

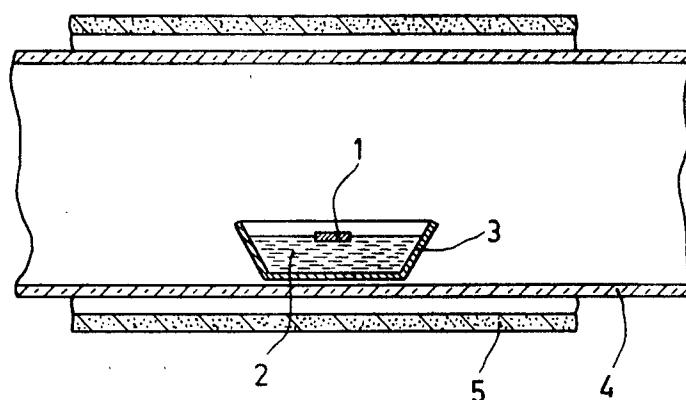
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METHOD OF CRYSTALLIZATION USING SOLVENT REMOVAL BY REACTION

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**METHOD OF CRYSTALLIZATION USING SOLVENT REMOVAL BY REACTION**

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6 Claims

**ABSTRACT OF THE DISCLOSURE**

A method of manufacturing crystals of semiconductor materials in which a seed crystal is brought into contact with a molten saturated solution of the semiconductor material while a gas is supplied to the atmosphere above the solution which reacts with solvent at the temperature of the melt to form a volatile compound so that the solvent is extracted from the surface layer and a state of over-saturation is caused in this layer.

This invention relates to the manufacture of crystals intended more particularly for semiconductor devices.

It is known that semiconductor crystals may be obtained by bringing a seed crystal into contact with a melt of the semiconductor material and maintaining a temperature gradient in the junction layer so that the seed crystal grows.

As a matter of fact, this method can be used only with materials, such as silicon and germanium, which can be melted at acceptable temperatures.

It is also known that silicon carbide can grow on a seed crystal from a molten saturated solution in chromium at an acceptable temperature. This substance is usable as a solvent, since the silicon carbide is satisfactorily soluble in it and this solvent is not absorbed by the crystal to a troublesome extent. This method has been carried out at atmospheric pressure in an inert gas at a temperature slightly above the melting point of the solution, namely approximately 1800° C. As a result of the small temperature difference between the seed crystal and the solution the growing rate of the crystal was low to a troublesome extent.

This may be considerably improved by crystallising at a reduced gas pressure whereby the solvent evaporates. A state of oversaturation is then caused in the surface layer with which the seed crystal is in contact, resulting in a crystal growth which is sped up considerably.

It is also known that such a method is also interesting for semiconductor materials other than silicon carbides. This holds good not only for semiconductor compounds, such as gallium phosphide, which cannot be crystallised directly from a melt or with great difficulty only, but also for semiconductor elementary materials, such as silicon, which when dissolved in a low-melting temperature solvent, for example tin, can be crystallised at comparatively low temperatures.

However, as previously mentioned, the solvent must then have not only an acceptable solubility of the semiconductor material and not be absorbed by the crystal to a troublesome extent, but also have so high a vapour pressure at the melting temperature that sufficiently rapid evaporation of the solvent and a rapid crystal growth, as the case may be at reduced pressure, take place.

The latter requirement as regards the solvent results in that the choice of a solvent for crystallising a given semiconductor is greatly limited and in certain cases a serviceable solvent will not even be available.

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An object of the invention is to mitigate this disadvantage.

The present invention underlies recognition of the fact that the state of oversaturation can be obtained in a simple manner by chemical means instead of by physical removal of solvent by evaporation, possibly at reduced pressure.

The invention relates to a method of manufacturing crystals, e.g. crystals for semiconductor devices, in which a seed crystal is brought into contact with a molten saturated solution of a semiconductor material so that the seed crystal grows, and it is characterized in that a gas is supplied to the atmosphere above the solution which gas reacts with the solvent at the temperature of the melt, thus forming a volatile compound so that solvent is extracted from the surface layer and a state of oversaturation is caused in this layer.

This method of removing solvent has a less limiting influence on the choice of the solvent or at least an influence which is limiting in another sense than in the case when the said removal is to take place by evaporation at reduced pressure. In fact, the majority of substances which can be used as solvents, such as gallium with gallium phosphide, silicon with silicon carbide and tin with silicon, exhibit a low vapour pressure at their melting point. Chromium, which can be used as a solvent for silicon carbide, is a favourable exception in this respect. However, many of the usable solvents at their melting temperatures readily form volatile compounds with gaseous reagents, such as oxygen, sulphur and halogen, so that solvent may rapidly be extracted from the solution.

**EXAMPLE 1**

As shown in the drawing, a seed crystal 1 of gallium phosphide is laid on the surface of a saturated solution 2 consisting of 4 mol percent of gallium phosphide in gallium, which solution is contained in a graphite vessel 3 placed in a quartz tube 4 and maintained in a molten state in argon at atmospheric pressure at a temperature of 1050° C. by means of an oven 5.

Subsequently a chlorine flow of 50 cm. per minute is passed through the quartz tube 4, causing solvent (gallium) to be extracted from the melt while forming volatile gallium chloride, so that oversaturation occurs in the surface layer and the gallium phosphide seed crystal grows at a rate of more than 30 $\mu$  per hour.

In conclusion, it should be noted that the method according to the invention can also be carried out in such manner that the seed crystal is fixed in position relative to the graphite crucible, the seed crystal being able to grow due to the solvent disappearing and the level of the liquid in the crucible falling correspondingly.

**EXAMPLE 2**

By means of a similar device as has been described in Example 1, a solution of 5 at. percent of silicon in tin in a quartz vessel is maintained in the molten state at 900° C.

On passing through the vessel hydrochloric acid gas of atmospheric pressure at a rate of 100 cm. per minute a silicon seed crystal laid on the solution grows at a rate of 25 $\mu$  per hour. This growth takes place due to the oversaturation in the surface layer which is caused by the extraction of solvent (tin) in the form of volatile tin chloride from the solution.

If solvent is extracted from the solution by evaporation in an argon atmosphere at a pressure of 10 mms., a crystal growth of only 10 $\mu$  per hour is obtained at the same temperature.

What is claimed is:

1. A method of growing crystals for use in semiconductor devices comprising the steps of forming a molten saturated solution of a semiconductor material in a solvent,

bringing into contact with a surface layer of the molten solution a seed crystal of said semiconductor material, and supplying to the atmosphere above the molten solution a gaseous reagent which reacts with the solvent at the melt temperature to form a volatile compound which vaporizes from said surface layer removing solvent from said molten solution and super-saturating said molten solution whereby semiconductor material is precipitated onto the seed crystal causing growth thereof.

2. A method as claimed in claim 1, wherein the semiconductor material is selected from the group consisting of silicon, silicon carbide and gallium phosphide.

3. A method as claimed in claim 2 wherein the semiconductor material is gallium phosphide and the solvent is gallium.

4. A method as claimed in claim 2 wherein the semiconductor material is silicon and the solvent is tin.

5. A method as claimed in claim 2 wherein the semiconductor material is silicon carbide and the solvent is silicon or chromium.

6. A method as claimed in claim 2 wherein the gaseous reagent is oxygen, sulfur or a halogen.

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