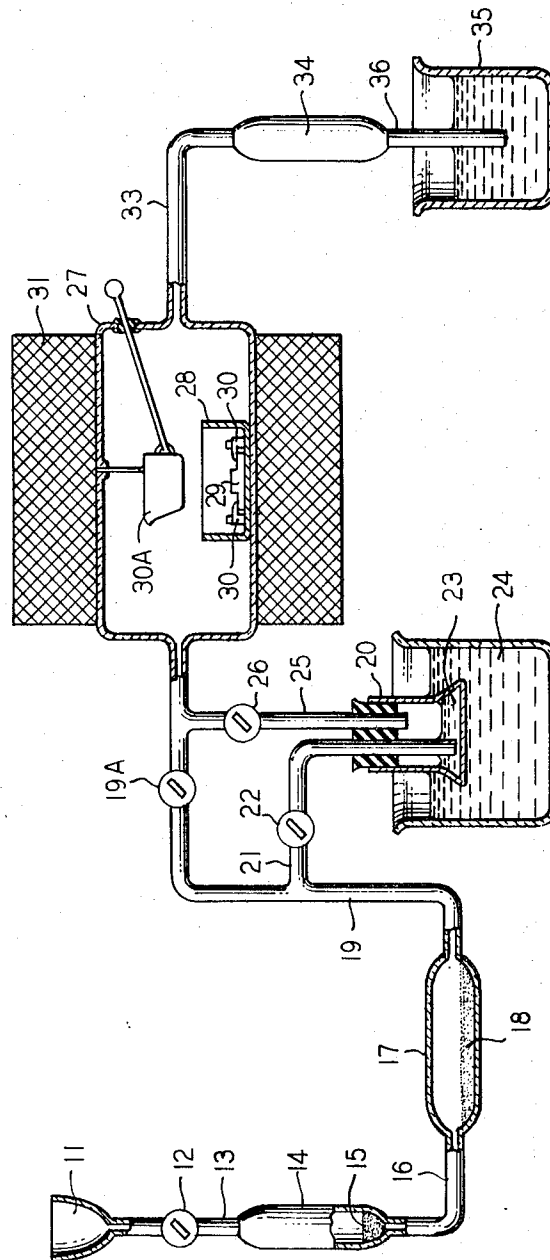


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CRYSTAL GROWTH TECHNIQUE
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CRYSTAL GROWTH TECHNIQUE

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6 Claims

ABSTRACT OF THE DISCLOSURE

Growth of crystalline materials is effected by providing a liquid-alloy solution comprising an agent and the material to be grown at a point intermediate a vapor and the desired site of crystal growth. In the operation of the process, the vapor selectively removes the agent from the liquid-alloy solution by chemical reaction therewith, so resulting in supersaturation of the liquid-alloy solution with respect to the material to be grown and crystal growth.

This invention relates to a technique for the growth of crystalline materials. More particularly, the present invention relates to a crystal growth procedure utilizing a chemical vapor etching technique.

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. Specifically, the inventive technique relates to the controlled growth of a crystalline body comprising a first material wherein a second material comprising an agent is contacted with a vapor including a material capable of chemically reacting with and removing the agent in vapor form from the second 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 sufficient to supersaturate the liquid solution with respect to the first material, the agent being removed from the solution continuously until the etching process is terminated or until the agent is completely exhausted.

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 process, substrates may or may not be present and, when present, may serve as a physical support and may be chosen to react or dissolve the agent.

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. 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 semiconductive materials, high melting refractory and ceramic crystals, in the bonding of similar or dissimilar materials and so forth.

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 an apparatus utilized in the practice of the present invention for the growth of crystalline bodies.

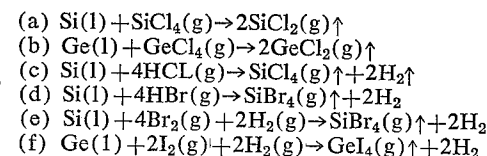
The term "agent" as applied herein denotes a broad class of operative materials which may be employed in

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 or admixed with one or more constituents of the desired crystalline material, or, if present, with one or more constituents of a substrate material.

Agents employed in the practice of the invention desirably evidence a vapor pressure over the liquid solution of the order of a few millimeters or less 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 the 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. 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 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, reaction 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. This step is also 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 chemical reaction used to selectively remove the agent may be furnished by any of the well known vapor transport processes, typical reactions being set forth below:



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

The apparatus shown includes a source of an inert gas, a saturating system and a reaction chamber. An inert 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 satu-

rator 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 inert gas is maintained by refrigerating saturator 20 with a suitable cold bath 24. Inert 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 container 28 containing a seed crystal 29 held in place by means of quartz fastener 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 platinum crystals are grown upon a platinum seed crystal by the described technique utilizing silicon as the agent and removing the silicon from the liquid-alloy solution with vaporous silicon tetrachloride.

A seed crystal of platinum is chosen as the substrate material and initially ground flat with a suitable abrasive. Argon is chosen as the carrier 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, a silicon-platinum alloy of the appropriate chemical composition is placed in container 30A and heater 31 is turned on to a temperature sufficient to melt the silicon-platinum alloy with argon flowing through the system. 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 removal of the agent (silicon) from the liquid-alloy solution initiated. The conditions employed in such techniques are well known to those skilled in the art.

During the course of the processing, the silicon tetrachloride vapor selectively removes the silicon agent from the liquid-alloy solution by chemically reacting therewith, so leading to a state of supersaturation of the solution with respect to platinum, thereby causing platinum to freeze out of solution together with a minute concentration of silicon at the interface between the platinum seed crystal and the liquid alloy, the seed crystal growing into the melt. Agitation of the melt during the processing increases the employable growth rate. 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, etc.

It will be understood by those skilled in the art that silicon 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 platinum. In much the same fashion, germanium, gallium arsenide, etc. 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 at a temperature below the melting temperature of the latter. Examples of the present invention are described in detail below. The 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 platinum crystals by the removal of silicon from a liquid-alloy solution of

platinum and silicon in an apparatus similar to that shown in the figure.

A platinum seed crystal, 10 mm. x 5 mm. x 1 mm. 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 a 5 minute etch in aqua regia.

Following, the seed crystal was placed in the apparatus and fastened by means of quartz holders. Thereafter, a platinum-silicon alloy of the appropriate composition (77 atomic percent Pt and 23 atomic percent Si) in solid form was placed in container 30A. Next, with valves 22 and 26 in the closed position and with valves 12 and 19A in the open position, argon was passed through the system and chamber 27 heated to 1000° 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. Subsequently, the temperature in chamber 27 was increased to 1020° C. for 10 minutes, so resulting in partial dissolution of the seed crystal.

The flow of argon through the system was maintained within the range of 200 to 300 cc. per minute, and the molar ratio of silicon tetrachloride to argon was maintained at approximately 0.1 to 0.01 by means of cold bath 24. The resultant platinum crystals were of macroscopic size and induced growth on all exposed faces.

EXAMPLE II

The procedure of Example I was repeated with the exception that the platinum seed crystal was not completely immersed in a liquid-alloy solution of platinum and silicon. The resultant platinum crystals were of macroscopic size and evidenced growth on all exposed faces.

EXAMPLE III

The procedure of Example II was repeated with the exception that two seed crystals of platinum were utilized and the liquid-alloy zone was situated at a point intermediate the two crystals. The removal of the silicon agent from the liquid-alloy zone again resulted in the freezing out of platinum at the solid-liquid interface and the ultimate bonding of the two seed crystals at a temperature of approximately 1000° C., a temperature significantly lower than that which would have been required to join such materials by any of the conventional prior art materials.

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 capable of reacting chemically with said agent, 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 remove said agent from the said solution in vapor form at the liquid-vapor interface, so resulting in supersaturation of 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 1 wherein said first material is immersed in said liquid solution.

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4. A process in accordance with the procedure of claim 1 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 of the surface of the said substrate.

5. 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.

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

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