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[54] GROWTH OF NEEDLELIKE VLS CRYSTALS

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[58] **Field of Search** .....117/106 A, 201

[56] **References Cited**

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[57] **ABSTRACT**

Single crystal material of needlelike 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.

2 Claims, No Drawings

GROWTH OF NEEDLELIKE VLS CRYSTALS

This application is a division of copending application Ser. No. 669,535, filed Sept. 21, 1967 now Pat. No. 3,505,127.

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 U.S. Pat. No. 3,346,414, granted 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 wherein a basic requirement is the presence of a needlelike 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 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 (in an excess beyond stoichiometry) into the liquid solution until the volume of the liquid solution is exhausted.

The invention has been described largely in terms of the growth of needlelike tapered gallium arsenide 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 technique described herein involves the growth of a crystalline body comprising a first material by a process wherein a second material comprising an agent, which is one component of the material to be grown, is contacted with a vapor containing a second component of the material to be grown, 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 upon reaction of the agent with the vapor and the attainment of supersaturation of the liquid solution with respect to the first material, so resulting in the initiation of crystal growth. Growth is continued until the agent is completely exhausted. 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. The agent may also contain a minor constituent desired in the material being crystallized.

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

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

d. Gaseous Cracking—$SiH_4(g) \rightarrow Si(s)+2H_2(g)$

e. Evaporation—Condensation—$Si(g) \rightarrow Si(s)$

The present invention may conveniently be described in detail by reference to an illustrative example in which sharpened gallium arsenide crystals are grown upon a gallium arsenide substrate by the reaction of a gallium agent with an excess beyond stoichiometry of arsenic.

A gallium arsenide wafer is chosen as the substrate material and initially ground flat with a suitable abrasive and etched. Following, the substrate is rinsed and dried in air after which gallium droplets are placed thereon. Then, the substrate is positioned in a quartz tube and a mixture of gaseous arsine and gallium trichloride admitted thereto, the volume of arsenic being in excess of that required to react with both the gallium present in the gaseous form and that present as agent. The system is then heated to a temperature within the range of 800° to 900° C.

During the course of the processing, gallium arsenide preferentially deposits at the site of the liquid droplet which eventually attains a state of supersaturation with respect to gallium arsenide, thereby causing gallium arsenide to freeze out of solution. As the process continues, the gallium agent is gradually consumed by reaction with the excess arsenic in the vapor so as to result in the exhaustion of the agent, thereby decreasing the volume of the liquid solution and the diameter of the growing crystal. Vapor-agent contact is continued until a state of exhaustion of the agent is attained and the process is then terminated.

An example of the present invention is described in detail below. This example 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

A gallium arsenide wafer, 2 mm. ×3 mm.×½ mm. with (111) and ($\overline{111}$) 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. The substrate was then heated in a hydrogen atmosphere to a temperature of about 800° C. Subsequently, a gaseous mixture comprising arsine (AsH_3), gallium trichloride ($GaCl_3$) and hydrogen was introduced into the system, the mol ratio of arsine to gallium trichloride being adjusted to yield an excess of arsenic beyond stoichiometry. 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 utilizing an agent which is one component of the material to be grown and introducing a vapor comprising an excess beyond stoichiometry of a second component of the material to be grown into the liquid solution until the volume of the liquid solution is exhausted, the agent chemically reacting with the vapor to yield the desired crystalline body.

2. A method in accordance with the procedure of claim 1 wherein said agent is gallium and said crystalline material is gallium arsenide, the said vapor comprising gallium trichloride and arsine, the arsine being present in an amount in excess of stoichiometry.

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