VAPOR-LIQUID-SOLID CRYSTAL GROWTH TECHNIQUE


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8 Claims

ABSTRACT OF THE DISCLOSURE

The controlled growth of a crystalline material upon a seed crystal is effected by means of the vapor-liquid-solid crystal growth mechanism, the seed crystal being physically isolated from the vapor source by immersion thereof in a liquid solution supersaturated with respect to the crystalline material.

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.


Briefly, the VLS technique involves growth of a crystalline body from a supersaturated liquid solution or liquid alloy zone in contact with the solid material being grown and exposed to a vapor. In the operation of the process, the liquid alloy zone is contacted with a vapor and 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 growth techniques from the standpoint of crystalline perfection and have, accordingly, been enthusiastically received by workers in the art. However, certain process limitations have precluded total exploitation of the technique. Thus, it has been found that the growth of macroscopic crystalline materials has been handicapped by large contact angles between the liquid alloy zones and the substrate, so resulting in “balling up” of an initially thin liquid alloy zone, and the growth of a plurality of independent needles. Additionally, it has been found that simultaneous vapor-solid deposition during the VLS growth process may be undesirable in that vapor-solid growth may compete with VLS growth. Accordingly, continued interest in VLS techniques has been focused upon these limitations.

In accordance with the present invention, a technique for effectively obviating these prior art limitations is described wherein crystalline materials of microscopic size are grown via the VLS mechanism, the solid or substrate material being present in the form of a seed crystal which is physically isolated from the vapor source by the liquid alloy zone, which is of sufficient thickness to avoid “balling up.” Studies have revealed that the isolated seed not only prevents chemical attack of an exposed substrate and VLS grown crystals by entering vapor or deleterious reaction products but also prevents concurrent vapor-solid deposition, thereby making possible a wider choice of vapor phase reactions. Furthermore, crystal growth from the seed into the melt has been found to be free of the inhibiting effect of inordinately large contact angles, thereby lifting the restrictive effect on the maximum diameter of crystal that may be grown. The inventive technique contemplates that at least 25 atom percent of the material to be grown comes from the vapor and in preferred embodiments at least 40 atom percent.

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 employed in the practice of the present invention.

The practice of the present invention involves the growth of crystalline body in accordance with the VLS technique described in the above-noted application.

Specifically, the technique involves the controlled growth of a crystalline body upon a seed crystal by a process wherein a material comprising a liquid solution of an agent saturated with respect to said crystalline body at the reaction temperature is contacted with a vapor containing at least one constituent of the material to be grown. During the operation of the process, the liquid solution attains supersaturation with respect to the crystalline body which freezes out of solution at the site of the solid-liquid interface, such being physically isolated from the vapor source. Isolation of the seed crystal from the vapor source is effected by immersion thereof in the liquid solution.

The term “agent,” as applied herein, denotes a broad class of operating materials which will 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 seed crystal. 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 and in the seed crystal 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.

As described above, deposition of a vaporous material is initiated at the site of the agent, a requirement being that the agent be placed in the desired site of crystalline growth in an independent manipulative step. This step is most conveniently effected by surrounding the said seed crystal with a liquid solution of the agent and the material to be grown so that the seed crystal is immersed therein. The desired crystalline material may be furnished by any of the well known vapor transport processes, typical reactions being set forth below:

REATIONS

(a) Disproportionation:

\[ 2\text{Si}_2\text{O}_3(g) = \text{Si}_3(s) + 2\text{Si}_4O(g) \]
(b) Decomposition:
$$\text{CuI}_2(g) \rightarrow \text{Cu}(s) + 2I(g)$$

(c) Reduction:
$$\text{CuI}_2(g) + \text{H}_2(g) \rightarrow \text{Cu}(s) + 2\text{HI}(g)$$
$$\text{SiC}_14(g) + 2\text{H}_2(g) \rightarrow 2\text{Si}(s) + 14\text{H}(g)$$

(d) Condensation:
$$\text{Zn}(g) + 2\text{Zn}(s)$$
$$\text{Ga}_2\text{O}(g) + 2\text{As}(g) + \text{H}_2(g) \rightarrow 2\text{GaAs}(s) + \text{H}_2\text{O}(g)$$
$$\text{Ga}_{2}\text{O}(g) + 2\text{P}(g) + \text{H}_2(g) \rightarrow 2\text{GaP}(s) + \text{H}_2\text{O}(g)$$
$$\text{Si}(g) \rightarrow \text{Si}(s)$$

(g) Gaseous Cracking:
$$\text{C}_2\text{H}_6(g) + 7\text{SiCl}_4(g) + 10\text{H}_2\text{O}(g) \rightarrow 7\text{Si}(s) + 28\text{HCl}(g)$$
$$\text{CH}_2\text{SiCl}_3(s) \rightarrow \text{Si}(s) + 3\text{HCl(g)}$$
$$\text{SiCl}_4(g) + \text{CCL}_4(g) + 4\text{H}_2(g) \rightarrow \text{Si}(s) + 8\text{HCl(g)}$$
$$\text{SiH}_2(s) + \text{CH}_2\text{SiCl}_3(s) \rightarrow \text{Si}(s) + \text{H}_2\text{Cl}_4(s)$$

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

(l) \text{SiH}_2(s) \rightarrow \text{Si}(s) + 2\text{H}_2(g)$$

With reference now more particularly to the figure, there is shown a schematic front elevation 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 contains 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 gases passing through saturator 20 emerge together with vaporized liquid via conduit 25 controlled by valve 26 and proceeds to reaction chamber 27. Chamber 27 may be a fused silica tube having disposed therein a container 28 containing a seed crystal 29 held in place by means of quartz fasteners 30. The agent employed herein is introduced to the system in liquid form from container 30A. Chamber 27 is suitably heated by means of RF heater 31. 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 seed crystal 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 seed crystal of substrate material and initially ground flat with a suitable abrasive end subsequently etched. Hydrogen is chosen as the reactive gas and silicon tetrachloride in liquid form is inserted in saturator 20.

Following, seed crystal 29 is placed in the apparatus of the figure and fastened by means of holders 30. Thereafter, gold-silicon alloy of the appropriate chemical composition is placed in container 30A and heater 31 is turned on to a temperature sufficient to melt the gold-silicon alloy. Next, the now liquid alloy is caused to flow around seed crystal 29 so as to result in the submersion thereof. Subsequently, the temperature of the system is elevated sufficiently to cause partial dissolution of the seed crystal, thereby presenting a clean crystal surface.

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 deposits in the liquid alloy zone which eventually attains a state of supersaturation with respect to silicon thereby causing silicon to migrate through the liquid alloy zone to the seed crystal where the silicon freezes out of solution at the interface between the seed and the liquid alloy, the seed crystal growing into the melt. Agitation of the melt during the processing increases the employable growth rate and decreases the statistical likelihood of spontaneous nucleation of silicon in the melt. Agitation may conveniently be effected by means of an encapsulated magnetic stirrer, by inductive stirring, by two or three-phase rotation of an electromagnetic field, by rotation of the seed crystal, and so forth.

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 its chemical stability. In much the same fashion, platinum, palladium, silver, copper, nickel, and so forth, 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 the material to be grown and that it be chemically inert.

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 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] faces was selected as the seed crystal. The crystal was ground flat on abrasive paper and given a bright etch to expose undamaged crystal surfaces. The etching procedure involved treating for three minutes with a 1:1 solution of hydrofluoric and nitric acids. Next, the etched substrate was washed with deionized water and dried in an oven at 110° C.

Following, the seed crystal was placed in the apparatus and fastened by means of quartz holders. Thereafter, gold-silicon alloy of the appropriate composition in solid form was placed in container 30A and heater 31 turned on to a temperature of 900° C., the alloy melting to form a liquid alloy. The container 30A was next tipped so as to result in the flow of liquid alloy around the seed crystal until it was completely submerged.

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, and chamber 27 was heated to 950° C. for a period of 10 minutes, so resulting in partial dissolution of the seed crystal.

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 in the liquid alloy zone for 2½ hours. The flow of hydrogen through the system was maintained within the range of 10 liters per minute, and the molar ratio of silicon tetrachloride to hydrogen was maintained at approximately 1/50 by means of cold bath 24. Agitation of the melt during the process was effected by means of inductive stirring. The resultant...
Example II

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 800° C. being used in the hydrogen reduction of germanium tetrachloride. The liquid alloy solution was obtained by adding a sufficient quantity of a solid gold-germanium alloy to container 30A and heating to a temperature of 750° C. before tipping upon the seed crystal. The resultant germanium crystals were of macroscopic size and evidenced growth on all exposed faces.

Example III

This example describes the growth of gallium arsenide crystals in accordance with the present invention.

A gallium arsenide wafer 2 mm. x 3 mm. x ½ mm. with (111) and (111) faces was chosen as the seed crystal. The wafer was ground flat and etched for 30 seconds with aqua regia. Next, the seed crystal was placed in a reaction chamber and a liquid mixture of gallium and gallium arsenide introduced thereto in the manner described so as to completely cover the seed crystal. Following, arsenic vapor was introduced by conventional means into the reaction chamber, the pressure being higher than the equilibrium vapor pressure of arsenic over the liquid alloy. The resultant gallium arsenide crystals were of high crystalline perfection and macroscopic in nature.

Example IV

The procedure of Example I was repeated with the exception that the vapor transport reaction employed was the hydrogen reduction of germanium tetrachloride. The liquid alloy solution was heated to 750° C., poured over the seed crystal and the vapor introduced thereto at a temperature of 800° C. The resultant germanium crystals were of macroscopic size.

What is claimed is:

1. A method for the controlled growth of a crystalline body upon a seed crystal which comprises the steps of contacting a liquid solution of a material comprising an agent saturated with respect to said seed crystal with a vapor comprising at least one constituent of the material to be grown and continuing said contacting for a time period sufficient to supersaturate the said solution with respect to said crystalline body, thereby initiating crystallization at the interface between said solution and said seed crystal, the said seed crystal being immersed in said solution thereby precluding direct contact between said vapor and said seed crystal, at least 25 atom percent of the material to be grown coming from the vapor.

2. A method in accordance with claim 1 wherein said seed crystal is silicon.

3. A method in accordance with claim 1 wherein said seed crystal is germanium.

4. A method in accordance with claim 1 wherein said seed crystal is gallium arsenide.

5. A method in accordance with claim 2 wherein said vapor is furnished by means of the hydrogen reduction of silicon tetrachloride.

6. A method in accordance with claim 2 wherein said vapor is furnished by means of the hydrogen reduction of germanium tetrachloride.

7. A method in accordance with claim 3 wherein said vapor is furnished by means of the hydrogen reduction of germanium tetrachloride.

8. A method in accordance with claim 4 wherein said vapor is arsenic.

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