

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

DRAWINGS ATTACHED

Method of Producing Dendrite Crystals

We, TEXAS INSTRUMENTS INCORPORATED, 13500 N. Central Expressway, Dallas, Texas, United States of America, a corporation organised and existing under the laws of the State of Delaware, United States of America do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to a method of producing dendrite crystals

As used herein and in the claims, the term "dendrite" means a flat single crystal semiconductor. The dendrite, when grown, is usually relatively long in a first axis, wide in a second axis, (width usually being less than the length), and extremely thin in a third axis (the thickness of the dendrite being much, less than in the width or length).

Successful methods for producing germanium dendrites having reasonably good electrical and physical properties have heretofore been proposed. In growing germanium dendrites a crucible containing germanium, (and usually containing, in addition to the germanium, a conductivity type determining impurity) is heated to a temperature in excess of the melting point of the germanium. The temperature of the melt is then lowered to a value very slightly in excess of the melting point of the germanium. A single crystal germanium seed is dipped into the centre portion of the melt and withdrawn vertically at a rate determined by the geometry of the dendrite desired. As the germanium seed makes contact with the melt, heat from the melt is transferred into the seed causing supercooling of the germanium melt. Since the melt in the vicinity of the crystal seed is supercooled, that part of the melt will solidify on the crystal seed and grow as a dendrite. Now, as crystallization

occurs, latent heat of fusion is given up to the melt. This heat of fusion must be sufficiently dissipated so that the melt in the vicinity of the dendrite is supercooled thereby promoting continued growth of the dendrite. To maintain a dynamic heat balance so that dendrite growth may be continuous, it is necessary to reduce the input heat rate to the melt to compensate for the latent heat of fusion given up to the melt as the dendrite crystallizes. If the heat balance is not maintained, dendrite growth will cease. If the melt temperature increases too much, no region of supercooling would exist. If the temperature decreased too much, the entire melt would freeze over.

From the foregoing discussion it is apparent that the temperature of the melt and the accompanying surroundings are important factors in the growing of dendrites. In attempts to grow silicon dendrites, however, another important factor was recognised, precluding the growth of silicon dendrites by the standard process used to grow germanium dendrites. The fact that molten silicon "wets" and adheres to almost every known substance was found to be a problem when the temperature of molten silicon is maintained extremely close to the freezing point. It is difficult to supercool silicon if the molten silicon is in physical contact with a solid substance. The solid substance "seeds" the melt, thus causing the molten silicon to freeze over.

The foregoing problem was encountered in the growing of silicon dendrites. Since the molten silicon would readily wet the side of the crucible, the entire melt would freeze over if the temperature was lowered to the critical range necessary in order to grow dendrites. The present invention provides a solution to this problem since only the portion of the melt in the immediate

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vicinity of the crystal seed need be super-cooled in order to grow dendrites. The solution provided by the present invention is also applicable to the growth of germanium dendrites, the invention providing an improvement in the control of the dendrite growth.

The present invention is a method of producing dendrite crystals from a melt capable of forming dendrites comprising the steps of placing a seed crystal in contact with the surface of said melt, cooling only the portion of said melt immediately adjacent the area of contact of said seed crystal and said melt to a temperature slightly below its freezing point, contemporaneously maintaining the temperature of the remainder of said melt slightly above its freezing point and drawing the seed crystal away from the melt.

Embodiments of the invention will now be described, by way of example, with reference to the accompanying drawing, in which:—

Figure 1 is a sectional view of a crucible containing molten semiconductor material with a dendrite growing from a single crystal seed;

Figure 2 is a top view of the crucible showing the orientation of the heat sink provided by the present invention;

Figure 3 is a view similar to Fig. 1, illustrating another embodiment of the present invention; and

Figure 4 is a view similar to Fig. 1, illustrating yet another embodiment of the present invention.

Referring to Figure 1 there is shown a graphite crucible 2 surrounded by heating coils 8 (usually inductive heating coils). The graphite crucible 2 is provided with an opening 3 in the bottom. Quartz liner 4 fits snugly around the inside surface of crucible 2, the quartz liner having a projection 10 from the bottom as shown in Figure 1. Projection 10 defines a rectangular slot with a closed end 12, the slot being positioned directly over the opening 3 of the graphite crucible 2.

Silicon 6, doped with a conductivity type determining impurity, is placed within the quartz liner 4 and heated to a temperature in excess of the melting point, the atmosphere surrounding the melt at all times being inert. The level of the molten semiconductor is usually $\frac{1}{8}$ to $\frac{1}{4}$ inch above the top 12 of slot 10. The temperature is then lowered to within a degree or two of the freezing point. A single crystal seed 18, cut in the 1,1,2 crystal direction and held by a retractable chuck 22, is dipped into the molten silicon 6 so that it barely pierces the surface of the silicon in the immediate vicinity of the closed end 12 of slot 10. The seed 18 is held in the melt until the dendrite crystal begins to form. Then, the retractable chuck 22 draws the seed 18 and grow-

ing crystal 16 away from the melt.

In the present example the seed crystal 18 was dipped in the melt and held there for about 10 seconds. The temperature of the melt was from about 1425°C. to about 1435°C. The 10 second interval gave the crystal seed 18 a chance to fuse into the melt. After the 10 second interval the crystal was pulled from the melt at a rate of about 1 inch/minute. At the instant the crystal pull began the temperature of the melt was lowered by about 5°C. The temperature of the melt in the immediate vicinity of the formation of the dendrite is about 5° to 10° C. below the fusing point of silicon due to the heat sink 12 and dendrite 16. Thus a supercooling effect is present. The dendrite crystal began to grow with a geometry very similar to the top cross section 12 of the slot 10. It was found that the faster the pull rate the smaller the width and thickness dimensions of the dendrite will be. It is deemed significant, however, that the shape of the top 12 of the slot 10 essentially governed the shape and orientation in which the dendrite grew from the melt.

The temperature of the major portion of the molten silicon 6 in the melt is above 1420°C, the melting temperature of silicon. However, the temperature of the molten silicon 14 in the near vicinity of the dendrite crystal 13 and the end of the slot 12 is below the freezing temperature, and remains in a supercooled state during the growing of the dendrite. It is thought that the slot 12 acts as a conductor and removes heat to lower the temperature of the silicon 14 in the region of the dendrite crystal 16. The dendrite crystal 16 also conducts away a portion of this heat. Thus, a supercooled region 14 in the centre of the melt is created although the remainder of the melt is maintained at a temperature in excess of the melting point. In this manner the silicon melt is prevented from completely freezing throughout.

Referring to Figure 2 there is shown a top view of the crucible as shown in Figure 1, with like parts represented by like numerals. The numeral 3 denotes the opening in the bottom of the graphite crucible 2. Numeral 12 denotes the top of the projection 10 as seen in Figure 1. The slot 12 is shown as being rectangular in the instant case. However, a circular projection could have been used although it would not be possible to govern the orientation of the dendrite.

The invention contemplates the supercooling of a portion of the molten semiconductor contained in the crucible so that the temperature of the remainder of the melt may be maintained in excess of the melting temperature. Thus, embodiments other than described in the foregoing example have been used in the laboratory and found to work successfully. As shown in Figure 1 a gas

line 24 can be used to carry a cooling fluid 26 (preferably inert gas) to the inside of projection 10. The flow of gas simply increases the cooling effect of the top 12 of the projection 10, thus acting as an efficient heat sink.

As another example a projection 50 that was circular in cross section was used and is shown in Figure 3. A projection 50 protrudes from the bottom of the melt, the projection having an opening 48 in the top. Inert gas was flowed into the inner portion of the projection 50 through crucible opening 3, the inert gas striking the molten silicon at the opening 48. The molten silicon does not flow out through the hole 48 because of its viscous nature and the pressure caused by the flow of gas. Use of the hole 48 in the top of the projection 50 does not seem to provide better control than the embodiment as described with reference to Figure 1, although both embodiments gave satisfactory results.

Yet another embodiment that proved to be successful is as depicted in Figure 4. An inert gas stream 70 is flowed against the surface of the molten silicon in the region where the dendrite 16 is pulled from the melt. The inert gas stream 70 supercools that portion of the melt from which the crystal is formed.

In all embodiments described in the foregoing paragraphs the idea of supercooling only a portion of the melt is the same throughout, with various modifications of heat sinks being shown by the different embodiments. Because of the local temperature control that is gained over the region where the dendrite is formed, that control not being found in the prior art, the overall temperature of the melt need not be retained within as close tolerances as that necessary in the prior art. Thus, the present invention provides an improved method for growing dendrites, that method being applicable to germanium as well as silicon.

The invention has been described with reference to specific examples, the examples being preferred embodiments. It is intended that modifications, substitutions and changes should fall within the scope of the present invention that is defined and limited only by the appended claims.

WHAT WE CLAIM IS:—

1. A method of producing dendrite crystals from a melt capable of forming dendrites comprising the steps of placing a

seed crystal in contact with the surface of said melt, cooling only the portion of said melt immediately adjacent the area of contact of said seed crystal and said melt to a temperature slightly below its freezing point, contemporaneously maintaining the temperature of the remainder of said melt slightly above its freezing point and drawing the seed crystal away from the melt.

2. A method according to claim 1, wherein the melt is composed of either silicon or germanium.

3. A method according to either preceding claim, wherein the temperature slightly below the freezing point is 5° to 10°C. or thereabouts below the freezing point of said melt.

4. A method according to any preceding claim, wherein the cooling step is carried out by applying a heat sink to said portion of the melt.

5. A method as set forth in claim 4, wherein said heat sink is a jet of inert gas.

6. A method as set forth in claim 4, wherein said heat sink is a solid immersed in the melt.

7. A method as set forth in claim 4, wherein said heat sink is a solid member immersed in said melt below the contact area of the seed crystal and separated from said seed crystal by 1/8 inch to 1/4 inch.

8. A method as set forth in claim 4, wherein said heat sink is a non-circular solid immersed in said melt below the contact area of the seed crystal.

9. A method as set forth in claim 4, wherein said heat sink is a non-circular gas cooled solid immersed in the melt below the contact area of the seed crystal.

10. A method as set forth in claim 4, wherein said heat sink is an elongated slot immersed in said melt below the contact area of the seed crystal.

11. A method of producing dendrite crystals from a melt capable of forming dendrites, substantially as hereinbefore described with reference to Figs. 1 and 2, or Fig. 3, or Fig. 4 of the accompanying drawings.

12. Dendrite crystals when produced by the method of any preceding claims from a melt capable of forming dendrites.

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line 24 can be used to carry a cooling fluid 26 (preferably inert gas) to the inside of projection 10. The flow of gas simply increases the cooling effect of the top 12 of the projection 10, thus acting as an efficient heat sink.

As another example a projection 50 that was circular in cross section was used and is shown in Figure 3. A projection 50 protrudes from the bottom of the melt, the projection having an opening 48 in the top. Inert gas was flowed into the inner portion of the projection 50 through crucible opening 3, the inert gas striking the molten silicon at the opening 48. The molten silicon does not flow out through the hole 48 because of its viscous nature and the pressure caused by the flow of gas. Use of the hole 48 in the top of the projection 50 does not seem to provide better control than the embodiment as described with reference to Figure 1, although both embodiments gave satisfactory results.

Yet another embodiment that proved to be successful is as depicted in Figure 4. An inert gas stream 70 is flowed against the surface of the molten silicon in the region where the dendrite 16 is pulled from the melt. The inert gas stream 70 supercools that portion of the melt from which the crystal is formed.

In all embodiments described in the foregoing paragraphs the idea of supercooling only a portion of the melt is the same throughout, with various modifications of heat sinks being shown by the different embodiments. Because of the local temperature control that is gained over the region where the dendrite is formed, that control not being found in the prior art, the overall temperature of the melt need not be retained within as close tolerances as that necessary in the prior art. Thus, the present invention provides an improved method for growing dendrites, that method being applicable to germanium as well as silicon.

The invention has been described with reference to specific examples, the examples being preferred embodiments. It is intended that modifications, substitutions and changes should fall within the scope of the present invention that is defined and limited only by the appended claims.

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1. A method of producing dendrite crystals from a melt capable of forming dendrites comprising the steps of placing a

seed crystal in contact with the surface of said melt, cooling only the portion of said melt immediately adjacent the area of contact of said seed crystal and said melt to a temperature slightly below its freezing point, contemporaneously maintaining the temperature of the remainder of said melt slightly above its freezing point and drawing the seed crystal away from the melt.

2. A method according to claim 1, wherein the melt is composed of either silicon or germanium.

3. A method according to either preceding claim, wherein the temperature slightly below the freezing point is 5° to 10°C. or thereabouts below the freezing point of said melt.

4. A method according to any preceding claim, wherein the cooling step is carried out by applying a heat sink to said portion of the melt.

5. A method as set forth in claim 4, wherein said heat sink is a jet of inert gas.

6. A method as set forth in claim 4, wherein said heat sink is a solid immersed in the melt.

7. A method as set forth in claim 4, wherein said heat sink is a solid member immersed in said melt below the contact area of the seed crystal and separated from said seed crystal by 1/8 inch to 1 1/4 inch.

8. A method as set forth in claim 4, wherein said heat sink is a non-circular solid immersed in said melt below the contact area of the seed crystal.

9. A method as set forth in claim 4, wherein said heat sink is a non-circular gas cooled solid immersed in the melt below the contact area of the seed crystal.

10. A method as set forth in claim 4, wherein said heat sink is an elongated slot immersed in said melt below the contact area of the seed crystal.

11. A method of producing dendrite crystals from a melt capable of forming dendrites, substantially as hereinbefore described with reference to Figs. 1 and 2, or Fig. 3, or Fig. 4 of the accompanying drawings.

12. Dendrite crystals when produced by the method of any preceding claims from a melt capable of forming dendrites.

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