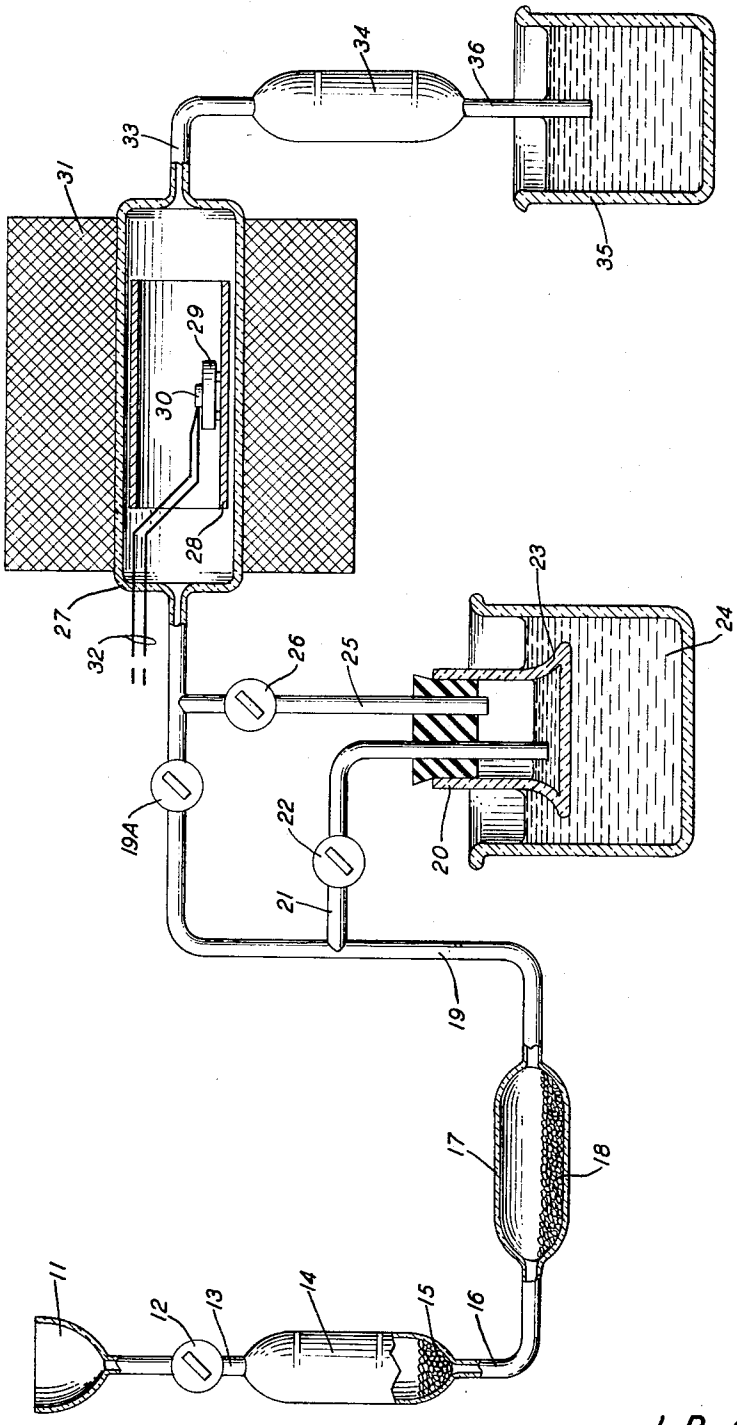
April 7, 1970 J. R. ARTHUR, JR., ET AL 3,505,127

VAPOR-LIQUID-SOLID CRYSTAL GROWTH TECHNIQUE FOR THE PRODUCTION OF NEEDLE-LIKE SINGLE CRYSTALS

Filed Sept. 21, 1967



INVENTORS J. R. ARTHUR, JR.
R. S. WAGNER

BY Edward M. Fink

ATTORNEY

United States Patent Office

3,505,127

Patented Apr. 7, 1970

3,505,127

VAPOR-LIQUID-SOLID CRYSTAL GROWTH TECHNIQUE FOR THE PRODUCTION OF NEEDLE-LIKE SINGLE CRYSTALS

John R. Arthur, Jr., Murray Hill, and Richard S. Wagner, Bernardsville, N.J., assignors to Bell Telephone Laboratories, Incorporated, Murray Hill, N.J., a corporation of New York

Filed Sept. 21, 1967, Ser. No. 669,535

Int. Cl. B01j *17/20*; C01b *33/00*

U.S. Cl. 148—1.6 3 Claims

ABSTRACT OF THE DISCLOSURE

Single crystal material of needle-like form may be obtained by means of the vapor-liquid-solid crystal growth technique, growth parameters of the growing crystalline material being controlled so as to result in the removal of the impurity agent and the concomitant decrease in the volume of the liquid solution and growth of crystalline materials evidencing sharp terminations.

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. 240,701, filed Jan. 28, 1964 now U.S. Patent 3,346,414, issued on Oct. 10, 1967.

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 crystals grown by conventional vapor-solid techniques and have, accordingly, been enthusiastically received by workers in the art; however, inherent limitations in the product have precluded total exploitation of the process. Studies have indicated that the tapered crystalline materials grown in accordance with this technique are of interest for use as field emission cold cathode emitters where in a basic requirement is the presence of a needle-like structure with a tip evidencing a radius of curvature less than 1 micron. Unfortunately, the crystalline materials grown in accordance with the well-known VLS procedure described in the copending application, alluded to hereinabove, have not proven entirely satisfactory for such purposes in that a cumbersome etching procedure has been required in order to obtain the desired radius of curvature. Accordingly, the interest of workers in the art has been focused upon this problem.

In accordance with the present invention, it has been determined that this prior art limitation may be effectively overcome by a novel procedure wherein the growth parameters are controlled so as to result in gradual removal of the impurity agent from the liquid solution. This end may be attained by (a) utilizing a deposition temperature such that the rate of evaporaton of the impurity agent is sufficient to decrease the volume of the liquid solution; (b) utilizing an agent having a distribution coefficient within the range of 10^{-2} to 10^{-1} whereby the agent is removed from the liquid by incorporation in the

crystalline material being grown; (c) selectively removing the agent from solution by means of a chemical reaction whereby a volatile compound is produced; (d) gradually reducing the rate of co-deposition in those situations wherein an agent manifesting a high vapor pressure is utilized; (e) utilizing an agent which is one component of the material to be grown and introducing a vapor comprising a second component of the material to be grown into the liquid solution until the volume of the liquid solution is exhausted; and (f) selected combinations of the foregoing alternatives.

The invention has been described largely in terms of the growth of needle-like tapered silicon crystals by the vapor-liquid-solid mechanism. However, it will be understood by those skilled in the art that such description is for purposes of exposition only and is not to be construed as restrictive in nature.

The invention will be more readily understood by reference to the following detailed description taken in conjunction with the accompanying drawing, wherein:

The figure is a schematic front elevational view of a typical apparatus utilized in the practice of the present invention.

The technique described herein involves the 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 site of the agent. 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. At this juncture in the growth process, the temperature of the system is gradually elevated to a point sufficient to cause the evaporation of the agent, thereby decreasing the volume of the liquid solution and the diameter of the growing crystal during the deposition process, vapor agent contact being continued until the agent has completely evaporated. Crystals grown in accordance with this technique have been found to evidence a conical shape having a tip diameter of the proportions previously noted.

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 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 may be required to evidence a vapor pressure over the liquid solution of sufficient magnitude to assure the continuous evaporation thereof at the operating temperatures. It will be evident from the requirements outlined that the constituent or constituents of the agent may 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. Thus, it may be desirable to utilize k factors of the order of 10^{-5}

wherein the vapor pressure of the agent is as small as 10^{-6} torr.

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, in the growth of needle-like VLS crystals in accordance with the invention, it is desirable that the contact angle between the liquid solution and the substrate or crystalline body be as high as 90° or greater.

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, and so forth. 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—$2SiI_2(g) \rightleftharpoons Si(s) + SiI_4(g)$

(b) Decomposition—$CuI_2(g) \rightleftharpoons Cu(s) + 2I(g)$

(c) Reduction—$CuI_2(g) + H_2(g) \rightleftharpoons Cu(s) + 2HI(g)$

$SiCl_4(g) + 2H_2(g) \rightleftharpoons Si(s) + 4HCl(g)$

(d) Gaseous cracking—$C_7H_8(g) + 7SiCl_4(g) + 10H_2(g) \rightarrow 7SiC(s) + 28HCl(g)$

$CH_3SiCl_3(g) \rightarrow SiC(s) + 3HCl(g)$

$SiCl_4(g) + CCl_4(g) + 4H_2(g) \rightarrow SiC(s) + 8HCl(g)$

$SiH_4(g) + CH_4(g) \rightarrow SiC(s) + 4H_2(g)$

(e) $SiH_4(g) \rightarrow Si(s) + 2H_2(g)$

(f) Evaporation-condensation—$Si(g) \rightarrow Si(s)$

With reference now more particularly to the figure, 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** containing purification medium **15**. Thereafter, the gas passes from trap **14** via conduit **16** and proceeds to a second trap **17** containing a purification medium **18**. 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 onto 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 sharpened 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 the figure.

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, 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 technique 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 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 until such time as it is desired to initiate the sharpening process. At this point, the temperature of the system is gradually elevated so as to result in the evaporation of the agent thereby decreasing the volume of the liquid solution and the diameter of the growing crystal. Evaporation is continued until a state of exhaustion of the agent is attained and the process is then terminated.

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 in accordance with the present invention by the hydrogen reduction of silicon tetrachloride in an apparatus similar to that shown in the figure.

A silicon wafer 15 mm. x 25 mm. x 1 mm. with {111} 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 following by a 4 minute treatment with a 1:2:6 solution of hydrofluoric, acetic and nitric acids. Next, the etched substrate was washed with deionized water and dried in an oven at 110° C.

Following, gold particles approximately 100 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 1050° 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 1½ hours, the flow of hydrogen through the system being maintined at approximately 350 $cm.^{-3}$ per minute, and the molar ratio of silicon tetrachloride to hydrogen being maintained at approximately 1–100 by means of cold bath **24**. At this point in the process, the temperature of the system was gradually elevated to 1150° C. and maintained at this temperature for one hour with a hydrogen flow of 450 $cm.^{-3}$ per minute, so resulting in the evaporation of the agent and a decrease in the volume of the liquid solution with a concomitant decrease of the diameter of the grow-

ing crystal until the agent was totally exhausted. The resultant needle-like crystals were found to be highly perfect in nature. A linear array of fine VLS grown silicon whisker emitters, approximately 1 mm. in length, grown upon a silicon substrate crystal were mounted approximately 3 mm. from a fluorescent screen anode placed perpendicular to the whisker axes. The substrate crystal containing the whiskers and the anode assembly was mounted in a glass ultra-high vacuum chamber which was baked at 300° C. for 12 hours in order to obtain a background gas pressure of 5×10^{-9} torr. After cooling the substrate crystal to 77° Kelvin with liquid nitrogen, current-voltage data was obtained, the data indicating that the current was due to field emission. The pattern on the fluorescent screen consisted of many randomly arrayed spots with a spread of approximately 2.5 mm. perpendicular to the line of emitters, and 5 mm. along the line of emitters, indicating that more than one whisker in the array was emitting since the maximum possible spread of emission from one whisker could not have extended more than 3 mm. due to the small emitter-anode separation.

EXAMPLE II

The procedure of Example I was repeated with the exception that the temperature of the system was maintained within the range of 1140°–1150° C. for a time period of approximately three hours, the flow of hydrogen through the system being maintained at approximately 450° $cm.^{-3}$ per minute. The resultant crystals were found to be evenly tapered with very sharp points having a tip diameter less than 1 micron.

EXAMPLE III

The procedure of Example I was repeated with the exception that the temperature of the system was maintained at 800° C. utilizing the thermal decomposition of silane as the vapor transport mechanism and tin as the agent. The process was continued until all the tin was exhausted by means of incorporation into the crystalline material being grown. The resultant crystals were found to be evenly tapered with very sharp points having a tip diameter less than 1 micron.

EXAMPLE IV

The procedure of Example III was repeated with the exception that copper was utilized as the agent and small amounts of silicon tetrachloride were introduced into the system during the process, so resulting in the chemical reaction of the copper with the silicon tetrachloride to yield copper chloride ($CuCl_2$). The process was continued until the agent was exhausted by total reaction with the silicon tetrachloride, so resulting in the formation of evenly tapered crystals with sharp points having a tip diameter less than 1 micron.

EXAMPLE V

A gallium arsenide wafer, 2 mm. x 3 mm. x ½ mm. with (111) and ($\overline{1}\overline{1}\overline{1}$) 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 droplets were then placed upon the surface of the etched substrate which was then positioned in a quartz tube. Next, a mixture of gaseous arsenic (As_2) at a pressure of 10^{-6} torr and gaseous gallium at a pressure of 5×10^{-7} torr obtained from a gallium arsenide crystal heated to 700° C., was introduced into the system and the temperature of the system elevated to 500° C. The reaction continued until the gallium agent was completely exhausted, so resulting in a plurality of tapered sharp gallium arsenide points having a tip diameter less than 1 micron.

What is claimed is:

1. In the 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 period sufficient to supersaturate the said solution with respect to the said first material, thereby initiating crystallization at the said site, the improvement which comprises controlling the growth parameters by effecting the gradual evaporation of said agent from the liquid solution, thereby decreasing the volume of the liquid solution and the diameter of the said rystalline body and continuing the process until the agent .s completely exhausted.

2. A process in accordance with the procedure of claim 1 wherein said crystalline body comprises silicon.

3. In the 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 period sufficient to supersaturate the said solution with respect to the said first material, thereby initiating crystallization at the said site, the improvement which comprises controlling the growth parameters by selectively removing the agent by reacting said agent with a material which forms a volatile compound with said agent, and volatilizing said compound, thereby decreasing the volume of the liquid solution and the diameter of the said crystalline body, and continuing the process until the agent is completely exhausted.

References Cited

UNITED STATES PATENTS

2,789,068	4/1957	Maserjian	148—185
3,346,414	10/1967	Ellis et al.	148—1.6

OSCAR R. VERTIZ, Primary Examiner

H. S. MILLER, Assistant Examiner

U.S. Cl. X.R.

23—204, 273, 301; 148—1.5; 252—62.3