

[72] Inventors **Wilhelmus Franciscus Knippenberg; Gerrit Verspui, both of Emmasingel, Eindhoven; Johan Charles Marie Basart, Heeze, all of Netherlands**

[21] Appl. No. **815,678**

[22] Filed **Apr. 14, 1969**

[45] Patented **Jan. 4, 1972**

[73] Assignee **U.S. Phillips Corporation
New York, N.Y.**

[32] Priority **Apr. 13, 1968**

[33] **Netherlands**

[31] **6805300**

[56] **References Cited**

UNITED STATES PATENTS

3,493,431	2/1970	Wagner	117/201 X
3,346,414	10/1967	Ellis et al.	117/201 X

Primary Examiner—Alfred L. Leavitt
Assistant Examiner—K. P. Glynn
Attorney—Frank R. Trifari

[54] **CRYSTALS, IN PARTICULAR CRYSTAL WHISKERS AND OBJECTS COMPRISING SUCH CRYSTALS**

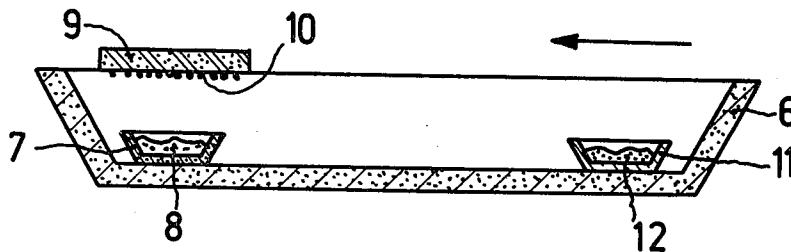
11 Claims, 3 Drawing Figs.

[52] U.S. Cl. 117/106,
117/201, 23/300

[51] Int. Cl. C23c 11/00,
C23c 13/00

[50] Field of Search 117/106,
201

ABSTRACT: A method of manufacturing filamentary crystals, i.e., whiskers, and controlling the growth thereof in which a substrate on which are provided particles of a metal powder is heated so that the metal particles melt and form molten droplets while an atmosphere containing the substance forming the crystals is passed over the substrate. The substrate is dissolved in the metal droplets and precipitates growing a filament of whisker epitaxially. The thickness of the crystal is then controlled by adjusting the partial pressure of the metal in the atmosphere which controls the size of the droplets. In some cases, a separate source of metal for controlling the partial pressure of the metal in the atmosphere is provided.



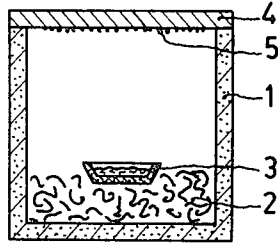


fig.1

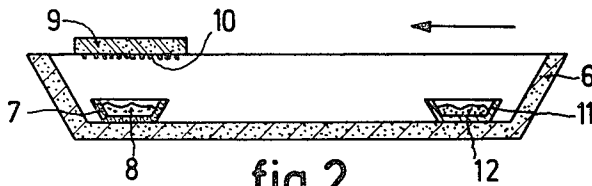


fig.2

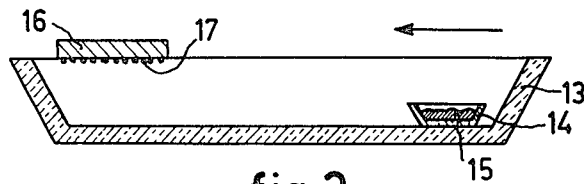


fig.3

INVENTORS
WILHELMUS F. KNIPPENBERG
BY GERRIT VERSPUI
JOHAN C. BASART

Frank R. Swifani
AGENT

CRYSTALS, IN PARTICULAR CRYSTAL WHISKERS AND OBJECTS COMPRISING SUCH CRYSTALS

The invention relates to the manufacture of crystals in which the crystal growth takes place by a VLS-mechanism. The invention relates in particular to the manufacture in this manner of thin filamentary crystals, sometimes referred to as whiskers, which are to be understood to mean herein elongate crystals independently of the shape of their transverse cross section. The invention moreover relates to crystals thus manufactured and to objects comprising such crystals.

Crystal growth by a VLS-mechanism (Vapour-Liquid-Solid) is described in Transactions of the "Metallurgical Society of the AIME" 233 (1965), 1053 et seq. In crystal growth of the above type the substance to be crystallized or its components are taken up from a gaseous phase by droplets provided locally on a substrate and consisting of a metal in which the substance to be crystallized is soluble, the substance being deposited on the substrate by the intermediation of the said droplets.

The crystal growth is strongly anisotropic and actually it takes place substantially only at right angles to the surface of the substrate. This is a result of the circumstance that the absorption of the substance to be crystallized or its components from the gaseous phase occurs preferentially at the free surface of the liquid metal phase, whereas the deposition takes place at the droplet-substrate-interface only.

The shape of the resulting crystal is slightly conical mainly as a result of the decrease of the volume of the metal droplets due to evaporation, particularly in the case of prolonged growth. Other factors also may possibly stimulate said conical growth, for example, as stated on page 1059 of the above-mentioned paper, a laminated growth on the side faces of the crystal. Moreover the evaporation of metal has for its result that the longitudinal growth of the crystals is limited.

One of the objects of the invention in VLS-growth is to control the thickness of the crystals and/or to obviate said limitation in longitudinal growth.

The invention relates to a method of manufacturing crystals, particularly filamentary crystals, such as whiskers, in which crystal growth takes place by a VLS-mechanism, which is characterized in that the thickness of the crystals during the growth is controlled by controlling the size of the droplets of the metal which in the VLS-growth serves as the liquid phase.

The influence of the factors which may cause thickness variations during the crystal growth can be completely compensated for by adjusting the size of the metal droplets by means of adjusting the above partial pressure so that crystals with a constant thickness are obtained. Alternatively, however, crystals with a previously determined variation in thickness can be obtained by varying the size of the droplets continuously or discontinuously during the growth by varying the said partial pressure. Further, since the metal droplets can be maintained, restriction in the longitudinal growth due to disappearance of the metal can be avoided.

For enlarging the droplets or keeping the size thereof constant a partial metal pressure in the crystallization atmosphere is required which is larger than that which is caused by evaporation of the metal droplets. Therefore an extra addition of metal is necessary.

For that purpose, the crystallization atmosphere is put into contact with a source of the metal or the metal compound, the partial metal pressure in the crystallization space being adjusted by the temperature to which said source is exposed.

In case the crystallization is not effected in a closed system but in a gas current the possibility occurs that this gas may be used as a transport medium for the metal and the compound, respectively, and the amount of metal supply or drain, may be controlled by means of the flow rate of the gas.

For temporarily reducing the droplets forced removal of metal may be obtained by temporarily reducing the gas pressure and/or temporarily lowering the temperature of a metal source if present. For the same purpose, in case crystallization is carried out in a gas current, temporarily the gas being conducted through the crystallization space may be given a con-

tent of the metal or the metal compound which is lower than that in the crystallization atmosphere or may be entirely free from them.

According to another embodiment of the method a substance is added to the gas current which reacts with the metal while forming a volatile compound so that metal of the droplets is carried away with the gas.

A favorable condition in supplying and removing metal via the gaseous phase for adjusting the droplet size is that this occurs preferentially at the liquid metal surface, similar to the absorption from the gaseous phase of the substance to be crystallized and its components, respectively.

When any metal deposition on the side faces of the crystals occurs a favorable use of this deposition may be made in the case these crystals are destined in the form of whiskers, to reinforce materials which do not or poorly wet the crystals as such. This is the case, for example, with whiskers of silicon carbide which are not wetted by most of the metals and alloys but in the presence of an adhering metal deposition also show a more effective adhesion to metals, in which they are incorporated by introducing them into a melt of such a metal for improving the mechanical properties.

The metal deposition on the crystals may be promoted, if required, by strongly increasing for a short period of time the partial pressure of the metal vapor prior to terminating the crystal growth.

On the other hand eventually undesired metal deposition may be removed by grinding or etching.

The crystals obtained according to the invention are of advantage for various uses in technology.

For example, it is of importance to have the disposal of long crystals, particularly whiskers, of constant thicknesses for electronic and mechanical uses, in which separate crystals are used and constant properties over a large length are required.

In addition, whiskerlike crystals with discontinuously varying thicknesses may be of advantage for reinforcing materials, because the presence of thickened portions ensure that the crystals are satisfactorily moved mechanically in the material.

Insofar as the crystals according to the invention are built up from semiconductive substances and are destined for electronic uses, the conductivity properties thereof may be adjusted, as is known, by incorporating dopes. As is likewise known, these additions may be incorporated in the crystals during their growth via the gaseous phase or in an aftertreatment by diffusion.

In order that the invention may be readily carried into effect, a few examples thereof will now be described in greater detail, reference being made to the accompanying drawing.

EXAMPLE I

Filamentary silicon carbide crystals were formed by means of a device as shown in FIG. 1 of the drawing.

In this figure, reference number 1 denotes a graphite crucible, 60 mm. high, 45 mm. inside diameter, 53 mm. outside diameter. 3 gm. of silicon dioxide 2 are provided in the crucible in which a graphite tray 3 was placed. A lid of sintered silicon carbide 4 on which iron grains 5 smaller than 5 mm. were provided, was placed on the crucible 1. The assembly was placed in a quartz tube (not shown) in which a hydrogen atmosphere was maintained of approximately atmospheric pressure. Around the quartz tube an inductance coil (not shown) is provided for heating the graphite crucible.

a. Upon heating at 1,250° C. a silicon and carbon containing hydrogen atmosphere was built up in the crucible. By the iron grains 5 silicon and carbon were taken up herefrom, the grains melting and silicon carbide growing from the resulting liquid phase according to a VLS-mechanism—epitaxially onto the silicon carbide lid 4, serving as a substrate. One of the formed crystals had a thickness of 24 μm . at its base which, after a growth of 1 mm., had reduced at its growing end to 19 μm . and, upon further growth over $\frac{1}{2}$ mm., had reduced at its growing end to 16.5 μm . in a period of time of 19 hours. In the

same period, another crystal had grown over a length of 1 mm., the thickness having reduced from $34\mu\text{m}$. at its base to $29\mu\text{m}$. at its growing end.

Herewith the known conical crystal growth as a result of evaporation at the surface of the liquid metal phase upon VLS-growth is illustrated.

b. If according to the invention 3 gm. of iron powder were provided in the tray 3 and the crystallization of silicon carbide was carried out for 42 hours at $1,230^\circ\text{C}$. under otherwise the same conditions, the partial iron pressure was increased so that the iron droplets even increase in size and the formed crystals become gradually thicker in the direction of growth. For example, the thickness of a crystal which had a base of $8.4\mu\text{m}$. had increased in thickness at its growing end to $9\mu\text{m}$. after a growth of 3 mm. and to $10.8\mu\text{m}$. after a further growth of 0.7 mm.

EXAMPLE II

As shown in FIG. 2 a graphite crucible 7 containing quartz grains 8 was provided in a graphite boat 6. Above the crucible 7 a plate 9 of sublimated silicon carbide of 20 mm. diameter was arranged. On the side of the plate 9 facing the crucible 7, iron grains 10 smaller than $5\mu\text{m}$. were provided. Furthermore a quartz tray 11 containing 1 gm. of iron powder 12 was placed in the graphite boat 6.

The assembly was arranged in a tube of sintered aluminum oxide (not shown) which was surrounded by a tubular electric furnace (not shown).

Hydrogen was led through the tube in the direction of the arrow at a rate of 25 liters per hour. By means of the furnace the graphite boat 6 was heated so that the part which comprises the tray 7 was heated at a temperature of $1,260^\circ\text{C}$. while the part comprising the tray 11, (the iron source) assumed a temperature of $1,180^\circ\text{C}$.

By heating for 40 hours, silicon carbide crystals having substantially constant thicknesses throughout their lengths grew on the plate 9. For example, over a length of a few centimeters and a thickness of about $10\mu\text{m}$., no or only slight variations in thickness were found such as just a local deviation of approximately $0.5\mu\text{m}$.

EXAMPLE III

As shown in FIG. 3, an aluminum oxide tray 14 containing 0.5 gm. of gold 15 was placed in a boat of sintered aluminum oxide 13. A disk of silicon 16, 20 mm. diameter, containing at its lower side gold grains 17 of approximately $10\mu\text{m}$. was provided on the boat 13.

The assembly was arranged in an aluminum oxide tube, (not shown) which was surrounded by a tubular electric furnace.

Hydrogen with 2 mol percent SiCl_4 was conducted through the tube in the direction of the arrow at a rate of 10 l. per hour.

a. By means of the oven the assembly was heated at $1,050^\circ\text{C}$. for 16 hours. Silicon whiskers the diameter of which increased in the longitudinal direction, for example, from 9 to $20\mu\text{m}$. over a length of 5 mm., grew on the plate 16.

b. By intermittently adding blasts of chlorine to a gas current in a quantity of 1 vol. percent of the gas, whiskers were

obtained the thickness of which locally dropped considerably.

c. If the tray 14 (the gold source) was heated to $1,150^\circ\text{C}$. while the temperature at the place where the crystal growth took place (the silicon substrate 16) was maintained at $1,050^\circ\text{C}$., an increase of the thickness takes place in the longitudinal direction as described in the embodiment sub a of this example.

What is claimed is:

1. A method of manufacturing filamentary of constant thickness crystals comprising the steps of exposing a substrate having thereon metal particles to a gaseous atmosphere containing both the material to be deposited in crystalline form on the substrate and vapors of said metal particles heating the substrate to a temperature at which the metal particles become molten and form metal droplets which dissolve the material to be deposited therein which precipitates on the substrate and forms filamentary crystals, and controlling the thickness of the deposited crystals by adjusting the partial pressure of the metal in said atmosphere.

2. A method as claimed in claim 1, wherein obtaining crystals of constant thicknesses, the influence of the factors which may cause thickness variations during the crystal growth are compensated for by adjusting the size of the metal droplets by means of adjusting the said partial pressure.

3. A method as claimed in claim 1, wherein the size of the metal droplets is varied by varying the said partial pressure so as to obtain crystals having a previously determined variation in thickness.

4. A method as claimed in claim 1, wherein the partial metal pressure in the crystallization space is controlled by means of a separate source of the metal, the partial metal pressure in the crystallization space being adjusted by the temperature to which said source is exposed.

5. A method as claimed in claim 4, characterized in that the partial pressure of the metal is increased by increasing the temperature of the source of the metal.

6. A method as claimed in claim 4 wherein the crystallization is carried out in a gas current and the size of the metal droplets is controlled by controlling the rate of flow of the gas.

7. A method as claimed in claim 1 wherein the partial pressure of the metal is temporarily reduced by temporarily reducing the gas pressure.

8. A method as claimed in claim 6, wherein the partial pressure in the crystallization space is temporarily reduced by temporarily leading through a current of gas having a content of the metal which is lower than that in the crystallization atmosphere.

9. A method as claimed in claim 7, wherein a gas current is led through the crystallization space to which temporarily a substance is added which reacts with the metal forming a volatile compound of it.

10. A method as claimed in claim 1 wherein for manufacturing crystals with a metal coating, the partial pressure of the metal in the crystallization atmosphere is increased for a short period of time prior to terminating the crystallization growth.

11. A method as claimed in claim 4 in which the partial pressure of the metal is temporarily reduced by temporarily decreasing the temperature of the metal source.

* * * * *

60

65

70

75