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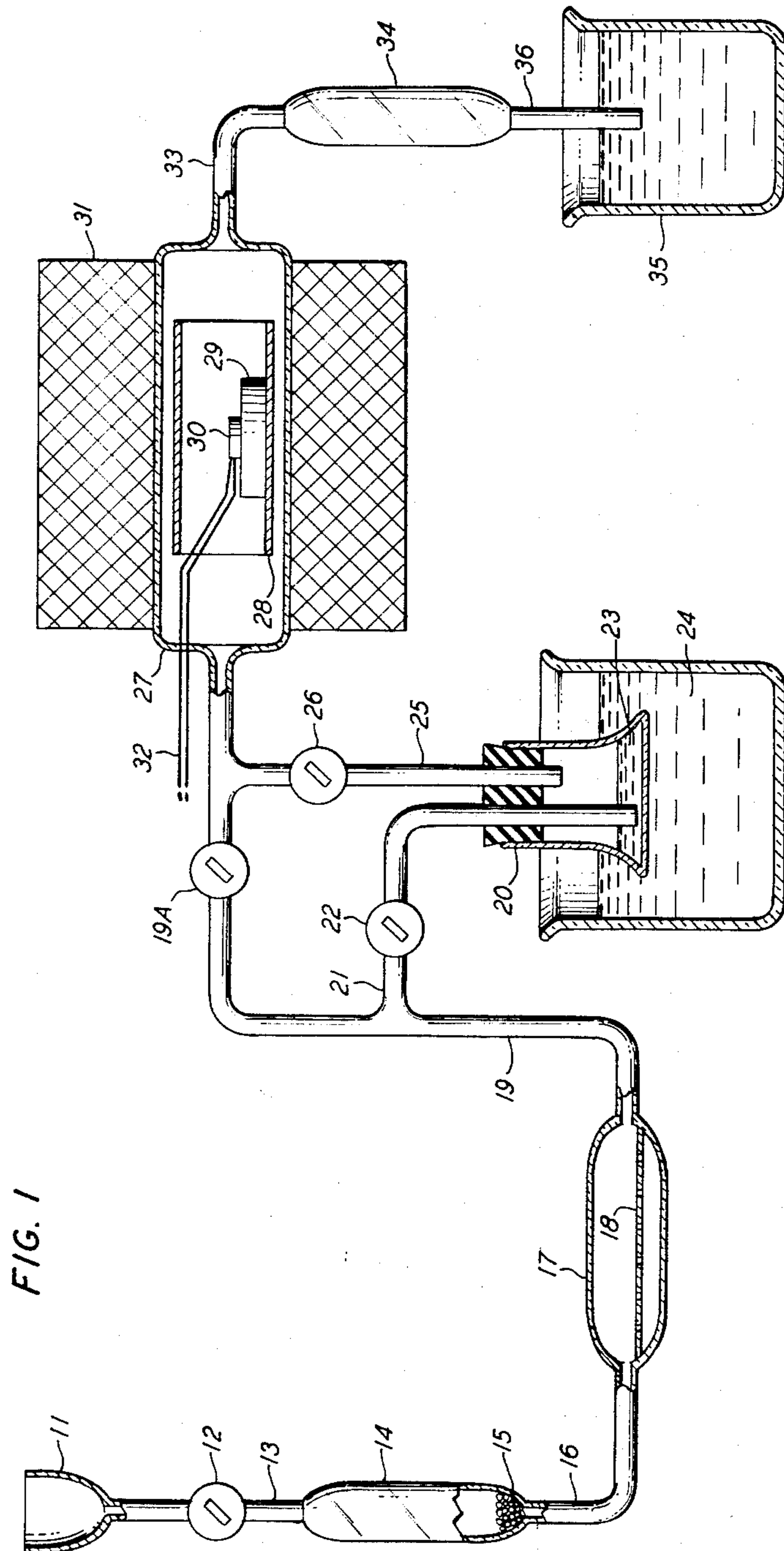
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3,346,414

VAPOR-LIQUID-SOLID CRYSTAL GROWTH TECHNIQUE

Filed Jan. 28, 1964

2 Sheets-Sheet 1



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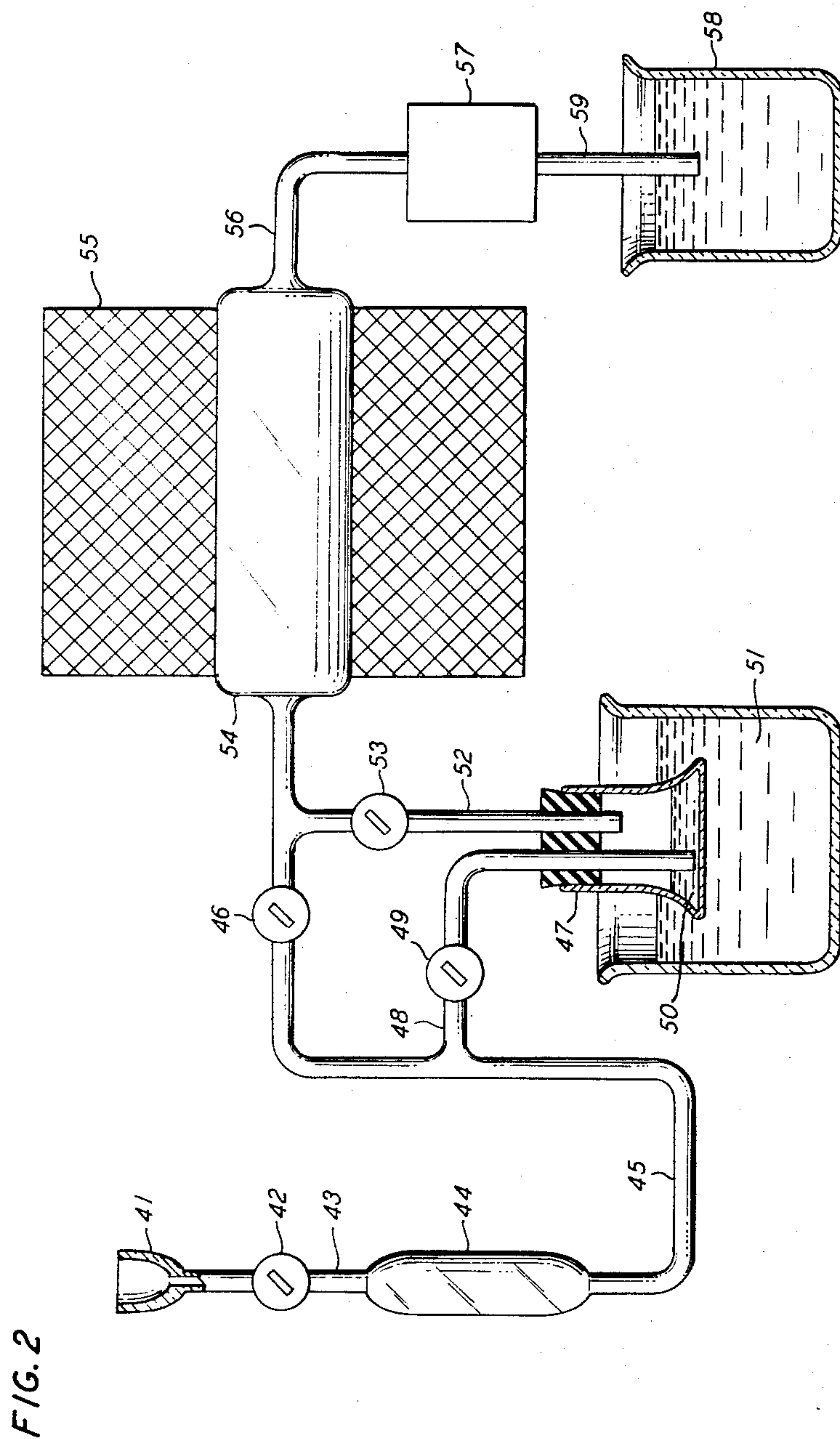
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1

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VAPOR-LIQUID-SOLID CRYSTAL GROWTH TECHNIQUE

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ABSTRACT OF THE DISCLOSURE

The controlled growth of acicular and macroscopic crystals as well as epitaxial layers is effected by providing an alloying agent at the desired site of crystal growth, heating the agent to a temperature sufficient to cause the formation of a liquid solution and exposing the solution to a vapor containing at least one constituent of the desired crystal.

This invention relates to a technique for the growth of crystalline materials.

In accordance with the present invention, a crystallization mechanism is described wherein crystallization is initiated upon the formation of a liquid layer which is saturated with respect to at least one of the constituents of the desired crystalline material.

More particularly, the present inventive technique is directed to the controlled growth of a crystalline body comprising a first material wherein a second material comprising an "agent" is contacted with a vapor comprising the said first material, the said agent being such that it is capable of forming a liquid solution comprising the said agent and the said first material, in which solution the said agent is maintained at a temperature above the initial freezing temperature of the solution and from which the said first material freezes out of solution at the site of the agent. Vapor-agent contact is continued for a time sufficient to supersaturate the liquid solution with respect to the first material.

It is the nature of the invention that crystal growth is initiated at the site of the agent, a requirement being that the agent be placed at the desired site of crystal growth in a separate manipulative step.

In the operation of the described technique, substrates may or may not be present, and when present may serve as a physical support, completely unreactive with respect to the agent, or may be chosen to react with or dissolve the agent. However, as long as the essential conditions outlined above are met, the choice of a substrate is dependent upon practical considerations, for example, heat resistance, avoidance of contamination, et cetera.

Preferred embodiments of the present invention utilize a substrate which is single crystalline, at least over the area of the desired site of crystal growth, and oriented. Still further embodiments are directed to the growth of crystalline bodies which follow the orientation of a substrate material.

The inventive technique is of particular interest for use in the growth of semiconductor materials, superconducting compositions, high melting refractory and ceramic crystals, luminescent materials, including optical maser compositions, p-n, n-n and n-p-n configurations, magnetic oxides, et cetera.

The invention will be better understood by reference to the following description taken in conjunction with the accompanying drawing forming a part thereof and from the appended claims wherein:

FIG. 1 is a schematic front elevational view of an

2

apparatus utilized in the practice of the present invention for the growth of crystalline bodies; and

FIG. 2 is a schematic front elevational view of another apparatus suitable for the growth of crystalline bodies in accordance with the invention.

The term "agent" as applied herein denotes a broad class of operative materials which may be employed in the practice of the present invention. Agents may be selected from among elements, compounds, solutions or multiphase mixtures, such as eutectic compositions. Further, the agent may be alloyed with or admixed with one or more constituents of the desired crystalline material or, if present, with one or more constituents of a substrate material. The agent may also be or contain a minor constituent desired in the material being crystallized, for example, an acceptor or donor in a semiconductor material or an activating element in a maser crystal.

Agents employed in the practice of the invention desirably evidence a vapor pressure over the liquid solution of the order of a few millimeters of mercury in order to avoid excess loss thereof. It will be evident from the requirements outlined that the constituent or constituents of the agent must evidence a distribution coefficient k less than unity, k being defined as the ratio of the concentration of the constituent or constituents of the agent in the desired crystalline material to its concentration in the liquid solution from which the desired crystalline material is grown. Selection of a particular agent having desired minimum or maximum values of k is dependent upon the specific crystalline material being grown and the vapor transport reaction selected. However, for the growth of crystalline bodies of specific lengths, in accordance with certain embodiments herein, k may be of the order of 0.1 or lower whereas in the growth of crystalline bodies of large area and small thickness, k may be of the order of 0.5 and greater.

Still another property influencing the selection of an agent is the wetting characteristic of the liquid solution containing the agent, with respect to the substrate and the desired crystalline material. Thus, for example, in the growth of acicular crystals it may be desirable that the contact angle between the liquid solution and the substrate or crystalline body be as high as 90° or greater, whereas in the growth of crystalline bodies of large area and small thickness from thin layers of liquid solution it is generally preferred that the contact angle be small, ranging down to 0°.

As described above, deposition of a vaporous material is initiated at the site of the agent, a requirement being that the agent be placed at the desired site of crystalline growth in an independent manipulative step. Several techniques are available for providing the agent at the desired site of growth. For example, it may be convenient to place the agent in the growth region by manual means or to deposit films of the agent of prescribed thicknesses by evaporation, electroplating, et cetera. Further, masks may be employed as desired to form specific arrays and patterns. It will be understood that the quantity of agent employed is self-regulating and of no criticality.

The desired crystalline material may be furnished by any of the well known vapor transport processes, typical reactions being set forth below.

(a) Disproportionation: $2\text{SiI}_2(\text{g}) \rightleftharpoons \text{Si}(\text{s}) + \text{SiI}_4(\text{g})$

(b) Decomposition: $\text{CuI}_2(\text{g}) \rightleftharpoons \text{Cu}(\text{s}) + 2\text{I}(\text{g})$

(c) Reduction:

$\text{CuI}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{Cu}(\text{s}) + 2\text{HI}(\text{g})$

$\text{SiCl}_4(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons \text{Si}(\text{s}) + 4\text{HCl}(\text{g})$

(d) Condensation: $\text{Zn}(\text{g}) \rightleftharpoons \text{Zn}(\text{s})$

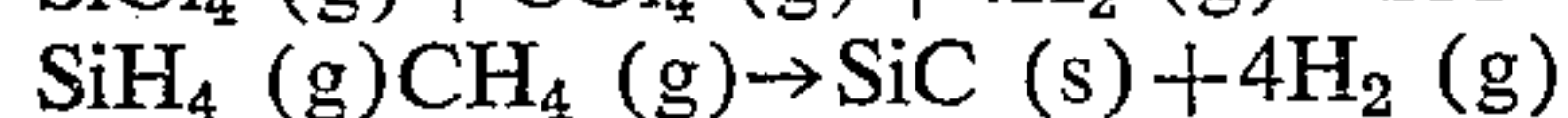
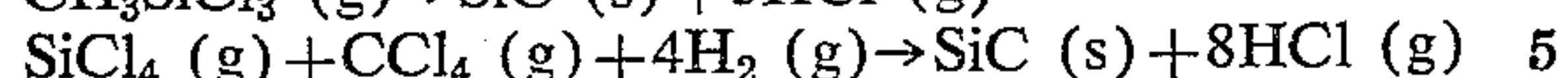
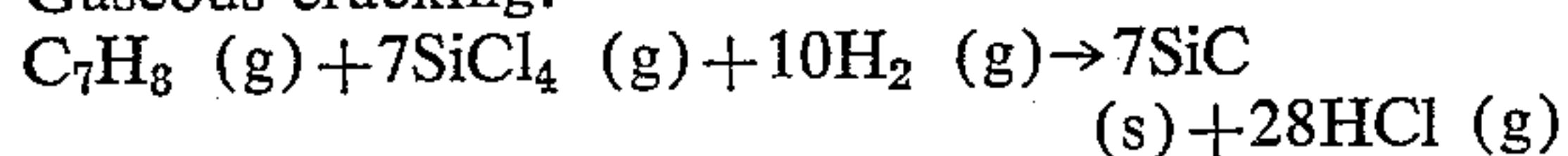
(e) $\text{Ga}_2\text{O}(\text{g}) + \text{As}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons 2\text{GaAs}(\text{s}) + \text{H}_2\text{O}(\text{g})$

(f) $\text{Ga}_2\text{O}(\text{g}) + \text{P}(\text{g}) + \text{H}(\text{g}) \rightleftharpoons 2\text{GaP}(\text{s}) + \text{H}_2\text{O}(\text{g})$

(g) Condensation: $\text{SiC}(\text{g}) \rightleftharpoons \text{SiC}(\text{s})$

3

(h) Gaseous cracking:

(i) $3\text{AlO} (\text{g}) \rightleftharpoons \text{Al}_2\text{O}_3 (\text{s}) + \text{Al} (\text{l})$ (j) $\text{Al}_2\text{Cl}_6 (\text{g}) + 3\text{H}_2\text{O} (\text{g}) \rightarrow \text{Al}_2\text{O}_3 (\text{s}) + 6\text{HCl} (\text{g})$ (k) $2\text{NbCl}_5 (\text{g}) + 2\text{CH}_4 (\text{g}) + \text{H}_2 (\text{g}) \rightarrow 2\text{NbC} (\text{s}) + 10\text{HCl} (\text{g})$ (l) $\text{SiH}_4 (\text{g}) \rightarrow \text{Si} (\text{s}) + 2\text{H}_2 (\text{g})$

With reference now more particularly to FIG. 1, there is shown a schematic front elevational view of an apparatus suitable for the growth of crystalline bodies by the described technique.

The apparatus shown includes a source of a reactive gas, a saturating system and a reaction chamber. A reactive gas is admitted into the system from source 11, controlled by valve 12, and passes via conduit 13 through a purification trap 14. Thereafter, the gas passes from trap 14 via conduit 16 and proceeds to a second trap 17 containing a purification medium. The now purified gas emerges from trap 17 via conduit 19, controlled by valve 19A, and may pass directly into the reaction chamber or first through a saturator 20 by means of conduit 21 controlled by valve 22, saturator 20 containing a suitable liquid 23. Control of the ratio of liquid 23 to reactive gas is maintained by refrigerating saturator 20 with a suitable cold bath 24. Reactive gas passing through saturator 20 emerges together with liquid 23 via conduit 25, controlled by valve 26 and proceeds to reaction chamber 27. Chamber 27 may be a fused silica tube, typically having disposed therein a cylinder 28 containing a pedestal 29 upon which a substrate 30 may be positioned. Chamber 27 suitably heated by means of RF heater 31, the temperature of substrate 30 being measured by thermocouple 32. The gaseous products of the reaction emerge from chamber 27 via conduit 33 and pass through trap 34 and on to an exhaust system 35 by means of conduit 36.

The present invention is conveniently described in detail by reference to an illustrative example in which silicon crystals are grown upon an oriented silicon substrate by the hydrogen reduction of silicon tetrachloride in accordance with the present invention, gold being employed as the agent, utilizing an apparatus of the type shown in FIG. 1.

An oriented single crystal of silicon is chosen as the substrate material and initially ground flat with a suitable abrasive. Hydrogen is chosen as the reactive gas and silicon tetrachloride in liquid form is inserted in saturator 20.

Following, small particles of gold are placed by manual means upon substrate 30 which is then positioned upon pedestal 29. Next, with valves 22 and 26 in the open position, the reactive gas (hydrogen) is permitted to flow through the system. Then, heater 31 is turned on and reaction chamber 27 heated to a temperature sufficient to alloy the gold with the silicon, so resulting in a plurality of molten alloy droplets containing silicon and gold.

Thereafter, valves 22 and 26 are turned to the open position, valve 19A closed and the reduction of silicon tetrachloride initiated. The conditions employed in such techniques are well known to those skilled in the art. (See, for example, Journal of the Electrochemical Society, volume 108, pages 649-653, 1961.)

During the course of the processing silicon preferentially deposits at the site of the liquid droplet which eventually attains a state of supersaturation with respect to silicon, thereby causing silicon to freeze out of solution together with a small concentration of gold at the interface between the solid silicon and the liquid alloy. As the process continues, the alloy droplet becomes displaced from the substrate crystal and rides atop the growing crystal.

4

It will be understood by those skilled in the art that gold has been chosen as an agent on the basis of its low distribution coefficient and the fact that it has little effect on the electrical properties of silicon. In much the same fashion, platinum, palladium, silver, copper, nickel et cetera, may be chosen or, in fact, any agent meeting the general criteria, that is that it be capable of forming a liquid solution comprising the agent and at least one constituent of the vapor other than the agent at a temperature below the melting temperature of the latter.

Several examples of the present invention are described in detail below. These examples and the illustration are included merely to aid in the understanding of the invention and variations may be made by one skilled in the art without departing from the spirit and scope of the invention.

Example I

This example describes the growth of silicon crystals by the hydrogen reduction of silicon tetrachloride in an apparatus similar to that shown in FIG. 1.

A silicon wafer, 15 mm. x 25 mm. x 1 mm. with (111) faces, was chosen as a substrate material. The substrate was then ground flat with an abrasive paper and given a bright etch to expose undamaged crystal surfaces. The etching procedure involved treating for 3 minutes with a 1:1 solution of hydrofluoric and nitric acids followed by a 4 minute treatment with a 1:2:6 solution of hydrofluoric, acetic and nitric acids. Next, the etched substrate was masked with deionized water and dried in an oven at 110° C.

Following, gold particles, approximately 50 microns in diameter were placed by manual means upon the etched substrate at the desired sites of crystalline growth. Then the substrate was positioned upon pedestal 29 in the apparatus.

Next, with valves 22 and 26 in the closed position and with valves 12 and 19A in the open position, hydrogen was passed through the system. Then RF furnace 31 was turned on and chamber 27 heated to 950° C. for a period of 10 minutes, so resulting in the formation of a plurality of molten alloy droplets containing silicon and gold.

Thereafter, valves 22 and 26 were opened, and valve 19A closed, thereby permitting hydrogen to pass through saturator 20 where silicon tetrachloride, obtained from commercial sources, was picked up and carried to chamber 27. Silicon was permitted to deposit at the sites of the alloy droplets for a period of 2½ hours. The flow of hydrogen through the system was maintained within the range of 300 to 360 cc. per minute and the molar ratio of SiCl_4 to H_2 was maintained at approximately 1:10 by means of cold bath 24. The resultant silicon crystals were acicular in nature, approximately 5 mm. in length and were found at each alloy site growing perpendicular to the substrate. The crystals were generally hexagonal in cross-section and of high crystalline perfection.

Example II

The procedure of Example I was repeated with the exception that nickel, palladium, silver, copper and platinum particles were placed upon the (111) faces of silicon single crystal substrates. In each case the reaction chamber was heated to 1050° C. and the process begun with a H_2 flow of 250 cc. per minute and a SiCl_4/H_2 ratio of 1:10, the reaction being permitted to continue to one hour. The resultant crystals of silicon in each case grew at the sites of the alloy formed between the agent, for example, Pd, Pt, et cetera, and the substrate were acicular in nature, approximately 5 mm. in length and grew perpendicular to the substrate. The crystals were hexagonal in cross-section.

5

Example III

The procedure of Example I was repeated with the exception that an oriented single crystal of germanium was employed as a substrate, a reaction temperature of 850° C. being used in the reduction process. The resultant crystals were acicular in nature, approximately 3 mm. in length and were found at each alloy site. The result crystals were germanium rich at the base and the germanium content continued decreasing from the base outwardly and ultimately became silicon rich.

Example IV

The procedure of Example I was repeated with the exception that gold particles having a diameter of approximately 3 mm. were employed as the agent. The resultant crystalline layers evidenced the same orientation as that of the substrate. It was noted that growth at 950° C. contrasts sharply with temperatures of 1200° C. commonly required for the growth of epitaxial layers of silicon.

With reference now more particularly to FIG. 2, there is shown a schematic front elevational view of another apparatus suitable for the growth of crystalline bodies in accordance with the present invention.

The apparatus shown includes a source of a gas, a saturating system and a reaction chamber. The gas is admitted into the system from source 41 controlled by valve 42 and passes via conduit 43 through purification trap 44. Thereafter, the gas emerges from trap 44 via conduit 45 and either passes directly into the reaction chamber, controlled by valve 46 or through saturator 47 by means of conduit 48 controlled by valve 49. Gas passing through saturator 47 emerges together with vapors of a liquid 50 contained in saturator 47, which is refrigerated by cold bath 51, via conduit 52, controlled by valve 53, and proceeds to reaction chamber 54. Chamber 54 is heated by means of an electrical resistance furnace 55. The gaseous products of reaction emerge from chamber 54 via conduit 56 and pass through flowmeter 57 and exhaust 58 by means of conduit 59.

Example V

This example describes the growth of gallium arsenide crystals in an apparatus similar to that shown in FIG. 2. Hydrogen was employed as the gas; saturator 47 contained distilled water refrigerated by a mixture of water and ice and chamber 54 was a fused silica tube 5/8" I.D. x 10".

A gallium arsenide wafer, 2 mm. x 3 mm. x 1/2 mm. with (111) and (111) faces was chosen as the substrate. The wafer was ground flat with 305 emery and etched for 30 seconds with aqua regia. Next, the etched substrate was rinsed in deionized water and dried in air. Gallium was smeared on a portion of the surface of the etched substrate which was then positioned in quartz tube 54. Next, a source of essentially pure gallium arsenide (0.2 g.) was inserted in chamber 54 upstream from the substrate. Following, with valves 49 and 53 in the closed position and with valves 42 and 46 in the open position, hydrogen was passed through the system and furnace 55 turned on.

Next, valves 49 and 53 were turned to the open position, and valve 46 to the closed position, thereby permitting hydrogen to pass through the saturating system, so carrying water to the reaction chamber wherein the source was maintained at 970° C. and the substrate at 790° C., the following reaction occurring:



The flow of hydrogen saturated with water was maintained at a rate of approximately 35 ml./min. The reaction continued for 2 1/2 hours. The resultant crystals of gallium arsenide were of acicular form, approximately 5 mm. in length and were found at the site of the gallium agent.

6

Example VI

The procedure of Example V was repeated with the exception that gold filings were employed as an alloying agent rather than gallium. The source was maintained at 1010° C. and the substrate at 830° C. The resultant acicular crystals of gallium arsenide were in blade and needle form, approximately 5 mm. in length and grew at each site of the filings.

Example VII

The procedure of Example V was repeated with the exception that palladium chloride was placed upon the surface of the gallium arsenide and decomposed in hydrogen at 860° C. to yield palladium as the alloying agent. The source was maintained at 970° C. and the substrate at 860° C. The resultant acicular crystals of gallium arsenide were in blade and needle form approximately 5 mm. in length and grew at each site of the palladium chloride.

Example VIII

The procedure of Example VI was repeated with the exception that a polycrystalline gallium phosphide substrate and a gallium phosphide source was employed. The source was maintained at 995° C. and the substrate at 875° C. The resultant acicular crystals of gallium phosphide were in blade and needle form, approximately 3 mm. in length and grew at each site of the filings.

While the invention has been described in detail in the foregoing specification and the drawing similarly illustrates the same, the aforesaid is by way of illustration only and is not restrictive in character. The several modifications which will readily suggest themselves to persons skilled in the art are all considered within the scope of the invention, reference being had to the appended claims.

What is claimed is:

1. A process for the controlled growth of a crystalline body comprising a first material at a given site, comprising providing a second material comprising an agent at the said site, contacting the said second material with a vapor comprising the said first material, the said agent being such that it is capable of forming a liquid solution comprising the said agent and the said first material, the said second material being maintained at a temperature above the initial freezing temperature of the said solution and continuing the said contacting for a time sufficient to supersaturate the said solution with respect to the said first material thereby initiating crystallization at the said site.
2. A process in accordance with the procedure of claim 1 in which the said vapor is provided at the said site only at a time subsequent to the placement of the said agent.
3. A process in accordance with the procedure of claim 2 wherein said agent is provided as at least one body in free space.
4. A process in accordance with the procedure of claim 2 wherein said agent is in contact with at least one selected site upon a substrate, the said substrate being maintained at the said temperature at the said selected site, and in which crystallization proceeds out of solution on the surface of the said substrate.
5. A process in accordance with the procedure of claim 4 wherein the said site defines a single crystalline section of a substrate.
6. A process in accordance with the procedure of claim 5 wherein said crystalline body is essentially cubic and in which the said substrate is single crystalline at least over the area of the desired site of the crystal growth.
7. A process in accordance with the procedure of claim 4 wherein the said selected site is of lesser area than that of the said substrate surface of which it is a part.
8. A process in accordance with the procedure of claim 4 wherein the said agent is a desired component of the said crystalline material.

7

9. A process in accordance with the procedure of claim 8 wherein the solubility of said agent is appreciable and wherein said agent is replenished by additional inclusions in said vapor.

10. A process in accordance with the procedure of claim 6 wherein the said substrate is silicon. 5

11. A process in accordance with the procedure of claim 6 wherein the said substrate is single crystal gallium arsenide.

12. A process in accordance with the procedure of claim 6 wherein the said substrate is gallium phosphide. 10

13. A process in accordance with the procedure of

8

claim 2 wherein the distribution coefficient of the said agent in the said crystalline material is less than 0.1.

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