

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
18 November 2004 (18.11.2004)

PCT

(10) International Publication Number
WO 2004/100221 A2

(51) International Patent Classification⁷:

H01L

(21) International Application Number:

PCT/US2004/013057

(22) International Filing Date: 27 April 2004 (27.04.2004)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

10/426,200

30 April 2003 (30.04.2003)

US

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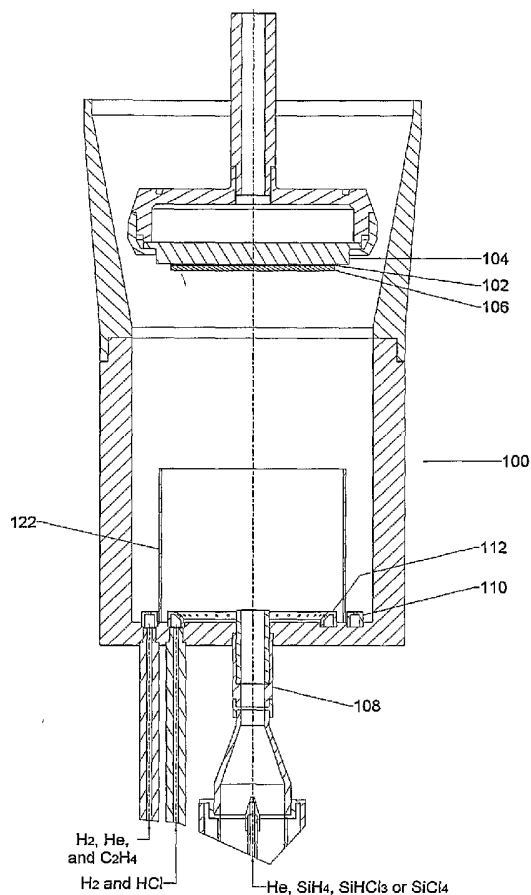
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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,

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(54) Title: PHASE CONTROLLED SUBLIMATION



(57) Abstract: A method of forming a silicon carbon compound. A silicon source is introduced into an environment. Silicon particles are formed therefrom. One or more hydrocarbons are introduced into the environment separately from the silicon source, thereby forming one or more silicon carbon compounds. A dissociation enhancer may be introduced into the environment to minimize silicon particle size prior to it joining the hydrocarbon source.



FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI,
SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, ML, MR, NE, SN, TD, TG).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Published:

— *without international search report and to be republished
upon receipt of that report*

PHASE CONTROLLED SUBLIMATION

FIELD OF THE INVENTION

The invention relates to crystal growth, and more particularly to silicon carbide
5 crystal growth.

BACKGROUND OF THE INVENTION

Silicon carbide (SiC) is a semiconductor material with properties highly suitable
for high power, high frequency, and high temperature applications. Its wide bandgap
10 make it suitable for high temperature applications and also as a substrate for
optoelectronic applications where blue and UV light is desired. Many applications
require a very high quality SiC crystal to minimize device defects and failures. Such high
quality silicon carbide is difficult to produce in an efficient manner. Technical obstacles
have remained that have inhibited the widespread use of silicon carbide. Reduction in
15 defects must be achieved to realize the full potential of silicon carbide in the electronics
industry. Silicon carbide substrates are typically perforated by tiny holes called
micropipes at a density of 15 – 30 mp/cm² on good material. The diameter is also small,
only 3" on commercially available material. To make a viable business low cost, high
quality, four-inch (minimum) wafers must be produced.

20 The standard way of growing SiC is by seeded sublimation growth. A graphite
crucible is filled with SiC powder and a SiC single crystal seed is attached to the lid of
the crucible, which is then sealed. The system is heated to temperatures above 2000°C
where SiC sublimates. Temperatures must be quite high to make sure the SiC powder
sublimes appreciably. If a thermal gradient is applied such that the seed is colder than the
25 source material, transport will take place from the source to the seed. If the pressure is
lowered to a few torr, the material transport is enhanced. Unfortunately, the method has
some drawbacks. Micropipe density is significant. Purity is also often a problem. Due
to the way the thermodynamics work for the sublimation, the growth is generally rich in
silicon (Si) at the beginning, with diminishing amount of Si at the end of the growth. This
30 has severe implications on the yield of semi-insulating wafers since the material will be
n-type at the start of the growth and p-type at the end.

The length of the grown crystals, commonly called boules, is also limited to the amount of silicon carbide source material in the system. Typical boule lengths are 20 – 25 mm.

High Temperature Chemical Vapor Deposition (HTCVD) can also be used to produce silicon carbide crystals. Gases carrying the Si and C needed for the growth replace a powder source material. In the entrance region, silane and ethylene react and nucleate in the gas phase to form micro-particles of Si_xC_y . Carbon is sometimes omitted and is then grabbed from graphite walls of the crucible. Micro-particles of SiC are formed and are moved into a main chamber where the temperature is much higher. Here the particles sublime and move towards a colder substrate through the aid of a carrier gas and the thermal gradient.

Unlike seeded sublimation growth, HTCVD is an open system, and is therefore run at significantly higher pressures to avoid problems with sublimation (evaporation) of the sample.

Material properties of HTCVD grown silicon carbide are usually much better than that of the sublimation grown crystals, however, the defect density could still use improvement, growth rates are low (< 1 mm/hr), and temperatures are high which stresses the crucible and insulation materials making the system drift.

Accordingly, there is a need for a lower temperature silicon carbide growth method that produces high quality crystals with a minimum amount of defects, and at higher growth rates (greater than 1mm/hr).

SUMMARY OF THE INVENTION

Embodiments of the present invention include a method of forming a silicon carbon compound. A silicon source is introduced into an environment such as the inlet to a HTCVD chamber. Silicon particles or droplets are formed from the silicon source. Hydrogen chloride is preferably introduced separately into the hot zone to reduce the size of the silicon particles before they meet with the hydrocarbon source that is also brought in separately. The purpose is to minimize the size of the Si_xC_y micro-particles before they reach the sublimation zone of the reactor. The growth rate is determined entirely by the ability to sublime the micro-particles. The larger the size of the particles the more

difficult it will be to sublime them and the higher the temperature and delta T which lead to deterioration of the grown crystal. If the size can be reduced, more material can be injected per time unit and hence the growth rate will increase while maintaining the same temperature and delta T. The silane and hydrocarbon components are thus ideally kept
5 apart since the silane will decompose to form small liquid droplets that are easier to dissociate thermally and/or chemically.

The silane and hydrocarbon may be introduced together as is done in HTCVD where these gases form SiC micro-crystals directly. However, in this case the separately introduced HCl will likely not be as effective in reducing particle size because the rate of
10 reaction between Si and HCl is much greater than that of SiC and HCl. In a preferred embodiment, the silicon source, hydrocarbons and HCl are introduced separately into the environment, so that the HCl is allowed to react with the silicon droplets prior to joining with the hydrocarbon source. An additional separation such as a short cylindrical wall between the hydrocarbon flow and the HCl/silicon mix may be needed in order to obtain
15 full effect of the chemical and thermal dissociation of the silicon clusters.

The invention further includes a silicon carbide crystal grown according to the inventive methods, and a semiconductor device incorporating such a silicon carbide crystal.

20 DESCRIPTION OF THE DRAWING

The invention is best understood from the following detailed description when read with the accompanying drawing.

FIGURE 1 depicts a sublimation chamber according to an illustrative embodiment of the invention.

25 DETAILED DESCRIPTION OF THE INVENTION

Embodiments of the present invention provide a method of forming compounds of potentially higher quality than compounds formed by traditional methods. The higher quality may reflect lower micropipe concentration and/or more uniform structure
30 throughout the crystal. The method can be applied to formation of many compounds, but

is particularly suitable to the formation of silicon carbide. As such, the invention will be described as it relates to silicon carbide.

Prior art silicon carbide formation by HTCVD is accomplished by allowing a gas mixture of silicon-containing compounds and hydrocarbons to react in a chamber inlet section to form Si_xC_y particles, and then passing these particles into a significantly hotter crucible where they sublime. There is little control of the particle size other than the pressure and the concentration of the precursor gases. In an illustrative embodiment of the present invention, however, silicon carbide cluster size is controlled by the addition of HCl and by separation of the Si source and the hydrocarbon source. Clusters of Si are allowed to form in the inlet region in order to make the material transport efficient, however, as soon as the clusters reach a hot zone of the growth chamber, these clusters or droplets are reduced in size by addition of HCl and by the heat before the flow of Si joins with a hydrocarbon flow. In a further embodiment of the invention, the HCl is omitted, particularly if the particle size is small enough so that the heat can dissociate the particles by itself without the aid of HCl. In an illustrative embodiment of the invention, the silicon source is transported in the chamber and the hydrocarbon is transported separated from the silicon source. The two streams of gas meet in the hot chamber, preferably in the sublimation zone that is the hottest part of the graphite assembly in the growth chamber. Since the temperature is significantly hotter when the gas flows meet, as compared to prior art methods, very small particles of SiC will be formed that may easily be sublimed. By eliminating or reducing pre-reaction between the silicon source and the hydrocarbons, and by additions of HCl brought in separately into the chamber, the size of silicon and silicon/carbon clusters can be reduced, allowing growth to occur at lower temperatures and/or higher pressures. There is a significant advantage to the separation of the source gases since the silane will form silicon droplets. It is relatively easy to dissociate these silicon droplets, for example by chemical and thermal means, which produce small particle sizes.

The silicon should meet the hydrocarbon flow at a distance from the surface on which the silicon carbide will be grown that is sufficient to allow the formed silicon-carbon particles to sublime before reaching the growing surface. In a preferred embodiment, the distance between the growing surface and the silicon/hydrocarbon

meeting area is in the range of about 30mm to 200mm. In a more preferred embodiment, the range is about 70mm to 120mm.

Although in the preferred embodiment of the invention, the silicon source is introduced into the chamber separately from all hydrocarbons, the invention includes a method wherein some hydrocarbons are added initially to the silicon source before the silicon source interacts with the main stream of hydrocarbons. In an illustrative embodiment, the amount of one or more hydrocarbons initially mixed with the silicon source is less than the amount in the main hydrocarbon flow. The flow rate of this second, smaller quantity of hydrocarbon is preferably less than 5sccm.

FIG. 1 shows a sublimation chamber 100 according to an illustrative embodiment of the invention. A seed crystal 102 is introduced onto a sample holder 104. The seed crystal and adjacent area is at a lower temperature than the chamber cavity. A single crystal 106 is then formed on seed crystal 102 by a sublimation process.

The sublimation process will be described as it relates to the formation of a silicon/carbon crystal. Broadly, the silicon and hydrocarbons react and form microcrystals before interacting at, or with, the substrate on which the crystal will be grown.

In an illustrative embodiment, a silicon source is introduced into an environment such as in chamber 100, forming silicon particles. FIG. 1 shows the silicon source being introduced through openings 108. The silicon source is preferably in a carrier gas such as helium, argon or other inert gas.

One or more hydrocarbons are preferably introduced into the environment separately from the silicon source. The hydrocarbon is transported via a carrier gas such as hydrogen, an inert gas or a combination thereof. The hydrogen decreases or eliminates deposition of carbon on the walls. When the hydrocarbon flow joins with the silicon flow small silicon carbide particles will form. The hydrocarbon is preferably ethylene but may be any other hydrocarbon or a mixture thereof.

FIG. 1 shows the hydrocarbons being introduced through openings 110. By introducing the hydrocarbons and the silicon into the chamber separately, the formation of large microcrystals or clusters can be reduced or eliminated. Optionally, walls 122 may be provided to further separate gas streams. As will be understood by those skilled

in the art, other chamber configurations are possible as long as sufficiently small microcrystals can be formed.

The separate silicon source produces liquid particles that are relatively easily dissociated. These droplets will readily dissolve when they reach high temperatures, allowing the hydrocarbons to easily react with them.

In an exemplary embodiment of the invention, a dissociation enhancer, such as hydrogen chloride, is introduced in the chamber through openings 112 to aid in the dissolving of silicon particles. The HCl may also facilitate dissociation of silicon/carbon compound crystals, thereby keeping them small. Introduction of HCl must be carefully controlled so that it does not react markedly with the crystal being formed. As shown in FIG. 1, the HCl is released into the chamber to interact with the silicon source prior to it joining the hydrocarbon flow.

Silane and the hydrocarbon may also be brought into a growth chamber together, and subsequently mixed with HCl to reduce particle size, however, the effect is not as significant as when the silicon and hydrocarbon is brought in separately. However, a small trickle of a hydrocarbon may be favorably added into the silicon flow in order to keep the particles more stable in case there is a problem with high levels of depositions on the sidewalls of the inlet. In this case the rest of the hydrocarbons are added separately as described previously.

The silicon source can be any silicon-containing compound from which silicon can be extracted for reaction with carbon. Examples include, silane, trichlorosilane, silicon tetrachloride, Si_2Cl_6 , Si_3Cl_8 or a combination of two or more of the aforementioned compounds. These compounds with the exception of silane will not decompose unless they are in contact with hydrogen. By separating them from the hydrogen until they reach a hot zone where sublimation or thermal dissociation occurs, cluster formation can be kept at a minimum. The result of the above-mentioned arrangement is a relatively small cluster size, which can result in a lower growth temperature or temperature gradient, a higher growth rate, and a better quality crystal. Preferably the growth temperature is below about 2400°C, and more preferably below about 2200°C.

The hydrocarbons are preferably in a carrier stream such as a stream containing hydrogen. The hydrogen can keep the hydrocarbons from being deposited as pyrolytic graphite. In a further embodiment the carrier gas contains helium.

The following are illustrative flow rate ranges:

- 5 silicon source: 300 standard cubic centimeter/minute-1 liter/minute
- hydrocarbon: 50 sccm-500 sccm
- hydrogen chloride: 100 sccm-300 sccm
- helium: 1 liter/min - 3 liters/min

The flow rates will depend, at least in part, on the size of the reactor.

- 10 The concentration of the silicon source is preferably greater than the concentration of the one or more hydrocarbons.

- The invention further includes a crystal formed according to the methods described herein, and a semiconductor device having such a crystal. The semiconductor device may be or include for example, a complimentary metal oxide semiconductor
- 15 (CMOS) device, micro-electro-mechanical (MEM) device, field effect transistor (FET), bipolar junction transistor (BJT), insulated gate bipolar transistor (IGBT), gate turn-off thyristor (GTO), or Schottky diode.

- While the invention has been described by illustrative embodiments, additional advantages and modifications will occur to those skilled in the art. Therefore, the
- 20 invention in its broader aspects is not limited to specific details shown and described herein. Modifications, for example, to the types of silicon sources and hydrocarbons, process parameters, types of crystals formed and crystal growth equipment, may be made without departing from the spirit and scope of the invention. Accordingly, it is intended that the invention not be limited to the specific illustrative embodiments, but be
 - 25 interpreted within the full spirit and scope of the appended claims and their equivalents.

Claimed is:

1. A method of forming a silicon carbon compound on a growing surface comprising:

introducing a silicon source into an environment;

5 forming silicon particles; and

introducing one or more hydrocarbons into the environment separately from the silicon source to form silicon-carbon particles;

wherein the one or more hydrocarbons are introduced at a distance from the growing surface sufficient to allow the formed silicon-carbon particles to sublime before reaching the growing surface, thereby forming one or more silicon carbon compounds on the growing surface.

2. The method of Claim 1 further comprising:

introducing hydrogen chloride into the environment.

15

3. The method of Claim 2 wherein the HCl is introduced into the environment separately from the silicon source and the hydrocarbon source.

4. The method of Claim 3 wherein the silicon particles formed meet with the

20 hydrogen chloride before meeting with the hydrocarbon flow.

5. The method of Claim 1 wherein the silicon source is selected from the group consisting of silane, trichlorosilane, silicon tetrachloride, Si_2Cl_6 , Si_3Cl_8 and a combination of two or more of the aforementioned compounds.

25

6. The method of Claim 5 wherein the silicon source is silane.

7. The method of Claim 1 wherein the silicon source is a chlorosilane and the method further comprises:

30 introducing hydrogen into the environment.

8- The method of Claim 1 wherein the one or more hydrocarbons are in a carrier stream containing hydrogen.

9. The method of Claim 1 wherein the concentration of silicon is greater than the
5 concentration of the one or more hydrocarbons.

10. The method of Claim 1 wherein the one or more hydrocarbons contains ethylene.

11. The method of Claim 1 wherein the silicon source is transported in a carrier gas.

12. The method of Claim 11 wherein the carrier gas is an inert gas.

13. The method of Claim 12 wherein the inert gas is helium.

14. The method of Claim 1 wherein the silicon source and the one or more
15 hydrocarbons are kept substantially separate until they reach the sublimation zone.

15. The method of Claim 1 wherein a second amount of one or more hydrocarbons is
introduced into the environment with the silicon source in addition to the one or more
20 hydrocarbons being introduced into the environment separately from the silicon source.

16. The method of Claim 15 wherein the flow of the second amount of hydrocarbons is
less than 5 sccm.

17. The method of Claim 1 performed at a temperature below about 2400°C.

18. The method of Claim 17 performed at a temperature of below about 2100°C.

19. The method of Claim 1 wherein the flow rate of silicon source is in a range of
30 about 300 standard cubic centimeter/minute-1 liter/minute.

20. The method of Claim 1 wherein the flow rate of hydrocarbon is in the range of about 50sccm-500sccm.
21. The method of Claim 1 wherein the flow rate of hydrogen chloride is in the range of about: 100sccm-300sccm.
22. The method of Claim 1 wherein the flow rate of helium is in the range of about 1liter/min - 3 liters/min.
23. The method of Claim 1 wherein the silicon source and the hydrocarbon source are physically separated within a growth chamber until they reach an area of predetermined temperature.
24. The method according to Claim 2 wherein the silicon and hydrogen chloride are physically separated from the hydrocarbon flow within a growth chamber until they reach an area of predetermined temperature.
25. The method according to Claim 2 wherein the silicon and hydrogen chloride are physically separated from the hydrocarbon flow within a growth chamber until the particle size is decreased to a predetermined size.
26. The method of claim 1 wherein the hydrocarbons are introduced into the environment at a distance of about 30mm to 200mm from the growing surface.
27. The method of claim 1 wherein the hydrocarbons are introduced into the environment at a distance of about 70mm to 120mm from the growing surface.
28. A silicon carbide crystal grown according to the method of Claim 1.
29. A semiconductor device comprising a silicon carbide crystal formed according to the method of Claim1.

30. A method of forming a silicon carbon compound comprising:
introducing a silicon source and one or more hydrocarbons into an environment;
and

5 subsequently introducing a dissociation enhancer into the environment.

31. The method of Claim 30 wherein the dissociation enhancer is HCl.

32. The method of Claim 30 wherein the silicon source is selected from the group
10 consisting of silane, trichlorosilane, silicon tetrachloride, Si_2Cl_6 , Si_3Cl_8 and a combination
of two or more of the aforementioned compounds.

33. The method of Claim 32 where the silicon source is silane.

15 34. A silicon carbide crystal formed according to Claim 30.

35. A semiconductor device comprising a silicon carbide crystal formed according to
the method of Claim 30.

FIGURE 1

