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Schmid et al.

[11] **4,256,530**

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[54] **CRYSTAL GROWING**

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[51] **Int. Cl.**[3] **C30B 9/04**; C30B 11/00; C30B 15/00

[52] **U.S. Cl.** .... **156/600**; 156/616 R; 156/617 SP; 156/DIG. 64; 156/DIG. 83

[58] **Field of Search** .... 156/DIG. 83, DIG. 64, 156/608, 617 R, 617 M, 617 V, 617 SP, 600, 616 R, 616 A; 422/248

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,265,528 8/1966 Bond 156/DIG. 83

Primary Examiner—Frank Sever

[57] **ABSTRACT**

In the growing of crystals, the formation of carbide contaminants is prevented by eliminating direct silica-graphite contact.

13 Claims, 2 Drawing Figures

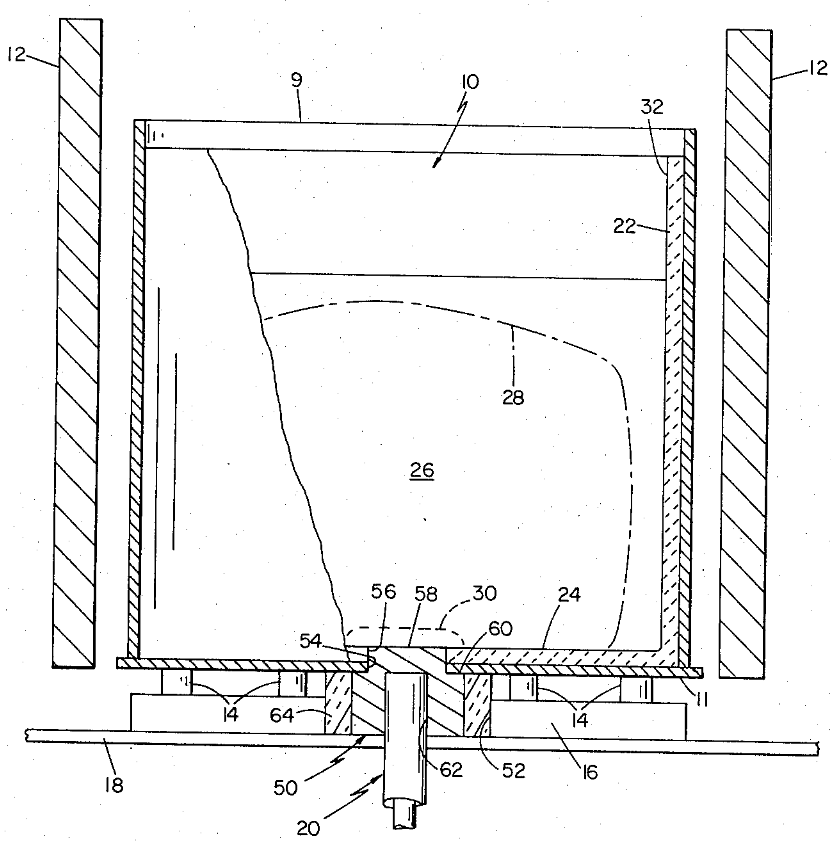
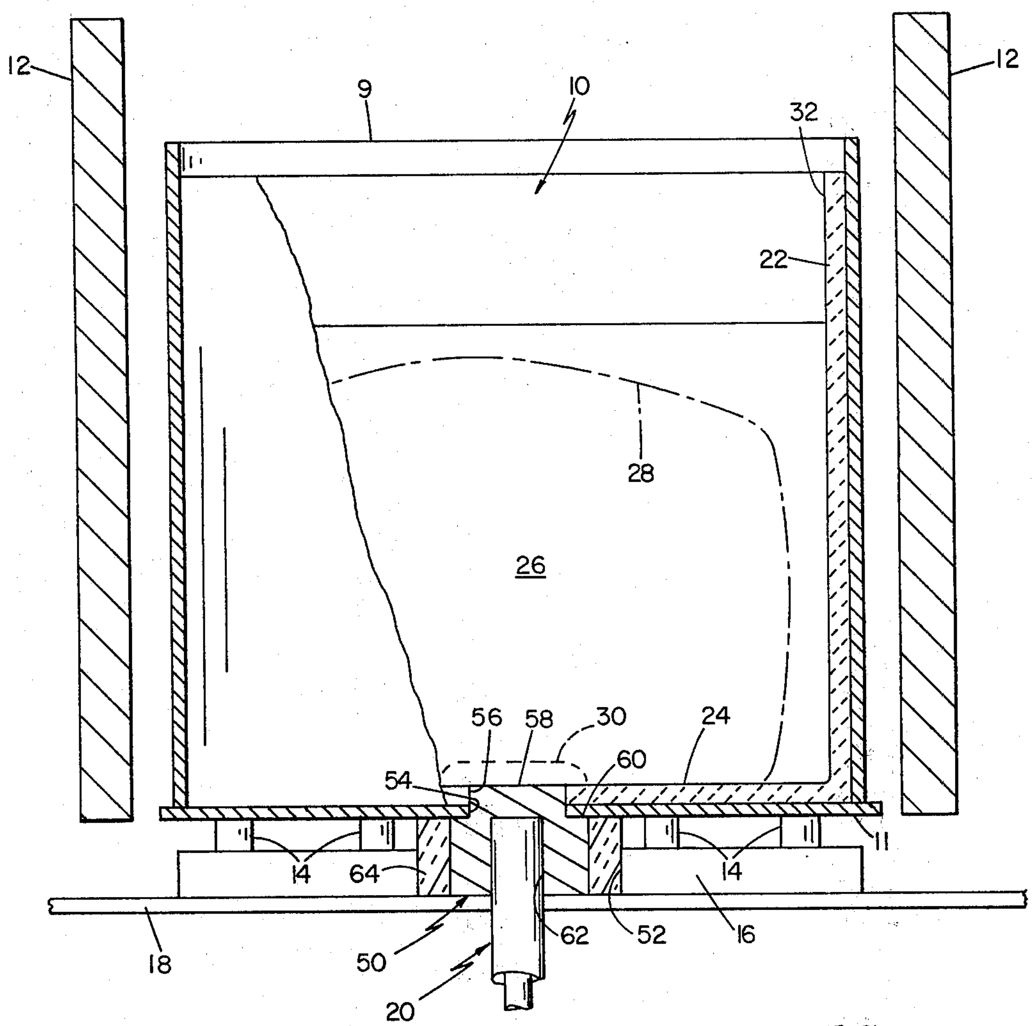


FIG 1



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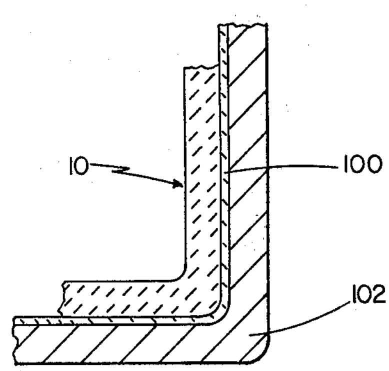

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FIG 2

CRYSTAL GROWING

The invention described herein was made in the performance of work under NASA Contract Number NAS 7-100, JPL No. 954,373 and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958 (72 Stat. 435; 42 U.S.C. 2457).

FIELD OF THE INVENTION

This invention relates to growing crystals, particularly of silicon, in vacuum environment.

BACKGROUND OF THE INVENTION

In the past, silicon crystals have been grown from the melt using both the well-known Czochralski crystal growth process and, more recently, the Heat Exchanger Method of crystal growth described in U.S. Pat. Nos. 3,653,432 and 3,898,051 (both of which patents are hereby incorporated by reference). In such processes, serious problems of silicon carbide impurity have been encountered when attempting to grow crystals at pressures below about 30 torr.

SUMMARY OF THE INVENTION

It has been discovered that, at pressures below about 30 torr and at the relatively high temperatures present during crystal growth, (for silicon, typically above 1685° K.), the silica crucible and surrounding graphite retainer generally used in silicon crystal growth react to form carbon monoxide (CO). The gaseous carbon monoxide is transported into the crucible where it contacts the silicon and forms silicon carbide (SiC), since silicon carbide is more stable than carbon monoxide. The unwanted silicon carbide contaminant can cause breakdown of crystallinity and incorporate carbon in silicon. The problem of carbon monoxide formation will be present whenever silica and graphite (carbon) are in contact; and unwanted carbide contaminants will result if the carbide of the crystal being grown is more stable than carbon monoxide.

It has further been discovered that the problem of unwanted carbide contaminants can be overcome by using molybdenum or some other refractory material that is free of elemental carbon, in place of graphite, to support the silica crucible or between the silica crucible and graphite retainer; or by coating the exterior of the crucible or interior of the retainer with refractory material. Either makes it possible to avoid direct silica-graphite (carbon) contact within the furnace.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Objects, features and advantages of the invention will appear from the following detailed description of the structure and use of a preferred practice thereof, taken together with the attached drawing in which:

FIG. 1 is a schematic view, partially in section, of a crucible, molybdenum retainer, conducting graphite plug, and insulation within the heating chamber of a casting furnace; and

FIG. 2 is a view of portions of a modified embodiment.

Referring now to FIG. 1, it illustrates a silica crucible **10** within the cylindrical heating chamber defined by the resistance heater **12** of a casting furnace of the type disclosed in U.S. Pat. No. 3,898,051. The crucible **10** rests on a molybdenum disc **11** which itself is supported by graphite rods **14** mounted on a graphite support plate **16** on the bottom **18** of the heating chamber, and is surrounded by a cylindrical molybdenum retainer **9**. A helium cooled molybdenum heat exchanger **20**, of the type disclosed in U.S. Pat. No. 3,653,432, extends through openings in the center of the plate **16** and bottom **18**.

Crucible **10** is about 6 in. (15 cm.) in height and diameter and its cylindrical wall **22** and base **24** are 0.15 in. (3.7 mm.) thick. Molybdenum disc **11** is about 0.040 in. (1 mm.) thick, and molybdenum retainer **9**, comprising a sheet of the same thickness rolled into cylindrical form, engages the exterior of cylinder wall **22**. A silicon ingot **26**, partially solidified according to the process described in aforementioned U.S. Pat. No. 3,898,051 is shown within the crucible. The solid-liquid interface **28** has advanced from the seed (shown in dashed lines at **30**) so that there is a thin annulus of liquid between it and the crucible wall (the temperature of which is above the melting point of silicon), and also liquid above it. When substantially all the liquid has been solidified, the temperature of the crucible wall will be permitted to drop below the silicon melting temperature, and the crucible and solidified ingot will then be cooled.

A stepped cylindrical graphite plug **50** (upper portion diameter 1.9 in., and lower portion diameter 2.5 in.) extends from bottom **18** upwardly through coaxial holes **52, 54, 56** in, respectively, plate **16**, molybdenum disc **11** and crucible base **24**. The top **58** of plug **50** is flush with the inside bottom surface of crucible base **24**. The seen **30** is placed over the plug **50** and the adjacent portion of crucible bottom **24** so as to cover opening **56**. The exterior of the plug upper portion fits loosely in openings **54, 56** to allow for thermal expansion; and the step **60** between the plug's upper smaller diameter and lower larger diameter portions engages the underside of plate **11**. A small quantity of silicon powder is placed in the area of opening **56** where seed **30**, crucible **10** and graphite plug **50** are in proximity. Heat exchanger **20** fits within a coaxial recess **62** in the bottom of plug **50**, with the top of the heat exchanger about ⅛ in. below the top **58** of the plug. A graphite felt insulation and/or molybdenum heat shield sleeve **64** closely surrounds the larger diameter portion of plug **50**, extending axially of the plug the full distance between bottom **18** and plate **11**. As shown, the exterior surface of insulation sleeve **64** engages the interior of opening **52**.

During crystal growth, the furnace heating chamber is evacuated to between 0.01 to 1 torr, and heated to between 1685° K. and 1735° K. At these temperatures and pressures, it has been found that any carbon (for example, a graphite crucible retainer) and silica (for example, a crucible) in direct contact will react to form gaseous carbon monoxide, CO, which occurs as per the following reactions:

$$SiO_2+3C \rightarrow SiC+2CO \quad (1)$$

$$SiO_2+C \rightarrow SiO+CO. \quad (2)$$

Each of these reactions is both pressure and temperature dependent. In the range of pressures and temperatures encountered in silicon crystal growth, the pressures of reactions (1) and (2) are, respectively:

$$\log P=11.62-1.57\times 10^4/T \quad (3)$$