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3,493,431

VAPOR-LIQUID-SOLID CRYSTAL GROWTH TECHNIQUE

Filed Nov. 25, 1966

2 Sheets-Sheet 1

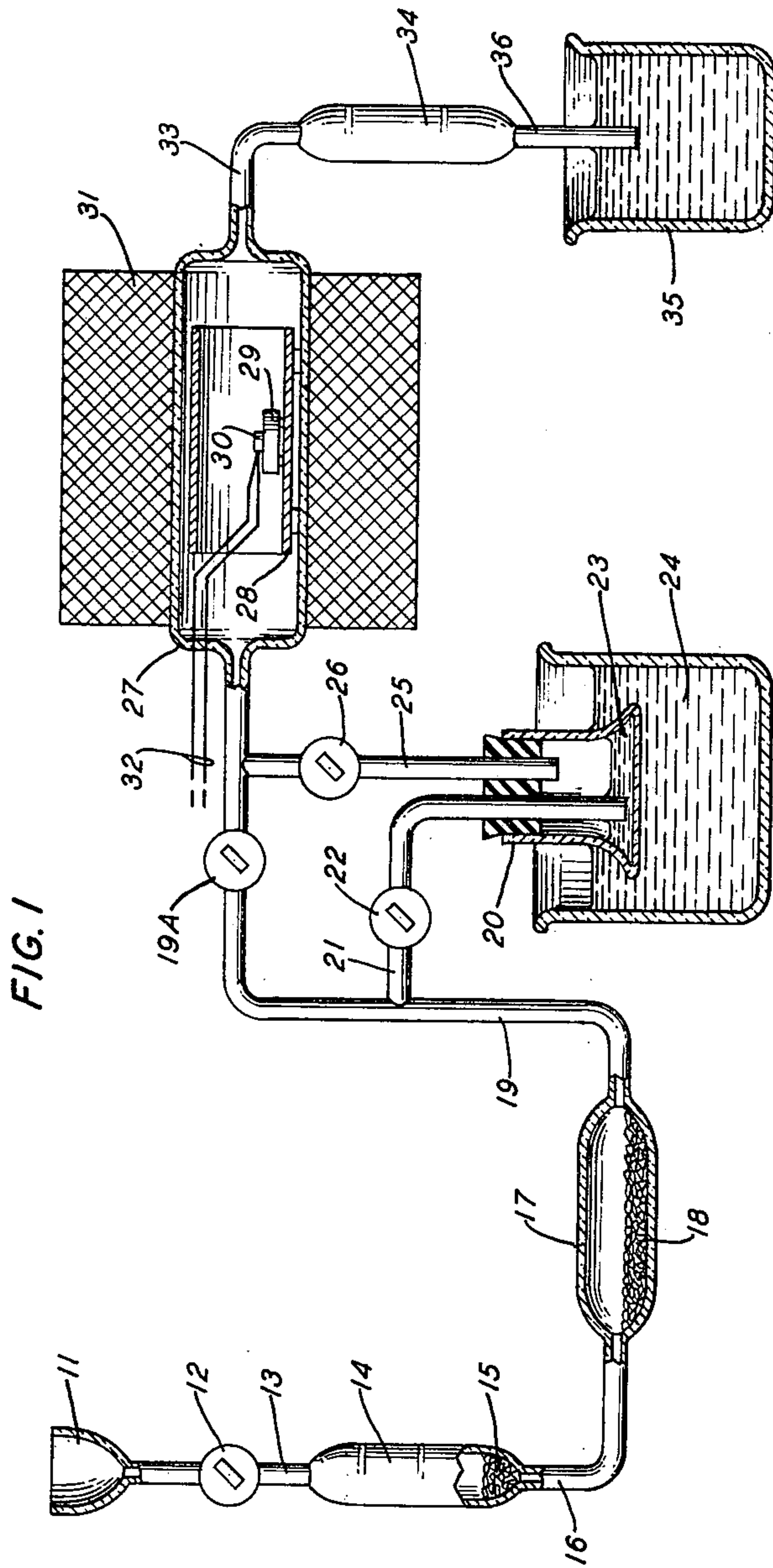


FIG. 1

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FIG. 2

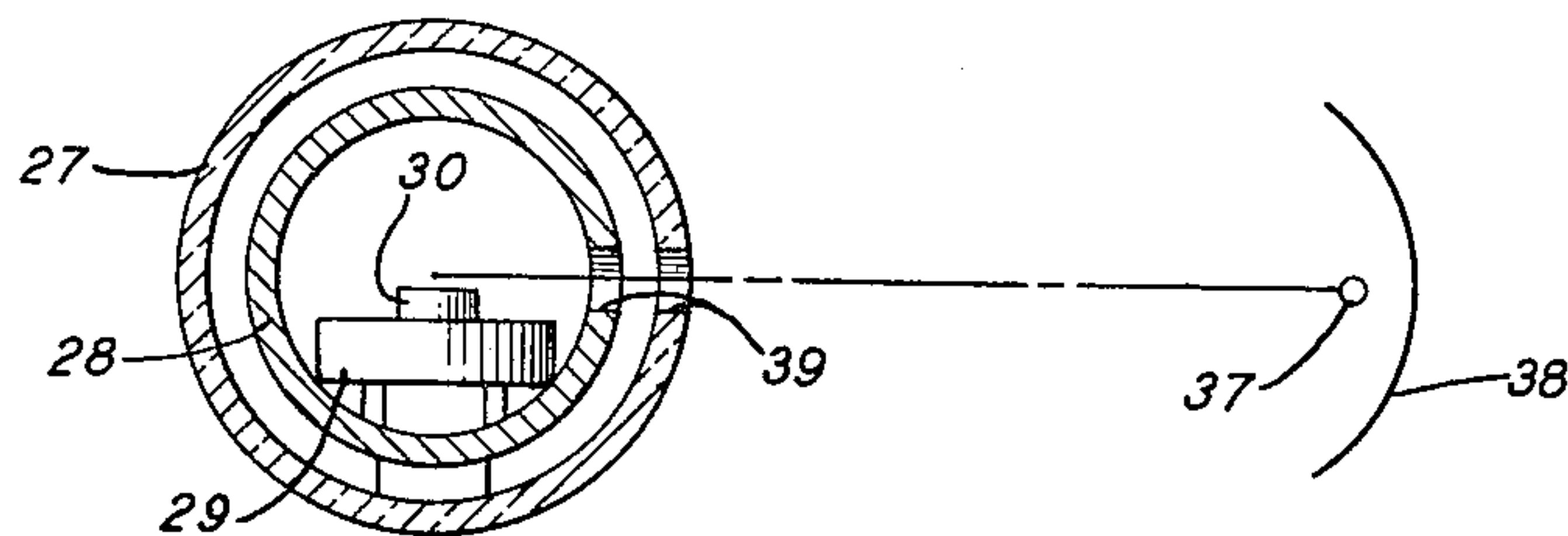


FIG. 3

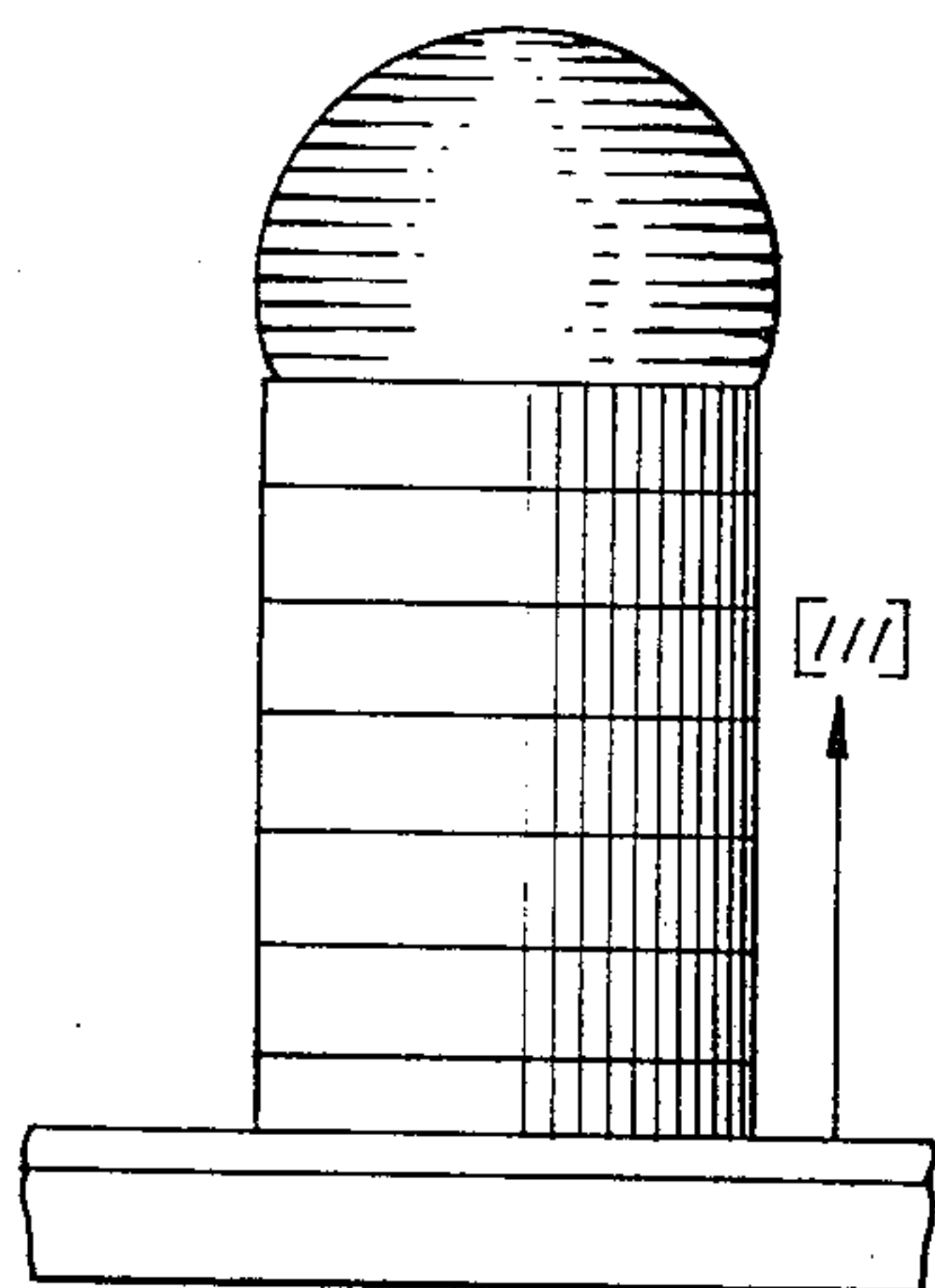


FIG. 4

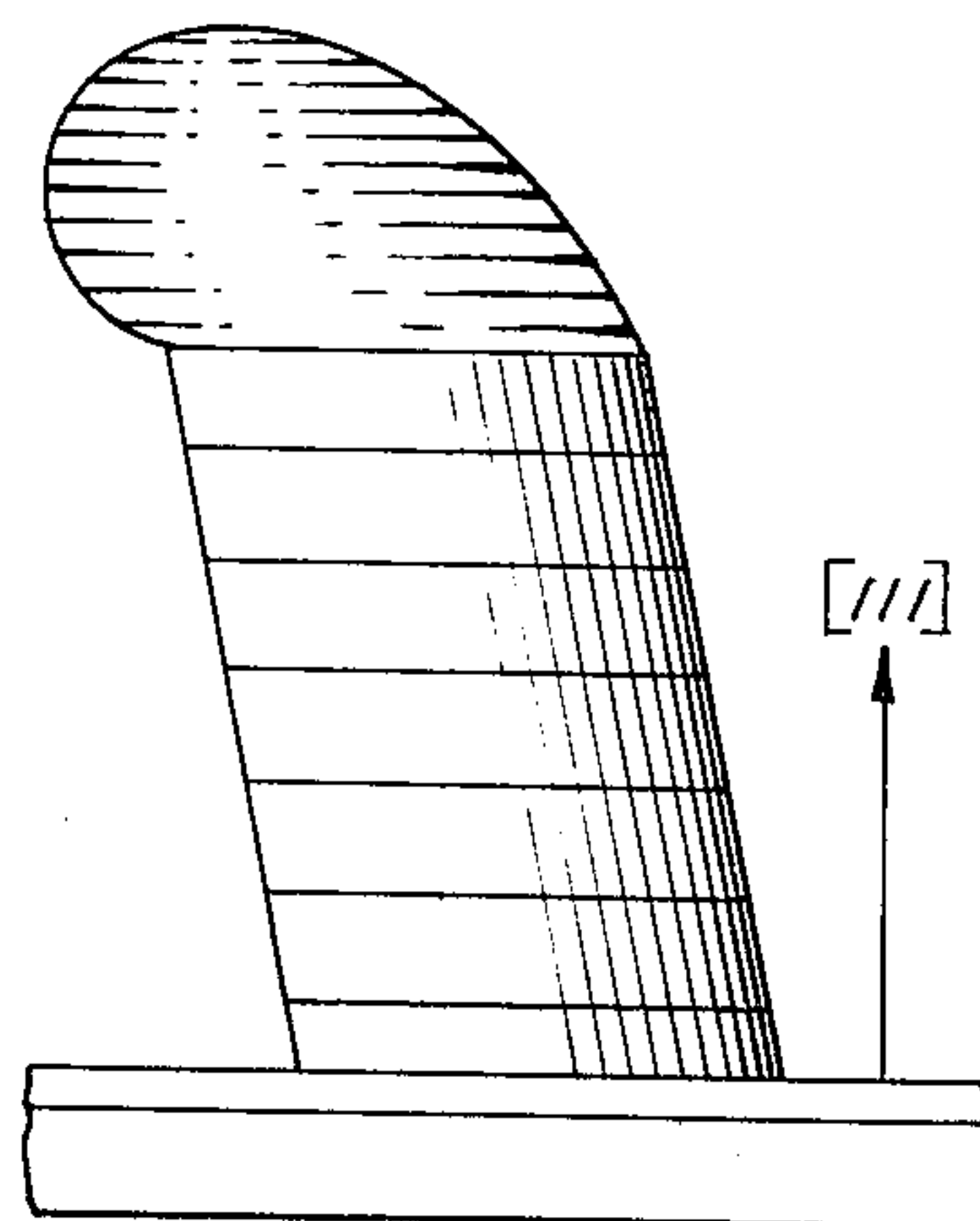
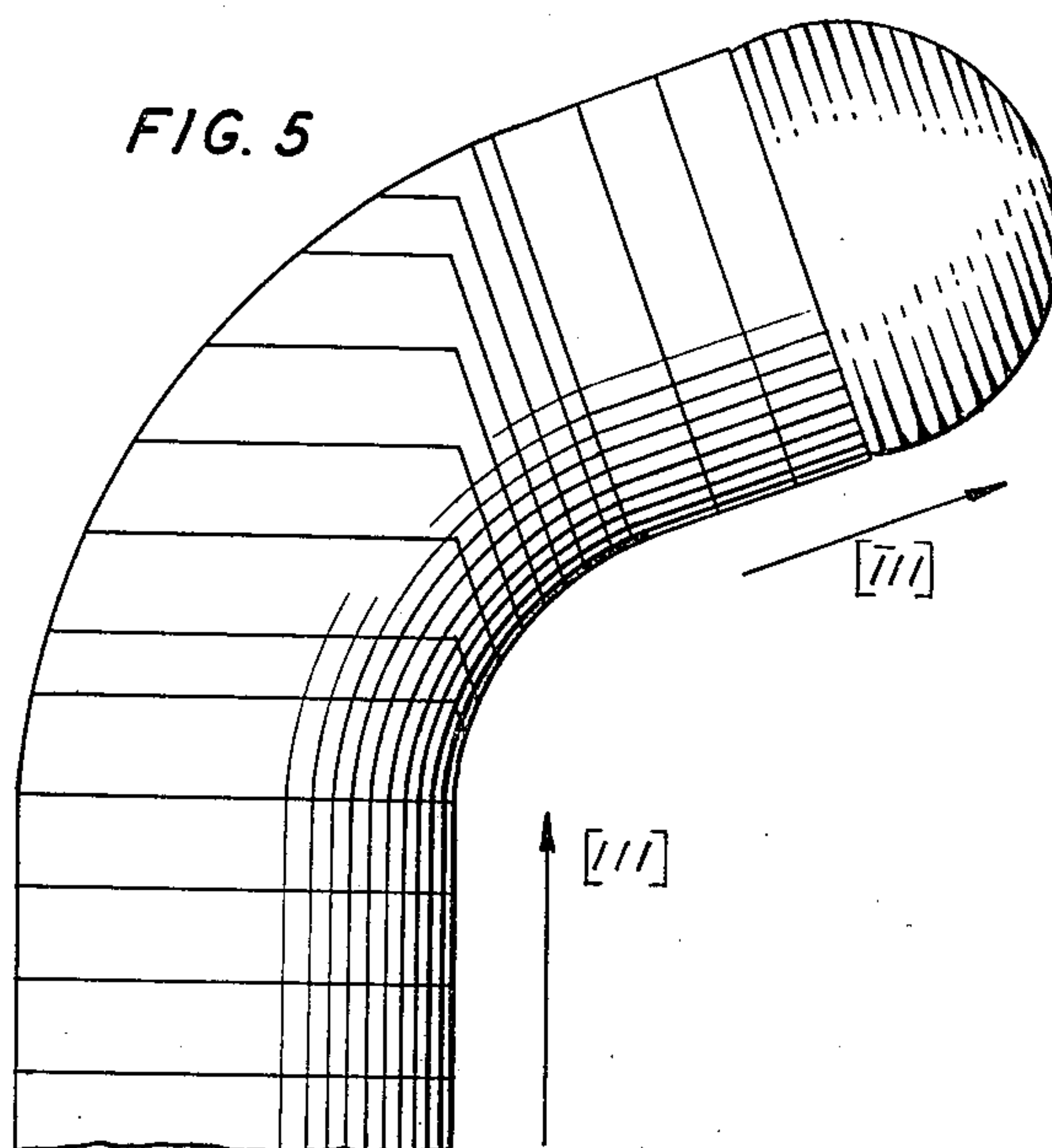


FIG. 5



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**VAPOR-LIQUID-SOLID CRYSTAL GROWTH
TECHNIQUE**

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10 Claims

ABSTRACT OF THE DISCLOSURE

The controlled growth of branched and/or kinked acicular and macroscopic crystals may be effected during vapor-liquid-solid crystal growth by alteration of the contact angle between the liquid alloy droplet and the substrate and/or alteration of interface morphology.

This invention relates to a technique for the growth of crystalline materials. More particularly, the present invention relates to a crystal growth procedure utilizing the vapor-liquid-solid mechanism.

Recently, considerable interest has been generated in a vapor-liquid-solid crystal growth technique, hereinafter designated "VLS," described by W. C. Ellis, W. G. Pfann, and R. S. Wagner in copending application, Ser. No. 340,701, now U.S. Patent 3,346,414, filed Jan. 28, 1964.

Briefly, this technique involves growth of a crystalline body from a supersaturated liquid solution or liquid alloy zone situated between a vapor and the solid material to be grown. In the operation of the process, a vapor is contacted with a liquid alloy zone, which is then permitted to attain supersaturation, so resulting in the solidification of the excess material at the solid-liquid interface and concurrent crystal growth.

Crystals grown in accordance with the VLS technique have been found superior to crystalline materials grown by conventional vapor-solid techniques from the standpoint of crystalline perfection and have, accordingly, been enthusiastically received by workers in the art. Unfortunately, it has been found that unconstrained growth of crystalline materials via the VLS mechanism typically occurs in only one direction, for example, for silicon $\langle 111 \rangle$, so precluding their use in device applications requiring materials evidencing growth in more than one direction.

In accordance with the present invention a technique for the growth of crystalline materials of a high degree of perfection evidencing growth in more than one direction is described. It has been determined that controlled growth of branched and/or kinked acicular and macroscopic crystals may be effected during VLS crystal growth by alteration of the contact angle between the liquid alloy zone and the solid material being grown (substrate) and/or alteration of solid-liquid interface morphology. These ends may be attained in an isothermal system by (a) applying a physical force, either mechanical or electromagnetic in nature, to the liquid-alloy zone, so resulting in an alteration of the contact angle configuration of the liquid-alloy zone and preferential growth in a new direction, or (b) effecting a sudden increase or decrease in temperature in the VLS process, so resulting in an alteration of interface morphology and growth in a new direction. Studies have further revealed that alteration of interface morphology may also be effected in a non-isothermal system by applying a lateral temperature gradient to the liquid-alloy zone during growth, thereby resulting in the formation of growth kinks.

The invention will be more readily understood by ref-

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erence to the following detailed description taken in conjunction with the accompanying drawing wherein:

FIG. 1 is a schematic front elevational view of a typical apparatus employed in the practice of the present invention;

FIG. 2 is a sectional view of a chamber and heat source utilized in a non-isothermal system wherein a lateral temperature gradient is applied to the liquid-alloy zone;

FIG. 3 is a front elevational view of a typical silicon crystal growth preferentially by VLS techniques in the $[111]$ direction;

FIG. 4 is a front elevational view of the crystal of FIG. 3 after the application of a physical force thereto during VLS crystal growth; and

FIG. 5 is a front elevational view of a crystal such as that shown in FIG. 3 after the application of a lateral temperature gradient during growth.

The practice of the present invention involves the growth of a crystalline body in accordance with the VLS technique described in the above-noted application. Briefly, the technique involves growth of a crystalline body comprising a first material by a process wherein a second material comprising an agent is contacted with a vapor containing the first material, the agent being such that it is capable of forming a liquid solution comprising the agent and the first material, in which solution the agent is maintained at a temperature above the initial freezing temperature of the solution and from which the first material freezes out of solution at the side of the solid-liquid interface. Vapor-agent contact is continued for a time period sufficient to supersaturate the liquid solution with respect to the first material, so resulting in the initiation of crystal growth.

The term "agent" as applied herein denotes a broad class of operative materials which may be employed in the practice of the VLS process. 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.

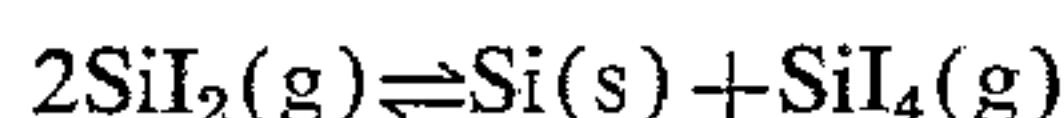
Agents employed in the practice of the invention desirably evidence a vapor pressure over the liquid solution of the order of a few millimeters of mercury or less in order to avoid excess loss thereof. It will be evident from the requirements outlined that the constituent or constituents of the agent 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 material to be 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 on the growth region by manual means or to deposit films of the agent of prescribed thickness by evaporation, electroplating, etc. Further, masks may be employed as desired to form specific arrays and patterns. The desired crystalline material may be furnished by any of the well known vapor transport processes, typical reactions being set forth below:

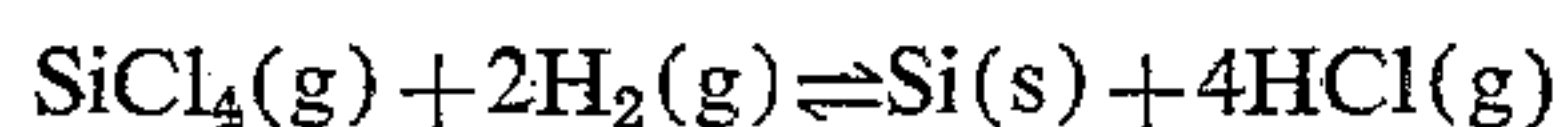
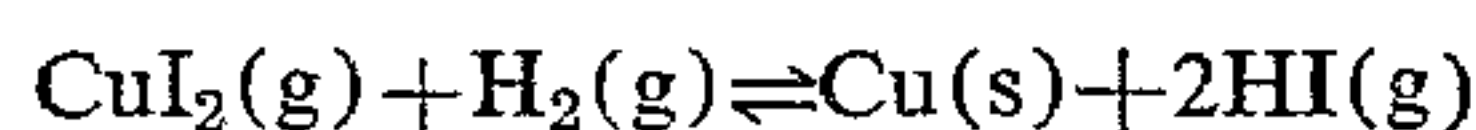
(a) Disproportionation



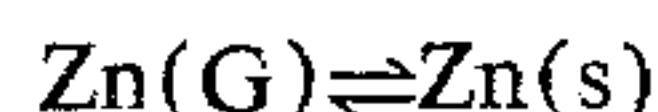
(b) Decomposition



(c) Reduction



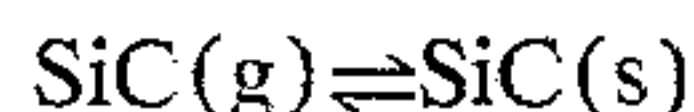
(d) Condensation



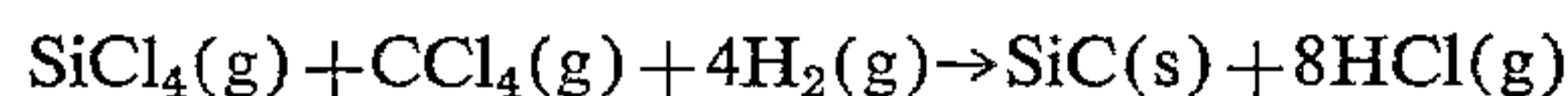
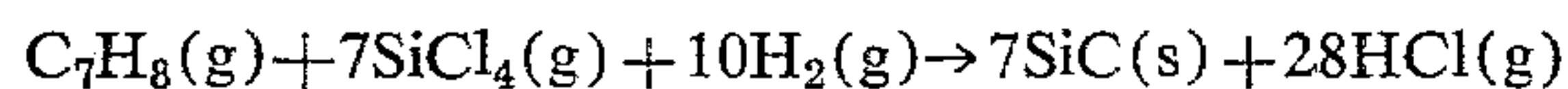
(e) $\text{Ga}_2\text{O}(\text{g}) + \text{As}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons 2\text{GaAs}(\text{s}) + \text{H}_2\text{O}(\text{g})$

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

(g) Condensation



(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 vaporized 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 vaporized 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 is 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.

With further reference now to FIG. 2, there is shown a front elevational view of a reaction chamber of the

type shown in FIG. 1 adapted with means for establishing a lateral temperature gradient during VLS growth. Shown in the figure is a heat source 37 provided with reflection means 38 for focusing said heat source upon window 39 in cylinder 28. In the operation of the process utilizing this embodiment a VLS crystal is first grown to a desired height with the heat source in the off position. Then, the heat source is turned on and focused upon the liquid alloy zone, thereby establishing a lateral temperature gradient and resulting in sufficient melt back to establish a change in interface morphology. VLS growth is continued with the heat source in the on position.

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 in which the chamber shown in FIG. 2 has been substituted.

An oriented single crystal of silicon was 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, vol. 108, pp. 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, preferential growth taking place in the [111] direction, as shown in FIG. 3. At a desired point in the processing, the heat source 37 is turned on and focused upon the liquid alloy droplet, so resulting in the establishment of a lateral temperature gradient. The temperature gradient results in an alteration of the contact angle configuration of the liquid droplet and the solid-liquid interface morphology, so that growth now occurs preferentially in a direction other than the [111], for example in the [11 $\bar{1}$] direction. Growth is continued until a crystal of a desired length is obtained. It will be understood by those skilled in the art that the means employed as a source of heat is not critical, a high powered lamp, a laser beam, etc. proving satisfactory. Similarly, the temperature is not critical and the degree of heating is merely that required to cause distortion of the alloy droplet, as observed visually.

As noted above, contact angle and an interface morphology during VLS crystal growth may be altered in an isothermal system by either (a) exertion of a physical force or (b) by means of sudden increases or decreases in the temperature of the liquid alloy zone during a hiatus in the process. Once again, the degree of physical force provided, as for example, by means of a gas stream, electromagnetic levitation, etc., is not critical nor is the degree of sudden cooling or heating, the degree of distortion of the alloy zone being the sole criterion

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for effecting a change in growth direction. For purposes of the present invention, however, temperature changes ranging up to 100° C. are considered satisfactory.

It will be further 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 1

This example describes the growth of kinked silicon crystals in accordance with the present invention 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.

The 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 SiCl₄ to H₂ was maintained at approximately 1:100 by means of cold bath 24. At this point in the process, valves 22, 26, 12, and 19A were closed and the temperature of the alloy droplet suddenly increased to 1000° C., thereby resulting in an increase in the volume of the droplet and an increase in contact angle since silicon melts at the solid-liquid interface. Heating was continued at 1000° C. until the droplet became unstable and ran down the side of the crystal. Thereafter, the temperature was lowered to 950° C., valves 22, 26, 12 and 19A opened and the VLS process continued, growth now occurring perpendicular to a new $\{111\}$ face.

EXAMPLE 2

The procedure of Example 1 was repeated with the exception that the temperature of the alloy droplet was suddenly decreased to 900° C. after cessation of the VLS process, so resulting in a reduction of the volume of the alloy droplet and the rupture thereof into two droplets.

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Then, the temperature was raised to 950° C. again and VLS continued by opening valves 22, 26, 12 and 19A. Growth was then noted perpendicular to the solid-liquid interface of both droplets, so resulting in a branched crystal.

EXAMPLE 3

The procedure of Example 1 was repeated with the exception that the VLS process was not interrupted. However, at a desired point in the process a high velocity gas stream was directed at the alloy droplet, so resulting in a change of the contact angle configuration of the liquid droplet. Continued growth was found not to be perpendicular to the original interface and deviated from the [111] direction.

What is claimed is:

1. In a method 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, the improvement which comprises halting the said vapor contacting, suddenly altering the temperature of said liquid solution for a time period sufficient to distort the configuration of said solution and continuing said vapor contacting.

2. A process in accordance with the procedure of claim 1 wherein said temperature is suddenly lowered.

3. A process in accordance with the procedure of claim 1 wherein said temperature is increased.

4. A process in accordance with the procedure of claim 1 wherein said substrate is silicon.

5. A process in accordance with the procedure of claim 2 wherein the temperature of said liquid source is lowered until said solution ruptures.

6. A process in accordance with claim 3 wherein the temperature of said solution is increased until said solution flows down the sides of said crystal.

7. In a method 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, the improvement which comprises altering the solid-liquid interface morphology by focusing a heat source upon said liquid solution during the course of the process.

8. In a method 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, the improvement which comprises mechanically altering the contact angle configuration of said liquid solution during the course of the process.

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9. A process in accordance with claim 8 wherein said altering is effected by causing a stream of gas to impinge upon said liquid solution.

10. A process in accordance with claim 8 wherein said altering is effected by electromagnetic means.

References Cited

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8

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5 ANDREW G. GOLIAN, Primary Examiner

U.S. Cl. X.R.

23-301; 117-106, 201; 148-16