gas mixture on a large number of flat substrates in a tubular space.

The substrates are arranged along the gas flow with increasing spaces between substrates from the substrate reached first by the mixture to the substrate reached last by the mixture.

Application to the epitaxial deposition of semiconductor compounds.

6 Claims, 5 Drawing Figures



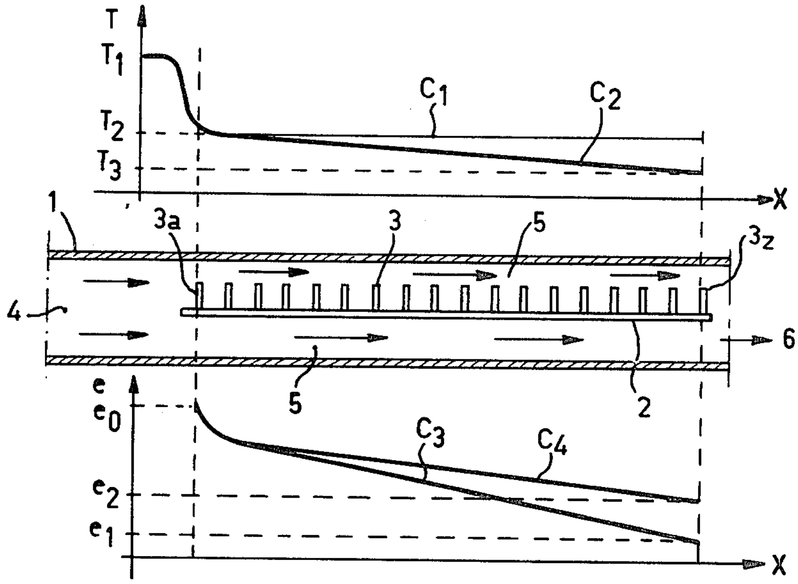


Fig.1

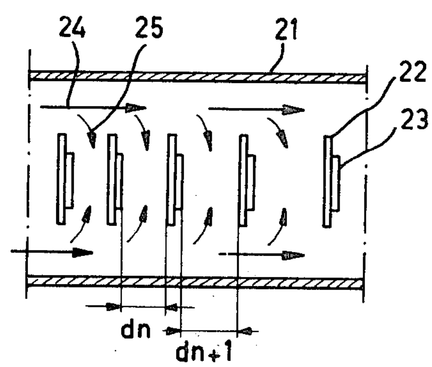


Fig. 2

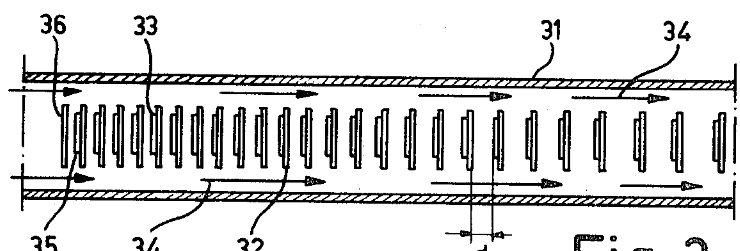


Fig.3

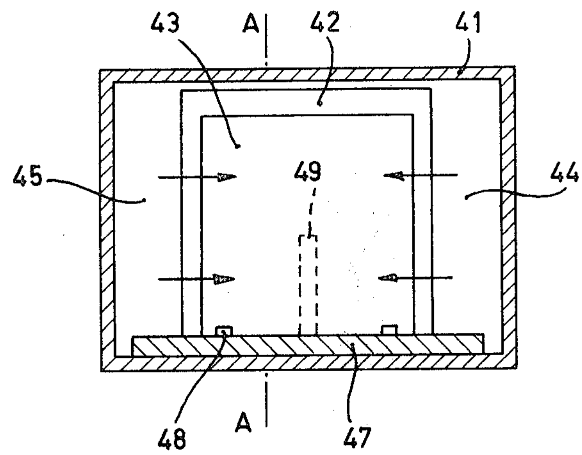


Fig. 4

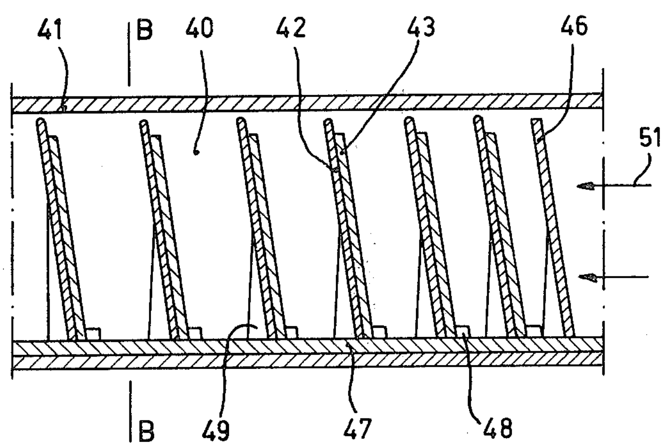


Fig. 5

VAPOUR-PHASE DEPOSITION METHOD

The present invention relates to a method of forming a deposit on a large number of flat substrates at a given temperature, according to which method the said substrates are provided in a zone of a tubular space, after which a gas mixture which contains the elements to be deposited and the temperature of which is higher than that of the said zone is conveyed into the said space in the direction of the substrates.

For depositing an epitaxial layer, for example, of semi-conductor material, on a suitable substrate from elements in the vapour phase, a shift of the equilibrium of a chemical reaction is usually employed: a gas mixture which is chemically stable at a temperature T_1 is passed over the substrate at a temperature T_2 which is lower than T_1. The reaction which the deposition causes upon contact of the substrate is very slow. Taking into account the small gas flow, the consumption of reacting elements is not negligible and is in particular much larger than during a diffusion operation, for example, that of a doping element in a semiconductor substrate in which the quantity of material actually diffused in the substrate is comparatively small.

When for series production the deposition operation is simultaneously carried out on the largest possible number of substrates, the latter should be provided in the same space and a gas flow with the elements should be conveyed over each of the substrates. If the substrates are provided parallel to the gas flow and are reached successively by the latter which flows laminarly over the receiving surfaces, the gas mixture gradually depletes in reaction elements and the thickness of the deposit decreases from the substrate which is nearest to the inlet of the reaction gas to the substrate which is farthest remote. It has been endeavoured to correct the effect of said depletion by means of a temperature gradient along the track of the gas flow. However, the possibilities of correction are restricted by the kinetics of the reaction, the gradient is difficult to maintain and involves a variation of the composition of the deposit and/or of a possible concentration of doping impurities when a doped semiconductor in concerned.

If the substrates have been provided in the form of a corn ear, either at right angles to the gas flow, or with a certain inclination in one direction or in the other, the drawback of the depletion of the gas flow of reaction elements has not been removed even in the case in which the support which is used for holding the substrates is in the form of a grating as is described, for example, in the U.S. Pat. No. 3,678,893, according to which the receiving surface of the substrates is directed downwards and opposite to the inlet of the gas flow; the substrates placed near the inlet of the reaction gas see their deposit grow more rapidly than that of the substrates which are farther remote from said inlet.

It is the object of the present invention to mitigate this drawback of the known method and to make it possible to obtain deposits of substantially the same thickness and quality on a larger number of substrates.

Another object of the invention is the compensation of the depletion of reaction elements of a gas flow which is used on a series of substrates placed along said flow, so as to obtain the same effect on said different substrates.

Another object of the invention is to obtain an epitaxial deposit of a thickness between certain tolerance limits on an assembly of crystalline substrates starting from elements in the gaseous phase.

According to the invention, the method of forming a deposit on a large number of flat substrates at a given temperature, according to which method the said substrates are provided in a zone of a tubular space, after which a gas mixture containing the elements which serve to be deposited and the temperature of which is higher than that of the said zone is conveyed into the said space in the direction of the said substrates, is characterized in that the said substrates are placed in such manner in places along the track of the gas mixture in the said space that the successive distances between adjacent substrates increase from the first substrate which is reached by the gas flow to the substrate which is nearest to the point of removal of the said flow.

The substrates are present laterally relative to the gas flow which forms the mixture in the tubular space and are not reached directly by said mixture; by diffusion from the said gas flow, the components of the mixture with the elements to be deposited can reach the receiving surfaces. The velocity of said diffusion is a function of various factors which depend on the gas flow itself and also on the intermediate space between the substrates. Applicants have found that the reaction rate and consequently the rate of deposition on a substrate was more rapid according as the intermediate space between said substrate and the adjacent substrate was larger. The gas mixture which supplies the elements to be deposited diffuses in the spaces between the substrates and depletes along the track thereof in the space due to the consumption of elements forming the deposit: the increase of the intermediate space between the substrates varies the diffusion circumstances and has for its object to compensate for the consequences of said depletion. The rates of deposition of the various substrates reach an equilibrium, the resulting thicknesses of deposition are substantially the same after a certain time.

The substrates generally consist of small plates which usually are rectangular or circular. Said substrates may have a small diameter or a less regular shape or dimensions differing from each other. Irrespective of the dimensions and the shape of the substrates, the diffusion effect of the gas flow is preferably ensured by securing each of the substrates on a support which is flat and thin and the surface of which exceeds that of the substrate and which is manufactured from a material on which the deposit cannot be effected chemically. Said supports mutually determine a succession of diffusion volumes in which the substrates are placed. The diffusion effect and the influence of the mutual distance between the substrates or the supports are thus used in the best of circumstances.

When the velocity of the gas flow is high, the danger is to be avoided of obtaining a difference in thickness, in deposition quality, between the substrates whose surface would be directed in the direction of flow of the gas mixture and of the substrates whose surface would be directed in the opposite direction. This danger is avoided by directing all the substrates in the same direction and by securing the substrates only to one face of each support when supports are used. The substrates are provided, for example, in such manner that their receiving surface is present opposite to the supply direction of the gas flow in the space. In this case no substrate is placed on the first support present opposite to the inlet of the gas mixture: this support serves as a screen.

In a preferred embodiment of the invention the tubular space in which the substrates are provided and into which the gas mixture is conveyed has a substantially rectangular cross-section and the substrate supports are also rectangular and placed in such manner that two symmetrical gas flows are formed of substantially identical rectangular cross-section; the diffusion occurs from said flow in two concurrent directions, which reduces the possible differences in deposition thickness on the same substrate.

In another embodiment of the invention the tubular space in which the substrates are placed and into which the gas mixture is conveyed has a circular cross-section and the substrates and supports are placed in the axis of the space.

The means which determine the position of the supports relative to the space, for example, a grating, are provided with the object of disturbing the gas flow in a minimum possible manner from which the diffusion to the substrates should occur nearly uniformly in order to minimize the differences in deposition thickness which may occur in one or another point of the substrate, in particular when said substrate has a comparatively large area.

Large quantities of substrates can be treated simultaneously in a tubular space used according to the invention. It is possible to treat several parallel rows of supports and substrates between which the flow of the gas mixture occurs in the same space having sufficient dimensions. The treatment of a large number of substrates in the same operation form a single gas supply ensures the homogeneity of the composition of the deposit which otherwise can be ensured with greater difficulty by a repetition of a treatment for each time a small number of substrates.

It is obvious that the space used for carrying out the method according to the invention can be directed in any manner. However, it is more advantageous to place said space in such manner that the receiving surface of the substrates is approximately vertical, which avoids the danger of contamination of the deposit by impurities which fall on said receiving surfaces under the influence of gravity.

The law of the enlargement of the intermediate space which is to enable the compensation of depletion of the gas mixture in elements which are necessary to form a deposit is determined experimentally; indeed the depletion along the gas flow is a function of numerous factors which depend especially on the deposited bodies, on the composition of the gas mixture, on the shape and on the dimensions of the space and on the temperatures of the gas mixture and the substrates. The enlargement of the intermediate spaces preferably is substantially linear. For example, in the case of supports the largest dimension of which is 20 to 80 mm, the minimum intermediate space is 5 to 15 mm and the enlargement is 0.5 to 2 mm per intermediate space. Experience teaches that it is advantageous to simultaneously use the two factors determining the rate of deposition on the substrates: on the one hand the temperature of the substrates, on the other hand the intermediate spaces between the substrates. The combination of a temperature gradient along a row of substrates and of an enlargement of the intermediate spaces between the substrates makes it possible to obtain a uniformity of the deposition thicknesses, simultaneously with a homogeneity of the composition of the deposit. For example, in the case of a deposit of a semiconductor material, the doping concentration can be kept constant for each individual substrate by simultaneously producing an enlargement of the intermediate spaces between substrates and a temperature gradient of one substrate to the other, while a single temperature gradient, even when this enables the partial compensation of the gradual depletion effect of the gas flow on the thickness of deposition, involves an undesired variation of the doping.

The invention may be used for depositing material which can be formed in the vapour phase by reaction of compounds the equilibrium of which is varied by reducing the temperature. The invention is used in particular for depositing semiconductor materials, polycrystalline or monocrystalline materials. The method according to the invention may be used in particular for the epitaxial monocrystalline deposition of semiconductor compounds which comprise at least one element of the columns II and III of the Periodic Table of elements and at least one element of the columns V and VI of said Table, for example, gallium arsenide phosphide which is deposited from gallium chloride and gaseous compounds of phosphorus and arsenic in a hydrogen flow. In that case, for example, silicon or oxidized silicon is used.

The present invention also relates to plates of crystalline semiconductor material with an epitaxial deposit which has been realized according to the method in the various embodiments described.

The invention will be described in greater detail with reference to the accompanying drawing, in which

FIG. 1 is a diagrammatic longitudinal cross-sectional view of a deposition device according to a known method with graphs indicating the temperatures used and the resulting thicknesses.

FIG. 2 is a diagrammatic longitudinal cross-sectional view showing an arrangement of substrates according to the invention.

FIG. 3 is a diagrammatic longitudinal cross-sectional view of a device for depositing according to the invention.

FIG. 4 is a cross-sectional view taken on the line BB of FIG. 5 of a device for depositing according to the invention.

FIG. 5 is a longitudinal cross-sectional view taken on the line AA of FIG. 4 of the same device.

In order to perform an epitaxial semiconductor deposit on a large number of substrates **3** (FIG. **1**), according to the known methods said substrates may be placed on a rack **2** which is placed in a tubular space. A gas mixture which chemically is in equilibrium at a temperature T_1 is conveyed at **4**, the substrates **3** being maintained at a temperature T_2 which is lower than T_1. During the track in the space the gas flow **5** depletes due to the consumption of deposited elements, and the gas mixture removed at **6** has a weaker concentration than in the supply thereof at **4** (the content of non-used side products of the reaction may be higher on the contrary). When the substrates **3** are present at the same mutual distance either because they are arranged at right angles to the gas flow as shown in FIG. **1**, or because they are arranged parallel to said flow, the thickness of the deposit obtained on the substrate is not regular because the substrates reached frist receive a thicker deposit than the substrates reached last. The difference in thickness between the first substrate **3***a* and the last 3z is considerable. The curve C_3 which is drawn with respect to the diagrammatic cross-section of the space shows the variation of the thickness obtained as a function of the distance X which separates one of the substrates from the substrate 3a. In order to diminish the difference between e_o, thickness of the deposit of the substrate 3a, and e_1, thickness of the deposit on the substrate 3z, a temperature gradient may be produced along the space **1**; the curve of the temperature T as a function of the distance X, which is C_1, in the case of a temperature which is equal for all the substrates, may then be replaced by the curve C_2. The gradual drop of the temperature of the substrates between T_1 and T_2 only very partly compensates for the depletion of the gas flow: deposition thicknesses are obtained according to the curve C_4 which are spread from e_o to $e_2 > e_1$.

In order to mitigate this drawback, according to the invention he substrates are placed, for example, in the manner as shown in FIG. **2**. Substrates **23** are secured to flat and thin supporting plates **22** perpendicularly to the gas flow indicated by the arrow **24** which flows in the longitudinal direction in a space **21** and diffuses towards the substrates **23** according to the directions denoted by the arrows **25**. The supports are placed in the space in such manner that a space is formed around it which forms a tube for passing the reaction gas mixture, the distances between each substrate and the adjacent support increasing in the direction of flow of the gas flow **24**; if the distance is equal to d_n for the substrate of the n^{th} order and d_{n+1} for the substrate of the $(n+1)^{th}$ order, one has $d_{n+1}>d_n$. The minimum mutual distance d_1 between the first substrate and the following support is determined as a function of the tolerance which is permitted for the uniformity of the thickness of the deposit on each substrate.

The receiving surfaces of the substrates shown in FIG. **2** are not present opposite to the inlet of the gas flow but in the opposite direction. The substrates **33** shown in FIG. **3** on the contrary are secured to supports **32** in a tubular space **31** and are present opposite to the supply direction of the vapour mixture which forms the gas flow **34**. The distance *d* between each substrate and the adjacent support increases in the direction of the gas flow. In order to avoid the direct contact of the reaction mixture with the substrate **35** reached first, a plate **36** which is identical to the support **32** is placed in front of said substrate **35**.

It is a similar measure which is taken in the device shown in FIGS. **4** and **5**. Rectangular substrates **43** bear on rectangular very slightly inclined supports **42** which form part of a plate **47**. Said supports are secured, for example, on the platform by means of angle pieces **49** of minimum dimensions in such manner that the diffusion in the space **40** between the supports and the substrates is not disturbed. The latter are held in place by gravity and due to the abument studs **48**. The platform **47** is placed in a tubular reactor **41** of a rectangular cross-section in such manner that two similar passages **44** and **45** remain on either side of the supports for the flow of the gas which enters at **51** and then diffuses in the spaces **40** the width of which gradually increases. The diffusion from the two gas flows occurs symmetrically.

A plate **46** which is identical to the supports **42** avoids that the first substrate is directly exposed to the gas flow which enters the space. An embodiment of the method according to the invention in a device analogous to that shown in FIGS. **4** and **5** will now be described hereinafter.

On a platform having **20** supports of oxidized silicon, **19** supports of gallium arsenide are provided. The dimensions of the supports are 40 × 40 mm and the mutual intermediate space *d* between the adjacent supports varies from 10 to 20 mm according to a substantially linear arithmetical series. The platform with its charge is placed in a tubular reactor having inside cross-sections of 70 × 40 mm, two passages of 40 × 15 mm being left free for the flow of the gas mixture on either side of the supports. The platform is directed so that the first support which does not support a substrate is present on the side of the gas supply which is also that of the minimum mutual intermediate space *d*.

The reactor is purified by means of hydrogen and then heated to the desired temperature, from which instant the substrates are maintained at a temperature between 750° and 800°C with a gradient of 10° between the various substrate ends. A gas mixture containing the elements which are to be deposited, including the possible doping elements, and diluted with hydrogen and heated to a temperature of approximately 900°C is conveyed to the platform with substrates with a total supply in the order to **10** liters per minute.

A deposit of gallium arsenide phosphide carried out in these conditions and having an average thickness of 60 micrometers shows a maximum difference of 5% between the thicknesses deposited on the various substrates, as well as a difference of less than 20% between the concentrations of doping impurities.

What is claimed is:

1. A method of forming a deposit on a large number of flat substrates by reaction of a gaseous mixture of compounds of the elements to be deposited, said method comprising passing a gas flow containing gaseous compounds of the elements to be deposited through the zone of a tubular space containing the substrates arranged with their flat surfaces substantially perpendicular to the direction of the gas flow and each substrate being separated from the next substrate by a distance that increases in the direction of the flow of the gas, said gas being heated to a temperature above that of said substrates and depositing said elements on said substrates.

2. A method as claimed in claim **1**, characterized in that each substrate is secured on a thin and flat support which has an area which is larger than that of the substrate secured thereto.

3. A method as claimed in claim **2**, characterized in that each support supports only one substrate on one surface, all the substrates with their receiving surface being directed in the same direction as the gas flow.

4. A method as claimed in claim **1**, characterized in that all the substrates are directed so that their receiving surfaces are directed towards the inlet of the gas flow in the space, the first support reached by the gas mixture supporting no substrate.

5. The method of claim **4** wherein the increase of the distances between substrates is substantially linear.

6. A flat crystalline semiconductor plate having a deposit obtained by the method of claim **1**.

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