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The Fox Group, Inc.

IN THE UNITED STATES DISTRICT COURT
FOR THE SOUTHERN DISTRICT OF NEW YORK

THE FOX GROUP, INC.,)
)
Plaintiff,)
)
v.)
) C.A. No.: 1:10-cv-03361-AKH
DOW CORNING CORPORATION,)
)
Defendant.) JURY TRIAL DEMANDED
)
)

AMENDED VERIFIED COMPLAINT FOR PATENT INFRINGEMENT

Plaintiff, The Fox Group, Inc. ("Fox"), through counsel, alleges as follows:

NATURE OF THE ACTION

1. This is an action seeking redress for patent infringement under the patent laws of the United States, Title 35, United States Code.

THE PARTIES

2. Plaintiff, The Fox Group, Inc. ("Fox"), is a California corporation, having its sole place of business at 39 Garrett Street, Warrenton, VA 20186. Fox recently changed its name in California to The Fox IP Holdings Group, Inc. Fox is registered to do business in Virginia as The Fox Group, Inc.

3. Defendant, Dow Corning Corporation ("Dow Corning"), is a Michigan corporation having a principal place of business at 2200 W. Salzburg Road, P.O. Box 994, Midland, Michigan 48686.

JURISDICTION AND VENUE

4. This Court has subject matter jurisdiction pursuant to 28 U.S.C. §§ 1331 and 1338(a), as well as 28 U.S.C. § 2201.

5. This Court has personal jurisdiction over Dow Corning, as Dow Corning has availed itself of jurisdiction in this court by filing the declaratory judgment action against Fox on April 21, 2010.

6. Venue is proper in this judicial district under 28 U.S.C. §§ 1391(b), 1391(c), and 1400(b). On April 21, 2010, Dow Corning filed a declaratory judgment complaint in this Court. A copy of Dow Corning's complaint is attached hereto as Exhibit A.

FACTUAL BACKGROUND

7. One of Fox's predecessors-in-interest began working on the development of silicon carbide substrates in the late 1980s. Fox's predecessor-in-interest achieved low levels of defects, namely micropipes, dislocations, and secondary phase inclusions, in its silicon carbide substrates. As early as 1997,

Fox's predecessor-in-interest filed a patent application that matured into one of the patents-in-suit that discloses and claims lower defect density levels than achieved by others in the field, namely: dislocation density of less than 10,000 per square centimeter; micropipe density of less than 10 per square centimeter; and secondary phase inclusion density of less than 10 per cubic centimeter.

8. Other companies, including Dow Corning, were not able to attain these claimed low defect density levels until years later. These low defect density levels are now "state of the art" defect densities, and silicon carbide that has these defect density levels infringe Fox's patents-in-suit.

9. Dow Corning manufactures and uses and offers for sale and sells silicon carbide substrates and epitaxial wafers.

10. On September 9, 2009, Dow Corning announced that it was producing and shipping in volume quantities its newest silicon carbide substrates and epitaxial wafers with "state-of-the-art defect densities" and that Dow Corning was "seeing an improvement in defect densities as the diameter increased." *See* Dow Corning Press Release, attached as Exhibit B, found at http://www.dowcorning.com/content/news/DCCSC_Final_Press_Release_9-09_with_claims.aspx). These substrates and wafers infringe the patents-in-suit.

11. At the time of Dow Corning's press release, the "state-of-the-art" defect densities satisfy the low defect density levels of Fox's patents. For example, at the 2008 European Conference on Silicon Carbide and Related Materials (ECSCRM), Dow Corning "reported that it had significantly improved micropipe densities, to about 10 such defects per square centimeter of material." *See* press release, attached as Exhibit C, found at http://www.semiconductor-today.com/news_items/2009/SEPT/DOWCORNING_150909.htm.

COUNT ONE: INFRINGEMENT OF U.S. PATENT NO. 6,534,026

12. Fox realleges and incorporates by reference each of paragraphs 1-11 above, as if fully set forth herein.

13. On March 18, 2003, the United States Patent and Trademark Office ("PTO") duly and lawfully issued U.S. Patent No. 6,534,026 ("the '026 patent"), entitled "Low Defect Density Silicon Carbide." A true and correct copy of the '026 patent is attached hereto as Exhibit D.

14. Fox is the owner by assignment of the '026 patent and has the exclusive right to make, use, import, offer for sale, and sell in the United States products covered by the '026 patent.

15. On information and belief, Dow Corning has been making, using, selling, and/or offering for sale silicon carbide wafers or substrates that infringe one or more claims of the '026 patent.

16. Dow Corning has been infringing the '026 patent and will continue to do so unless and until enjoined by this Court.

17. Dow Corning's acts of infringement of the '026 patent have caused Fox irreparable injury and damages, in an as-yet-undetermined amount and, unless and until enjoined by this Court, will continue to do so.

18. Fox gave Dow Corning notice of the infringement on February 23, 2007, and Dow Corning has continued to infringe in spite of this notice. Dow Corning's acts of infringement of the '026 patent have been and continue to be willful and deliberate.

19. Attached hereto as Exhibit E is a claim chart depicting that Dow Corning is infringing at least claim 1 of the '026 patent.

COUNT TWO: INFRINGEMENT OF U.S. PATENT NO. 6,562,130

20. Fox realleges and incorporates by reference each of paragraphs 1-19 above, as if fully set forth herein.

21. On May 13, 2003, the United States Patent and Trademark Office ("PTO") duly and legally issued U.S. Patent No. 6,562,130 ("the '130 patent"), entitled "Low Defect Axially Grown Single Crystal Silicon Carbide." A true and correct copy of the '130 patent is attached hereto as Exhibit F.

22. Fox is the owner by assignment of the '130 patent and has the exclusive right to make, use, import, offer for sale, and sell in the United States products covered by the '130 patent.

23. On information and belief, Dow Corning has been making, using, selling, and/or offering for sale silicon carbide wafers or substrates that infringe one or more claims of the '130 patent.

24. Dow Corning has been infringing the '130 patent and will continue to do so unless and until enjoined by this Court.

25. Dow Corning's acts of infringement of the '130 patent have caused Fox irreparable injury and damages, in an as-yet-undetermined amount and, unless and until enjoined by this Court, will continue to do so.

26. Fox gave Dow Corning notice of the infringement on February 23, 2007, and Dow Corning has continued to infringe in spite of this notice. Dow Corning's acts of infringement of the '130 patent have been and continue to be willful and deliberate.

27. Attached hereto as Exhibit G is a claim chart depicting that Dow Corning is infringing at least claim 1 of the '130 patent.

PRAYER FOR RELIEF

WHEREFORE, Fox respectfully requests the following relief:

A. the entry of judgment that Dow Corning has infringed one or more claims of the '026 and '130 patents;

B. a permanent injunction enjoining Dow Corning, its officers, agents, servants, employees, and attorneys, and those persons in active concert or participation with them, from further infringement of the '026 and '130 patents;

C. the entry of judgment awarding Fox compensatory damages for Dow Corning's infringement of the '026 and '130 patents;

D. the entry of judgment that Dow Corning's infringement of the '026 and '130 patents has been deliberate and willful;

E. the entry of judgment awarding Fox enhanced damages, up to three times the amount of compensatory damages against Dow Corning pursuant to 35 U.S.C. § 284;

F. the entry of judgment awarding Fox pre- and post-judgment interest on its damages, together with its costs and expenses;

G. the entry of judgment awarding Fox reasonable attorney fees pursuant to 35 U.S.C. § 285; such other relief as this Court may deem just and proper.

VERIFICATION

I declare under penalty of perjury that I have read the foregoing Verified Complaint and that the same is true and correct.

Executed on December 17, 2010.

THE FOX GROUP, INC.

Bernard P. O'Meara

Bernard P. O'Meara
President & CEO

Respectfully submitted,

Dated: December 17, 2010

By: [signature]
Griffith B. Price, Jr.

Griffith B. Price, Jr.
SDNY No. GP0560
Patrick J. Coyne
Hayley S. Weimer
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Attorneys for Plaintiff
THE FOX GROUP, INC.

CERTIFICATE OF SERVICE

I, Larry White, hereby certify that on December 17, 2010, true and correct copies of the foregoing **Amended Verified Complaint for Patent Infringement**, was served by the indicated means to the person at the addresses listed:

Via First Class Mail

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J. Peter Coll, Jr.
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EXHIBIT A

Judge Hellerstein

10 CIV 3361

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APR 2 2010
U.S.D.C. S.D. N.Y.
CASHIERS

UNITED STATES DISTRICT COURT

SOUTHERN DISTRICT OF NEW YORK

DOW CORNING CORPORATION,

Plaintiff,

v.

THE FOX GROUP, INC.,

Defendant.

Case No.

COMPLAINT FOR DECLARATORY JUDGMENT

DEMAND FOR JURY TRIAL

Plaintiff Dow Corning Corporation ("Dow Corning") for its Complaint against The Fox Group, Inc., ("Fox"), hereby alleges as follows:

NATURE OF THE ACTION

1. This is an action for a declaratory judgment of non-infringement and invalidity of United States Patent Nos. 6,534,026 (the "'026 patent") and 6,562,130 (the "'130 patent") (collectively, the "Patents-in-Suit") pursuant to the Declaratory Judgment Act, 28 U.S.C. §§ 2201-02, and the patent laws of the United States, 35 U.S.C. § 100 *et seq.*, and for such other relief as the Court deems just and proper.

THE PARTIES

2. Dow Corning is a Michigan corporation with its principal place of business at 2200 W. Salzburg Road, P.O. Box 994, Midland, Michigan 48686.

3. On information and belief, Fox is a New York corporation with a principal place of business at 200 Voyageur, Pointe Claire, Quebec, Canada.

JURISDICTION AND VENUE

4. The Court has exclusive subject matter jurisdiction pursuant to 28 U.S.C. §§ 1331, 1338(a), 1367, 2201, and 2202, and the patent laws of the United States, 35 U.S.C. § 1, *et seq.* Venue is proper in this judicial district pursuant to 28 U.S.C. §§ 1391 and 1400.

5. Fox purports to be the owner of all rights, title, and interest in and to the '026 patent and '130 patent.

6. On August 1, 2007, Barney O'Meara of Fox sent a letter to Mark Loboda of Dow Corning stating that "[w]hile Dow Corning may not be presently making SiC of low enough defect density that it falls within the claims of either '026 or '130, it is our belief that Dow Corning is attempting to do so. Should you succeed and with to commercialize such a product, Fox Group would be willing to discuss licensing and or other mutually beneficial business interactions."

7. On December 17, 2007, attorneys for Fox sent a letter to the Intellectual Property Group of Dow Corning, stating that "given the product quality improvement we have seen in the industry, it is doubtful that any manufacturer with defects higher than those claimed in the Fox Group patents will remain viable." Further, the letter stated that "[a] non exclusive license from

1 Fox Group is still available, and would ensure that Dow Corning will fix it's obligations under the
2 patents."

3 8. On September 29, 2009, Barney O'Meara of Fox sent an email to James Helwick
4 of Dow Corning, stating that, based on "state-of-the-art defect densities," Dow Corning's products
5 now have defect densities below 10^4 per cm^2. O'Meara further stated that Fox had
6 corresponded with Dow Corning "about two years ago" regarding "silicon carbide being made,
7 offered for sale, or sold" by Dow Corning, and that the '026 and '130 patents were "especially
8 relevant within our industry, as their claims are for SiC with defect densities below 10^4."
9 O'Meara concluded by stating that Fox "remains willing to license its intellectual property" and
10 suggests a meeting to discuss licensing.

11 9. On November 17, 2009, Fox sent a letter to the Sue K. McDonnell, Senior Vice
12 President & General Counsel of Dow Corning, alleging that Dow Corning infringed the Patents-
13 in-Suit. Specifically, the letter stated "there is reason to believe that Dow Corning's Silicon
14 Carbide is of such quality that it falls within our claims" and included a list of the patents owned
15 by the Fox Group, along with a statement that "we believe the most significant of the patents are
16 the '130 and '026." (Patents-in-Suit -- Exhibit A)

17 10. On November 20, 2009, Sharon Brady of Dow Corning sent a letter to Fox, stating
18 that Dow Corning was in receipt of the November 17 letter, and would respond after an internal
19 investigation.

20 11. On December 17, 2009, Fox sent a letter to Ms. Brady, thanking her for the
21 November 20 letter, and stating that Fox was now "offering very special terms for those who
22 accept licenses soon, but we are limiting the number of companies that will enjoy those terms."

23 12. On December 17, 2009, Timothy Troy of Dow Corning sent a letter to Fox, stating
24 that Fox was not the first to develop low-defect silicon carbide, that Dow Corning used a
25 manufacturing process that differed from the techniques described in the '026 and '130 patents,
26 and that the Dow Corning silicon carbide products were well outside the scope of any valid patent
27 protection available to the Fox Group, and that therefore, no license was needed or desired.

28 13. On December 29, 2009, Fox sent a letter to Mr. Troy, stating that Fox is not aware

1 of any prior art to its patents, that there are no process or apparatus limitations on the '026 or '130
2 patent claims, and reiterating that Fox is offering "particularly favorable licensing terms, but these
3 will be offered for only a few more weeks."

4 14. Dow Corning has not infringed and does not infringe, either directly or indirectly,
5 any valid and enforceable claim of the Patents-in-Suit, either literally or under the doctrine of
6 equivalents. A substantial controversy now exists between the parties which is of sufficient
7 immediacy and reality to warrant declaratory relief.

8 15. The Court has personal jurisdiction over Fox.

9 **FIRST CLAIM FOR RELIEF**

10 **(Declaratory Judgment of Non-Infringement of the '026 Patent)**

11 16. Dow Corning repeats and realleges each and every allegation in the foregoing
12 paragraphs as though fully set forth herein.

13 17. Dow Corning has not infringed and is not now infringing, either directly,
14 contributorily, or through inducement, willfully or otherwise, the '026 patent.

15 18. As a result of the acts described in the foregoing paragraphs, there exists a
16 substantial controversy of sufficient immediacy and reality to warrant the issuance of a
17 declaratory judgment.

18 19. A judicial declaration of non-infringement is necessary and appropriate so that
19 Dow Corning may ascertain its rights with respect to the '026 patent.

20 **SECOND CLAIM FOR RELIEF**

21 **(Declaratory Judgment of Non-infringement of the '130 Patent)**

22 20. Dow Corning repeats and realleges each and every allegation in the foregoing
23 paragraphs as though fully set forth herein.

24 21. Dow Corning has not infringed and is not now infringing, either directly,
25 contributorily, or through inducement, willfully or otherwise, the '130 patent.

26 22. As a result of the acts described in the foregoing paragraphs, there exists a
27 substantial controversy of sufficient immediacy and reality to warrant the issuance of a
28 declaratory judgment.

23. A judicial declaration of non-infringement is necessary and appropriate so that Dow may ascertain its rights with respect to the '130 patent.

THIRD CLAIM FOR RELIEF

(Declaratory Judgment of Invalidity of the '026 Patent)

24. Dow Corning repeats and realleges each and every allegation in the foregoing paragraphs as though fully set forth herein.

25. Dow Corning is informed and believes and thereon alleges that any and all allegedly infringed claims of the '026 patent are invalid for failure to satisfy the conditions for patentability set forth in 35 U.S.C. §§ 101, 102, 103 and/or 112.

26. As a result of the acts described in the foregoing paragraphs, there exists a substantial controversy of sufficient immediacy and reality to warrant the issuance of a declaratory judgment.

27. Dow Corning is entitled to a declaration that the allegedly infringed claims of the '026 patent are invalid.

FOURTH CLAIM FOR RELIEF

(Declaratory Judgment of Invalidity of the '130 Patent)

28. Dow Corning repeats and realleges each and every allegation in the foregoing paragraphs as though fully set forth herein.

29. Dow Corning is informed and believes and thereon alleges that any and all allegedly infringed claims of the '130 patent are invalid for failure to satisfy the conditions for patentability set forth in 35 U.S.C. §§ 101, 102, 103 and/or 112.

30. As a result of the acts described in the foregoing paragraphs, there exists a substantial controversy of sufficient immediacy and reality to warrant the issuance of a declaratory judgment.

31. Dow Corning is entitled to a declaration that the allegedly infringed claims of the '130 patent are invalid.

PRAYER FOR RELIEF

1 WHEREFORE, plaintiff Dow Corning requests that judgment against Fox be
2 entered as follows:
3 A. That Dow Corning does not infringe any of the Patents-in-Suit;
4 B. That the allegedly infringed claims of the Patents-in-Suit are invalid;
5 C. That the case is exceptional under 35 U.S.C. § 285 and that Dow Corning
6 be awarded its attorneys' fees, costs and expenses incurred in this action as provided by that
7 statute; and
8 D. That Dow Corning have such other and further relief as the Court may
9 deem just and proper.
10
11
12 Dated: April 21, 2010

Respectfully submitted,

ORRICK, HERRINGTON & SUTCLIFFE LLP

13
14 By ______________________
15 Robert M. Isackson
16 J. Peter Coll, Jr.
Richard S. Swope
Attorneys for Plaintiff
17 DOW CORNING CORPORATION
18
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EXHIBIT B

Compound Semiconductor Solutions

News and Upcoming Events

2009.09.09
Dow Corning Shipping Next Generation Silicon Carbide Wafers

Dow Corning Shipping Next Generation Silicon Carbide Wafers

New SiC Semiconductor Products Support Advancements of Power Electronics Market

Auburn, MI– Dow Corning is now shipping volumes of its newest silicon carbide (SiC) wafers based on technology breakthroughs in crystal growth announced late last year. These products provide state-of-the-art defect densities that enable high power semiconductor devices and reliable manufacturing performance.

"This is a significant step in our efforts to eliminate the technical and commercial limitations related to the broad adoption and growth of SiC semiconductor devices," said Jim Helwick, Director, Dow Corning Compound Semiconductor Solutions. The new technology has been incorporated into wafers sizes up to 4 inches in diameter thus far, with work underway to exploit in even larger diameter wafers up to 6 inches. "In fact, we are seeing an improvement in defect densities as the diameter is increased," he said.

Dow Corning SiC wafers can be used in high power electronic applications such as communications, solar and wind energy systems, electrical distribution, and hybrid and electric vehicles.

"We now have the wafer and epitaxy technology and high volume production capabilities to supply our customers' growing needs for affordable, leading edge quality SiC products," he said. "Dow Corning is committed to continuing its leadership in supplying materials solutions to a broad cross section of the global electronics industry. Our global expertise combined with our collaborative approach in working with customers enables us to deliver solutions that reliably perform, time after time."

To learn more about Dow Corning's advanced technologies for semiconductor applications, please visit http://www.dowcorning.com/compoundsemiconductor.

About Dow Corning

Dow Corning http://www.dowcorning.com provides performance-enhancing solutions to serve the diverse needs of more than 25,000 customers worldwide. A global leader in silicones, silicon-based technology and innovation, Dow Corning offers more than 7,000 products and services via the company's *Dow Corning®* and *XIAMETER®* brands. Dow Corning is a joint venture equally owned by The Dow Chemical Company and Corning, Incorporated. More than half of Dow Corning's annual sales are outside the United States.

< back to Compound Semiconductor Home Page

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EXHIBIT C

semiconductorTODAY
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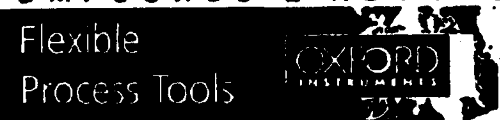

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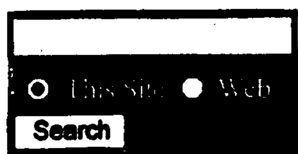

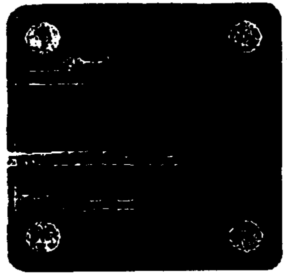

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News

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15 September 2009

Dow Corning ships low-defect 4-inch SiC substrates

Materials giant Dow Corning says that it is now shipping its low-defect silicon carbide (SiC) substrates in volume quantities.

Last year at the European Conference on Silicon Carbide and Related Materials (ECSCRM), the US-headquartered firm reported that it had significantly improved micropipe densities, to about 10 such defects per square centimeter of material.

Jim Helwick, the director of Dow Corning's Compound Semiconductor Solutions division, said that the progress detailed then had now been applied to commercial products: "The new technology has been incorporated into wafers sizes up to 4 inches in diameter thus far, with work underway to exploit [it] in even larger diameter wafers up to 6 inches… In fact, we are seeing an improvement in defect densities as the diameter is increased," he added.

Reducing the level of defects in SiC semiconductor material is seen as a significant step in the wide-bandgap semiconductor community's efforts to stimulate the broad adoption of SiC-based devices.

Those devices have the potential to be used in high-power electronic applications such as communications, solar and wind energy systems, electrical distribution, and hybrid and electric vehicles – provided that production yields are sufficiently high to allow cost-effective manufacturing.

"We now have the wafer and epitaxy technology and high-volume production capabilities to supply our customers' growing needs for affordable, leading-edge SiC products," Helwick said.

Dow's 4H-SiC material – the polytype most widely demanded for SiC electronics - has been available in 3-inch format for some time. On its website, the company quotes a typical bow of 6 microns for those wafers, and a typical warp of 17 microns.

The US firm is just one of a host of SiC wafer suppliers hoping to cash in on the anticipated market for wide-bandgap electronics as the technology becomes more widespread.

Rivals in Europe include France-based NovaSiC and Germany's SiCrystal, while in the US Dow Corning competes with the likes of Cree and SemiSouth. Over the past couple of years, the first Chinese competitor has also emerged, in the form of TankeBlue.

At the forthcoming International Conference on Silicon Carbide and Related Materials (ICSCRM) in Nuremberg, Germany next month, SiCrystal will give an invited talk on its own development of high-quality 4-inch SiC substrates.

Meanwhile, Japanese giant Nippon Steel will detail its progress towards large-diameter 4H-SiC crystals. In the past, Japanese car companies Honda and Nissan have been at the forefront of SiC device development for applications in electric vehicles.

See related item:

Merchant substrate market for GaN to reach $470m in 2013

Search: Dow Corning SiC substrates

Visit: www.dowcorning.com/compoundsemiconductor

Visit: www.icscrm2009.org

The author Michael Hatcher is a freelance journalist based in Bristol, UK.

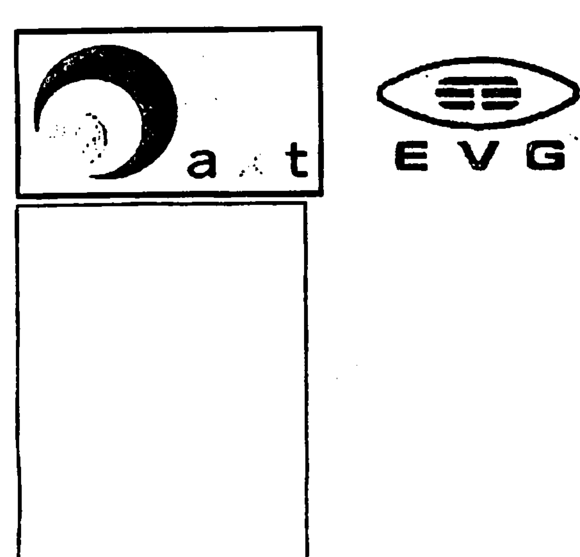

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EXHIBIT D

US006534026B2

(12) **United States Patent**
Vodakov et al.

(10) **Patent No.: US 6,534,026 B2**
(45) **Date of Patent: *Mar. 18, 2003**

(54) **LOW DEFECT DENSITY SILICON CARBIDE**

(75) Inventors: **Yury Alexandrovich Vodakov**, St. Petersburg (RU); **Mark Grigorievich Ramm**, Forest Hills, NY (US); **Evgeny Nikolaevich Mokhov**, St. Petersburg (RU); **Alexandr Dmitrievich Roenkov**, St. Petersburg (RU); **Yury Nikolaevich Makarov**, Richmond, VA (US); **Sergei Yurievich Karpov**, St. Petersburg (RU); **Mark Spiridonovich Ramm**, St. Petersburg (RU); **Heikki I. Helava**, Piedmont, CA (US)

(73) Assignee: **The Fox Group, Inc.**, Livermore, CA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **09/782,951**

(22) Filed: **Feb. 14, 2001**

(65) **Prior Publication Data**

US 2002/0049129 A1 Apr. 25, 2002

Related U.S. Application Data

(60) Provisional application No. 60/182,553, filed on Feb. 15, 2000.

(51) **Int. Cl.**[7] **C30B 23/06**
(52) **U.S. Cl.** **423/345**; 423/346; 117/951
(58) **Field of Search** 423/345, 346; 117/951

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Primary Examiner—Steven J. Bos
Assistant Examiner—Anthony Kuhar
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(57) **ABSTRACT**

A low defect (e.g., dislocation and micropipe) density silicon carbide (SiC) is provided as well as an apparatus and method for growing the same. The SiC crystal, grown using sublimation techniques, is preferably divided into two stages of growth. During the first stage of growth, the crystal grows in a normal direction while simultaneously expanding laterally. Although dislocations and other material defects may propagate within the axially grown material, defect propagation and generation in the laterally grown material are substantially reduced, if not altogether eliminated. After the crystal has expanded to the desired diameter, the second stage of growth begins in which lateral growth is suppressed and normal growth is enhanced. A substantially reduced defect density is maintained within the axially grown material that is based on the laterally grown first stage material.

14 Claims, 8 Drawing Sheets

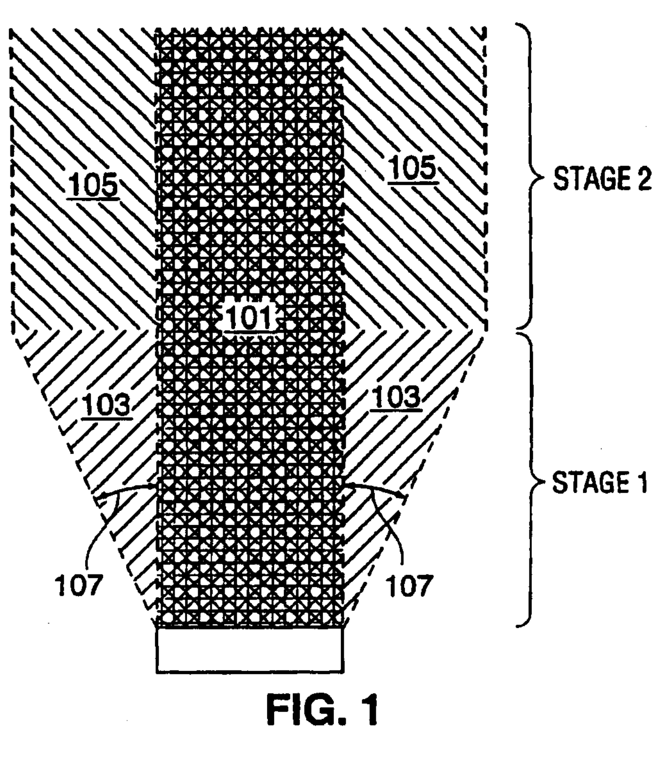

FIG. 1

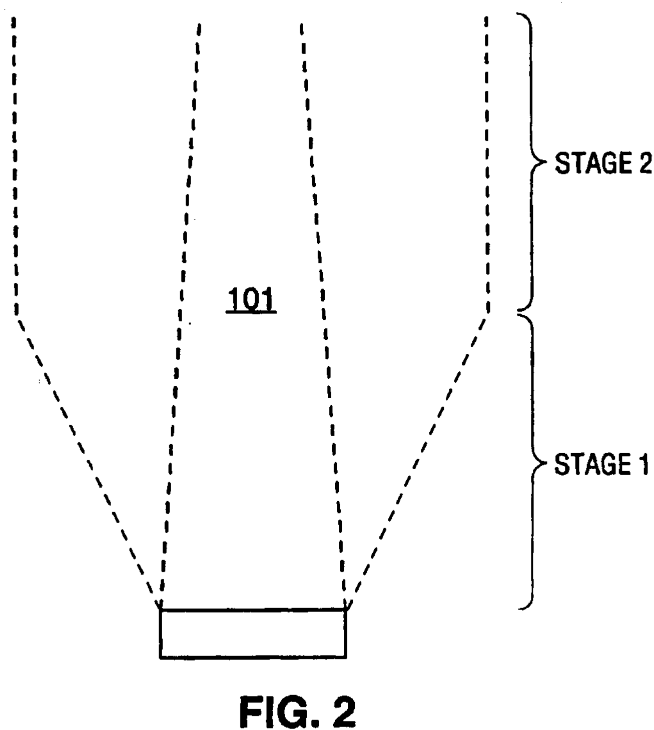

FIG. 2

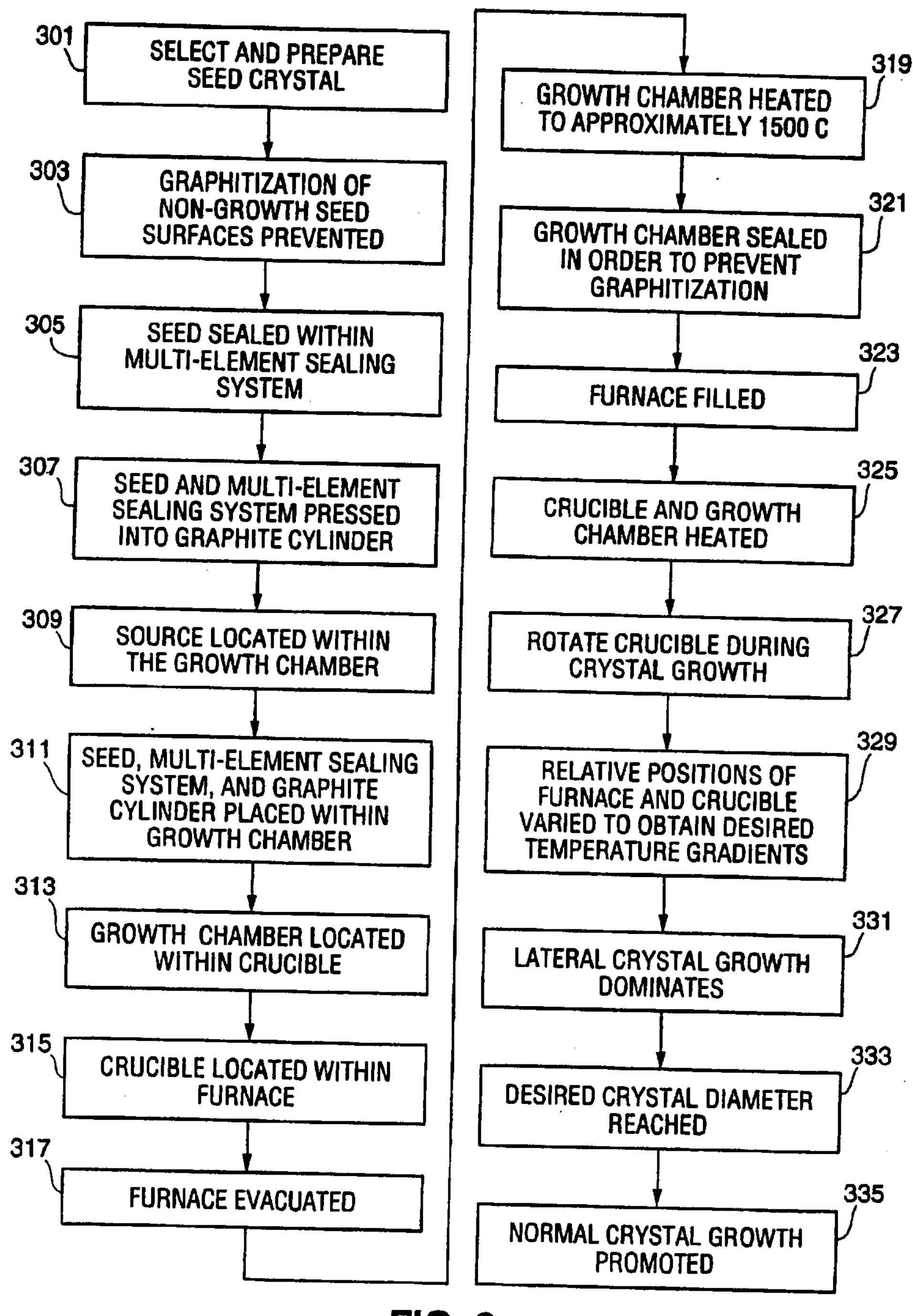

FIG. 3

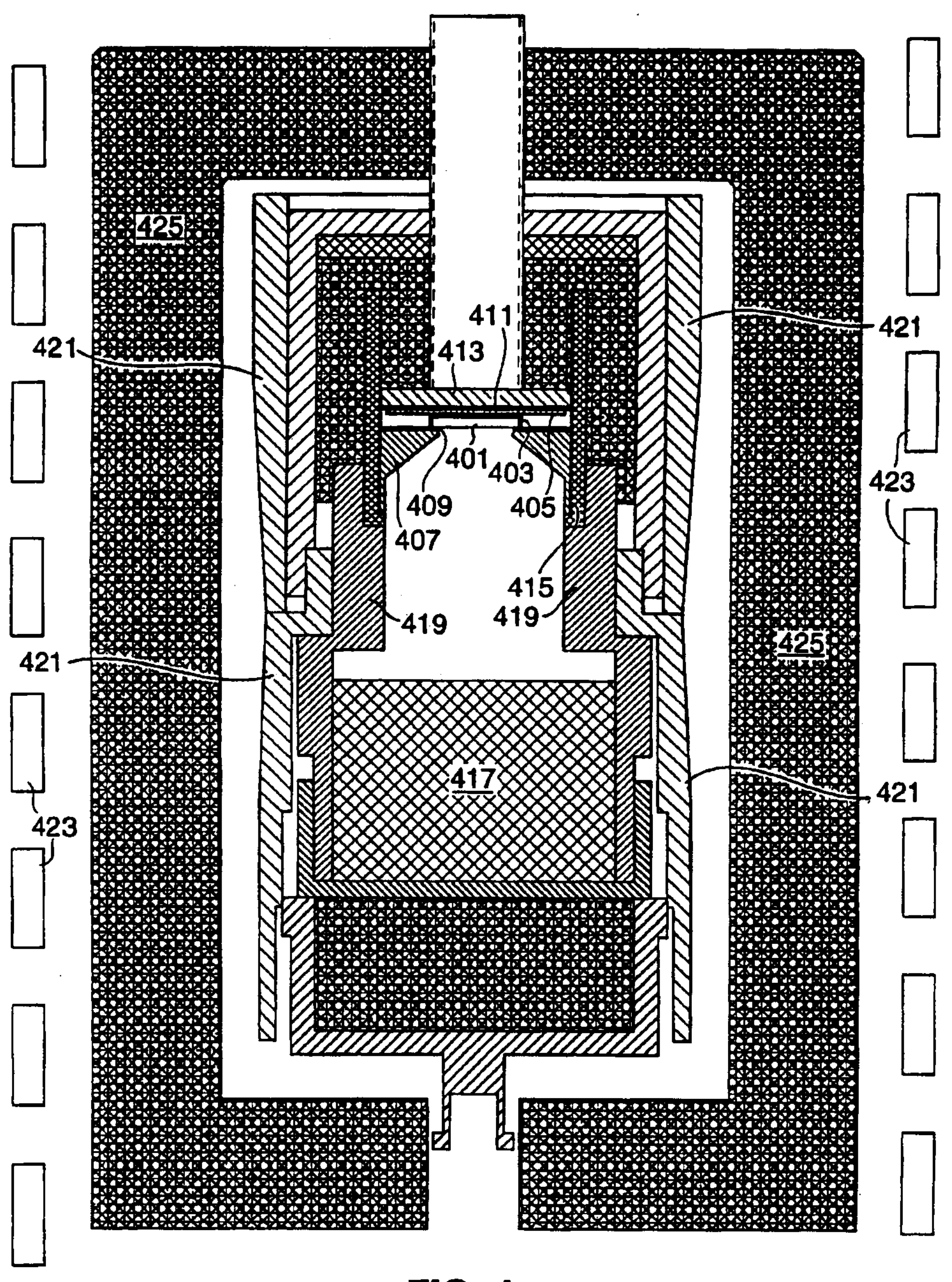

FIG. 4

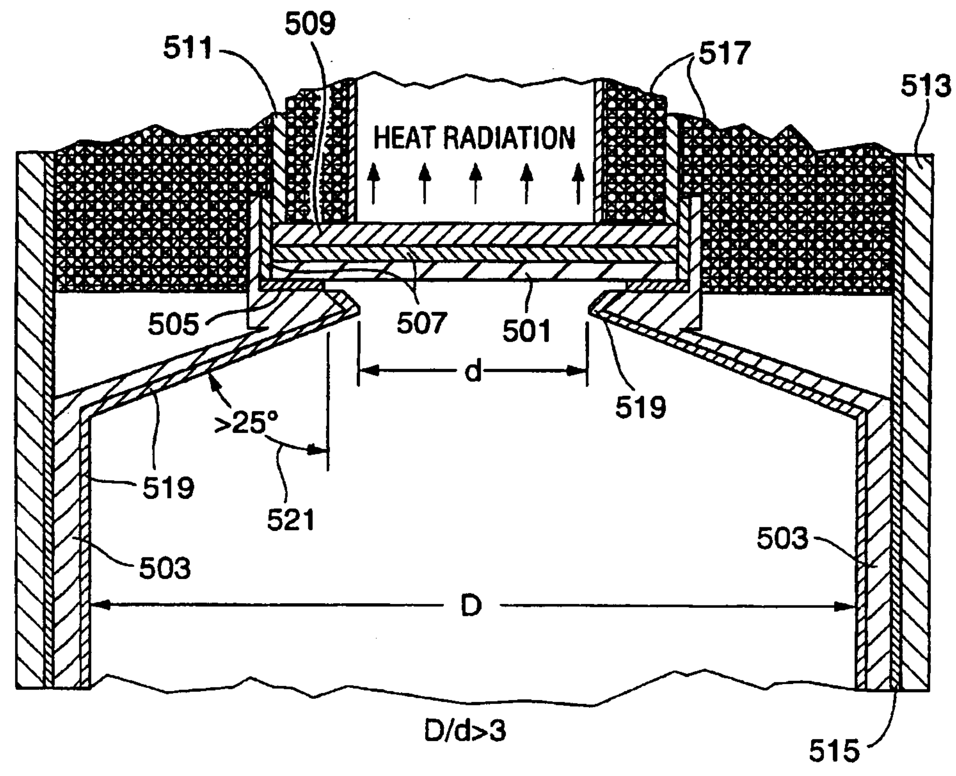

FIG. 5

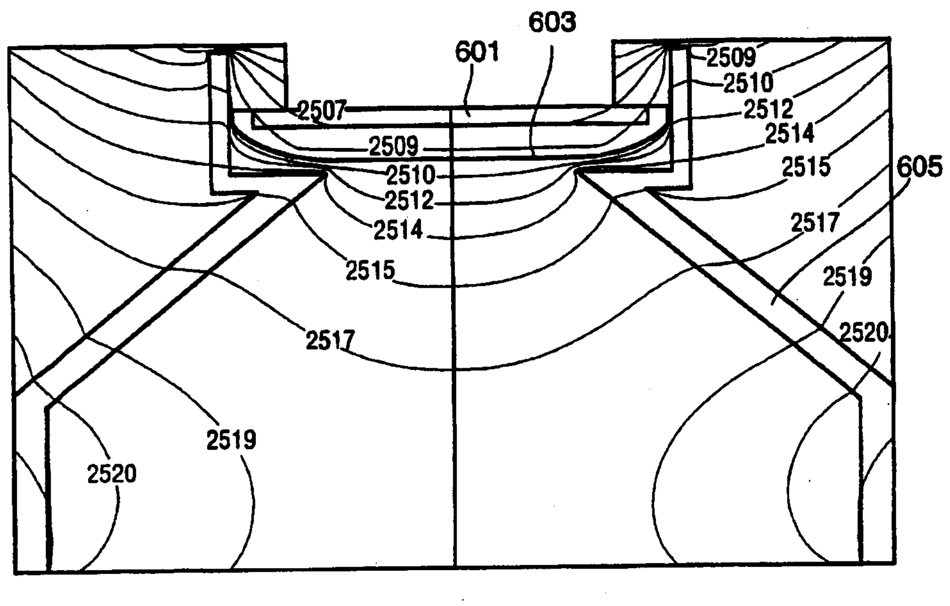

FIG. 6

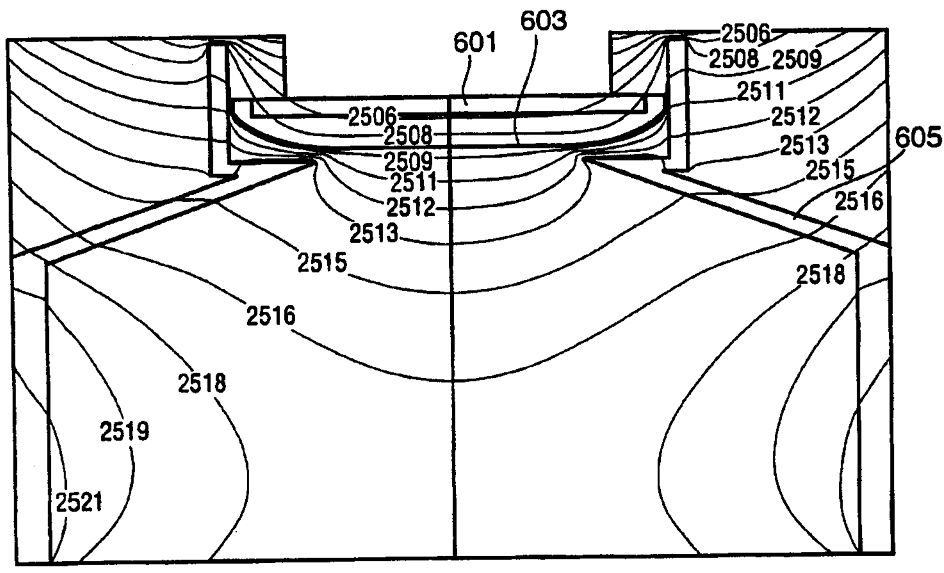

FIG. 7

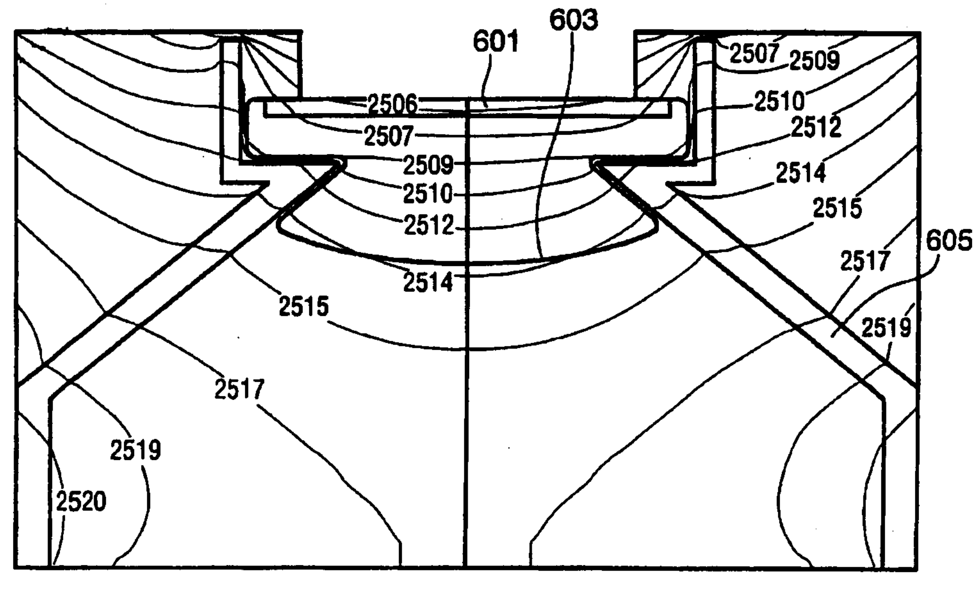

FIG. 8

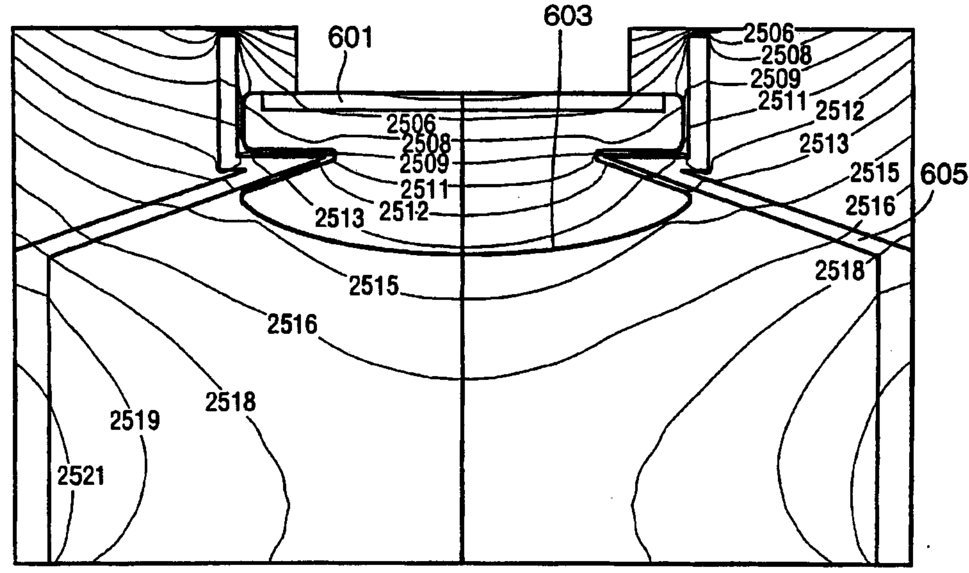

FIG. 9

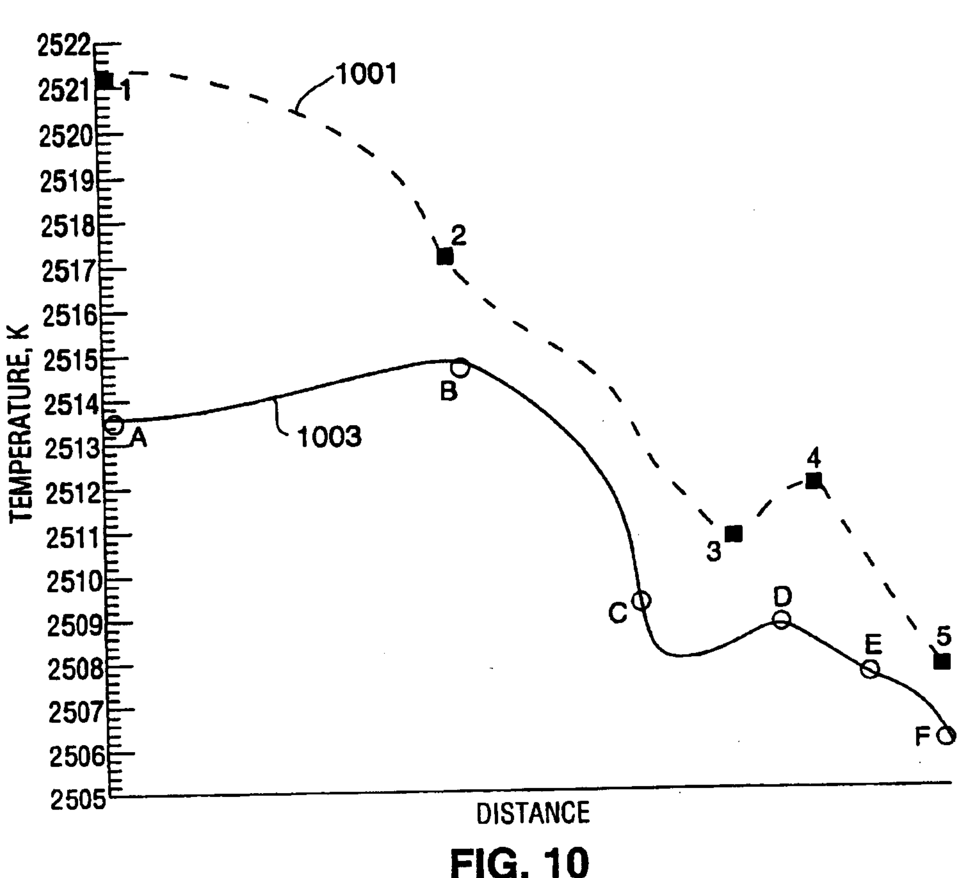

FIG. 10

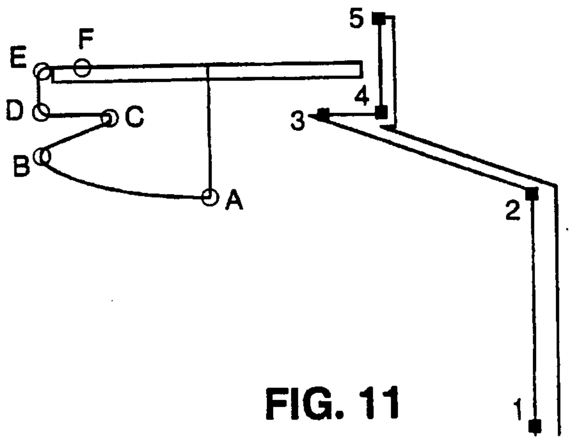

FIG. 11

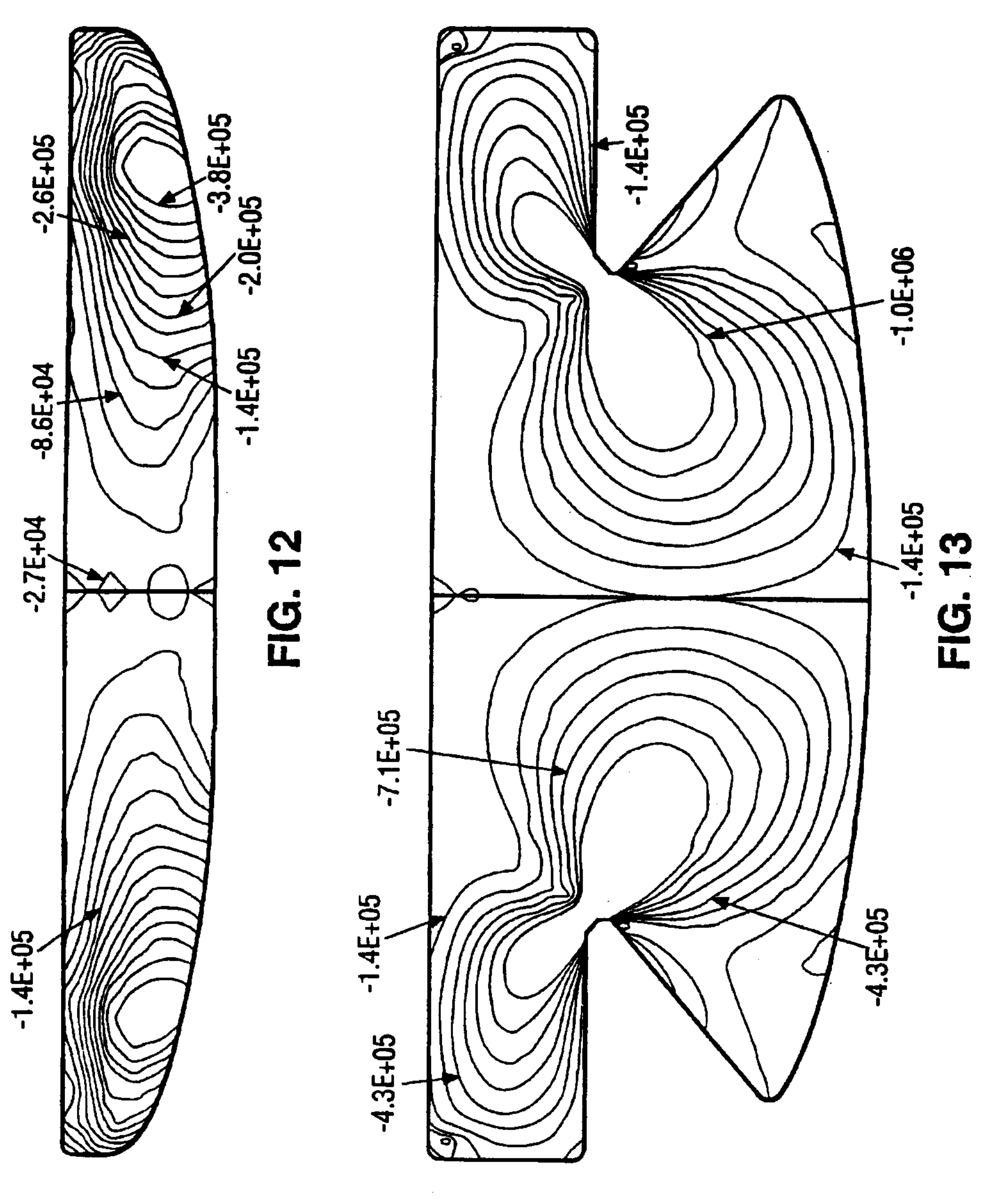

FIG. 12

FIG. 13

LOW DEFECT DENSITY SILICON CARBIDE

CROSS-REFERENCES TO RELATED APPLICATIONS

This application claims priority of U.S. Provisional Patent Application Serial No. 60/182,553, filed Feb. 15, 2000.

FIELD OF THE INVENTION

The present invention relates generally to silicon carbide and, more particularly, to a method and apparatus for growing low defect density silicon carbide.

BACKGROUND OF THE INVENTION

Silicon carbide (SiC) has a number of characteristics that make it an ideal candidate for a variety of semiconductor applications, primarily those requiring high power handling capabilities. Arguably the most important characteristic of SiC is its indirect bandgap, resulting in relatively high recombination lifetimes and the ability to produce higher voltage junctions than those that can be produced from a direct bandgap material. The large bandgap of this material also provides for negligible current leakage up to 500° C., thereby allowing for high temperature operation without excessive leakage current or thermal runaway. The switching frequency of SiC devices is much higher than that of a device fabricated from silicon or gallium arsenide due to SiC's high breakdown strength and the resultant reduction in minority carrier storage and associated switching losses. Lastly, due to the high junction temperature and the high thermal conductivity of SiC, devices fabricated from SiC have reduced cooling requirements.

Although semiconductor devices based on SiC offer vast improvements over devices fabricated from silicon, in order to realize these improvements materials must be fabricated with much lower defect densities than have been obtainable heretofore. As noted by the authors in the 1999 article entitled SiC Power Devices, Naval Research Reviews, Vol. 51, No. 1(1999), in order to scale up devices fabricated from SiC, the density of dislocations as well as the density of micropipes must be reduced. Conventional SiC material has a dislocation density between 10^5 and 10^6 per square centimeter and a micropipe density between 10^2 and 10^3 per square centimeter. Some extremely high quality SiC material has been grown with dislocation densities on the order of 10^4 per square centimeter. Unfortunately, even this dislocation density is at least an order of magnitude too high for many semiconductor applications. Id. at page 21.

U.S. Pat. No. 5,679,153 discloses a technique of growing SiC epitaxial layers using liquid phase epitaxy in which the density of micropipes is substantially reduced or eliminated. In one aspect of the disclosed technique, an epitaxial layer of SiC is formed on a bulk single crystal of SiC, the epitaxial layer being of sufficient thickness to close micropipe defects propagated from the bulk crystal. In order to form an electronically active region for device formation, a second epitaxial layer is formed on the first epitaxial layer by chemical vapor deposition. Based on this technique, SiC layers having micropipe densities of between 0 and 50 micropipes per square centimeter on the surface were claimed.

Although techniques have been disclosed to achieve SiC materials with low micropipe densities, these techniques do not lend themselves to growing bulk materials, i.e., materials that are at least a millimeter thick or more preferably, at least a centimeter thick. Additionally, these techniques do not impact the dislocation densities of the material. Accordingly, what is needed in the art is a technique of growing bulk SiC material with defect densities on the order of 10^3 per square centimeter, more preferably on the order of 10^2 per square centimeter, and even more preferably on the order of 10 or less dislocations per square centimeter. The present invention provides such a technique and the resultant material.

SUMMARY OF THE INVENTION

In accordance with the invention, a low defect density silicon carbide (SiC) is provided as well as an apparatus and method for growing the same. The SiC crystal, grown using sublimation techniques, is divided into two stages of growth. During the first stage of growth, the crystal grows in a normal direction while simultaneously expanding laterally. Preferably during this stage the ratio of the lateral growth rate to the axial growth rate is between 0.35 and 1.75. Although dislocations and other material defects may propagate within the axially grown material, defect propagation and generation in the laterally grown material are substantially reduced, if not altogether eliminated. After the crystal has expanded to the desired diameter, the second stage of growth begins in which lateral growth is suppressed and normal growth is enhanced. Preferably during this stage the ratio of the lateral growth rate to the axial growth rate is between 0.01 and 0.3, and more preferably between 0.1 and 0.3. A substantially reduced defect density is maintained within the axially grown material that is based on the laterally grown first stage material. Preferably during this stage the ratio of the lateral growth rate to the axial growth rate is between 0.01 and 0.3, and more preferably between 0.1 and 0.3. A substantially reduced defect density is maintained within the axially grown material that is based on the laterally grown first stage material.

In one aspect of the invention, a SiC material is provided with a low defect density, defects including both dislocations and micropipes. The defect density in the grown SiC is less than 10^4 per square centimeter, preferably less than 10^3 per square centimeter, more preferably less than 10^2 per square centimeter, and still more preferably less than 10 per square centimeter. In at least one embodiment, SiC is grown comprised of an axially grown region and a laterally grown region, the laterally grown region having the desired low defect density. In another embodiment of the invention, the SiC is comprised of a central region having a first defect density and a perimeter region encircling the central region that has a second defect density. The first defect density may be greater than 10^4 per square centimeter. The second defect density is substantially less than the first defect density and is less than 10^3 per square centimeter, preferably less than 10^2 per square centimeter, and more preferably less than 10 per square centimeter. In another embodiment of the invention, the SiC material is comprised of a SiC seed crystal, a first crystalline growth region initiating at a growth surface of the SiC seed crystal and following an axial growth path, and a second crystalline growth region of the desired defect density initiating at a growth surface of the SiC seed crystal and following a laterally expanding growth path. The defect density in the first crystalline growth region may be greater than 10^5 per square centimeter. The laterally expanding growth path is at an angle of at least 25 degrees, and preferably at least 45 degrees, from the normal, i.e., axial, growth path.

In another aspect of the invention, a method of growing a SiC material with a low dislocation density is provided. In at least one embodiment, a SiC seed crystal is introduced into a sublimation system wherein both axial and lateral

crystal growth is promoted, at least during one stage of growth. Propagation of dislocation defects, including micropipes, from the seed crystal into the laterally grown crystal is substantially reduced as is generation of dislocation defects within this region. In at least another embodiment of the invention, a SiC seed crystal is introduced into a sublimation system and heated to a temperature sufficient to cause sublimation. Temperature gradients within the sublimation system as well as temperature differentials between the crystallization growth front and adjacent surfaces promote a first stage of free space crystal expansion wherein the crystallization front expands both axially and laterally followed by a second stage of free space crystal expansion wherein the crystallization front expands axially while lateral expansion is suppressed.

In another aspect of the invention, an apparatus for use in growing a SiC material with a low dislocation density is provided. In at least one embodiment of the invention, the apparatus includes a ring element that promotes lateral crystal expansion, preferably through the use of a conical surface. The ring element may also be used to shield the edge of the SiC seed from the growth process. The ring element may also include a second surface, preferably conical, that promotes lateral crystal contraction. Preferably the ring element inner surfaces are comprised of either Ta_xC_y or Nb_xC_y. In at least one embodiment of the invention, the apparatus also includes a graphite heat sink coupled to a non-growth surface of the SiC seed crystal, a growth chamber with inner surfaces preferably comprised of either Ta_xC_y or Nb_xC_y, and means for applying temperature gradients to the crucible.

A further understanding of the nature and advantages of the present invention may be realized by reference to the remaining portions of the specification and the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 schematically illustrates the regions of defect free crystal growth in accordance with the invention;

FIG. 2 schematically illustrates a reduction in the core region during crystal growth;

FIG. 3 illustrates the basic methodology applied to achieve low defect density SiC;

FIG. 4 illustrates the preferred design of the sublimation system;

FIG. 5 illustrates a detailed cross-section of the critical growth region of the preferred design of the invention;

FIG. 6 illustrates the calculated temperature distribution within the growth cell and in the growing crystal for a ring element cone angle of 45 degrees and a growth period of approximately 4 hours;

FIG. 7 illustrates the calculated temperature distribution within the growth cell and in the growing crystal for a ring element cone angle of 70 degrees and a growth period of approximately 4 hours;

FIG. 8 illustrates the calculated temperature distribution within the growth cell and in the growing crystal for a ring element cone angle of 45 degrees and a growth period of approximately 22 hours;

FIG. 9 illustrates the calculated temperature distribution within the growth cell and in the growing crystal for a ring element cone angle of 70 degrees and a growth period of approximately 22 hours;

FIG. 10 illustrates a one dimensional temperature distribution over the ring element cell wall and the crystal interface;

FIG. 11 illustrates the ring element wall locations and the crystal interface locations that correspond to the data points shown in FIG. 10;

FIG. 12 illustrates the distribution of the principal component of the thermal elastic stress tensor as computed for the temperature distributions shown in FIG. 6; and

FIG. 13 illustrates the distribution of the principal component of the thermal elastic stress tensor as computed for the temperature distributions shown in FIG. 8.

DESCRIPTION OF THE SPECIFIC EMBODIMENTS

The dislocations in (0001) silicon carbide (SiC) seed crystals are primarily threading and screw dislocations in the <0001> crystal direction. Micropipe defects are basically screw dislocations with a Burger's vector that is so large that the core of the screw is empty. The inventors have found that by growing a crystal under the appropriate conditions in the radial direction (i.e., lateral direction) rather than the axial direction, the multiplication of <0001> dislocations is suppressed. Accordingly, under the appropriate conditions, a defect free SiC crystal can be grown using sublimation techniques.

In the preferred embodiment of the invention, as illustrated in FIG. 1, crystal growth is divided into two stages. During the first stage of growth, the crystal grows in a normal direction (i.e., vertically) while simultaneously expanding laterally. Preferably during this stage the ratio of the lateral growth rate to the axial growth rate is between 0.35 and 1.75. After the crystal has expanded to the desired diameter, lateral growth is suppressed while normal growth is enhanced (i.e., the second stage of growth). Preferably during this stage the ratio of the lateral growth rate to the axial growth rate is between 0.01 and 0.3, and more preferably between 0.1 and 0.3. In the preferred embodiment this ratio is not too low, thereby achieving a slightly convex growth surface and avoiding singularization of this surface. Lateral crystal growth is limited by the size of the crucible, which, in turn, is primarily limited by the ability to achieve the required temperature gradients.

According to the invention, although dislocations and other material defects propagate within core region 101, defect propagation and generation is substantially reduced, if not altogether eliminated, in the laterally grown area 103. Additionally, a substantially reduced defect density is maintained within the axially grown material that is based on the laterally grown material, i.e., regions 105. Preferably the growth conditions are chosen to reduce the size of core region 101 during growth as illustrated in FIG. 2.

In order to achieve defect free lateral crystal growth, the inventors have found that preferably a number of conditions are met. These conditions, discussed in further detail below, include:

(i) High quality seed crystal—Preferably the growth surface of the seed crystal is defect free, thereby minimizing the propagation of defects within the core region of the grown crystal.

(ii) Shielding the back surface of the seed crystal to prevent initiation of dislocations and other microscopic defects (e.g., planar defects) which can propagate through the crystal and impact the quality of the grown crystal.

(iii) Selection of the proper growth angle—Generally angle 107 in FIG. 1 must be greater than 25 degrees, and preferably greater than 45 degrees. This angle is

primarily determined by two factors; first, the vertical temperature gradient between the source and the seed crystal and second, the lateral temperature gradient between the center of the crucible and the crucible walls.

(iv) Selection of an appropriate seed crystal diameter—Generally the diameter of the seed crystal should be less than 30 percent of the diameter of the crystal to be grown.

(v) Prevention of polycrystalline growth—Requires the elimination of contact between the laterally growing material and the crucible side-walls thus insuring free-space expansion of the crystal. This is achieved by maintaining a temperature differential between the laterally growing crystal and the crucible side-walls.

FIG. 3 illustrates the basic methodology applied to achieve defect free SiC while corresponding FIG. 4 illustrates the preferred design for the furnace and crucible. Initially a SiC seed crystal 401 is selected and prepared. (Step 301) Seed crystal 401 can be grown using any of a number of well known techniques (e.g., Lely method). In the preferred embodiment a seed crystal with minimal defects is used, typically on the order of 10^5 per square centimeter or less. Also preferably the seed crystal has minimal, if any, micropipe defects. The ratio of the diameter of seed crystal 401 to the diameter of the crystal to be grown is preferably less than 0.3.

In the preferred embodiment of the invention, surface mechanical defects are removed from the surface of the seed crystal using conventional surface preparation techniques, e.g., grinding, polishing, and chemical etching. In this embodiment, approximately 50 microns is removed although the removal of additional material in excess of a 50 micron layer may be required in order to achieve the desired surface. Preferably the surface finish has an RMS roughness of 50 Angstroms or less.

During crystal growth, it is important to prevent graphitization. (Step 303) Accordingly, the back surface of seed crystal 401 is preferably shielded during evaporation. The preferred method of shielding the non-growth surfaces of seed crystal 401 is to place the growth surface of the crystal onto the flat, polished surface of a tantalum disk. Then the wafer is annealed in vacuum for a few minutes at 1700 to 1750° C., yielding a dense graphite layer 403 on those seed crystal surfaces not in contact with the tantalum disk. Once formed, back surface graphite layer 403 is coupled to a holder 405. Preferably holder 405 is comprised of graphite or pyrographite and a graphite based glue is used to couple seed crystal 401 to holder 405, the glue eliminating voids in the joint between the two surfaces. In addition to helping to prevent graphitization, the above-described crystal seating process also prevents localized temperature non-uniformities in the seating area that arise from having voids between the back surface of the seed crystal and the crucible lid (e.g., the seed holder).

In an alternate embodiment, the dense graphite layer 403 is grown on all seed crystal surfaces and subsequently removed from the growth surface, for example using an epi-polishing technique.

In order to shield the non-growth seed surfaces of the seed crystal from evaporation, in the preferred embodiment of the invention seed crystal 401 is sealed within a multi-element system that includes a ring element 407. (Step 305) Ring element 407 is not only integral to the sealing system, it also helps to shape the desired lateral growth of the crystal. The outer surface of element 407 is cylindrical while the inner surfaces are generally conical and coated with Ta_xC_y or Nb_xC_y. Preferably the inner surfaces of element 407 are comprised of a pair of conical surfaces as shown in FIG. 4.

Seed crystal 401 is pressed and sealed to ring element 407 using a gas impermeable graphite foil 409. As shown, the inner diameter of the portion of ring element 407 adjacent to seed crystal 401 as well as the interposed gas impermeable foil 409 is smaller than the outer diameter of crystal 401. Accordingly, the edge of crystal 401 is unexposed, thus controlling growth of crystal defects that typically would originate at the crystal edge, the crystal edge defined as the juncture of the crystal face surface and the crystal side surface. In addition to preventing exposure of the crystal edge, ring element 407 provides a means of achieving the desired lateral temperature gradient and thus, as previously noted, provides a means of controlling the lateral growth of the crystal.

In the preferred embodiment of the invention, the inner surface of ring element 407 is comprised of a pair of conical surfaces, the pair of conical surfaces providing a slight necking down of the crystal growth surface. As such, prior to undergoing lateral expansion, the crystal growth surface undergoes an initial period of contraction. In an alternate embodiment, ring element 407 is comprised of a single conical inner surface that defines the laterally expanding crystal surface. In an alternate embodiment, ring element 407 is comprised of a single conical inner surface that defines the laterally expanding crystal surface and a non-conical inner surface immediately adjacent to the seed crystal that insures that the crystal growth interface initially undergoes a period of contraction prior to undergoing lateral expansion. As in the preferred embodiment, in the alternate embodiments the inner diameter of the portion of element 407 in contact with foil 409 (and adjacent to crystal 401) is smaller than the outer diameter of seed crystal 401, thus controlling growth of edge defects.

A second gas impermeable graphite foil 411 is used to seal the back surface of seed crystal 401 and holder 405 to a graphite heat sink 413. Foil 411 helps to achieve a good thermal contact between crystal 401/holder 405 and heat sink 413, the thermal contact preferably being continuous across the entire heat sink interface. As shown, the outer diameter of graphite heat sink 413 is substantially equal to the outer diameter of ring element 407. The stack, comprised of heat sink 413, holder 405, seed crystal 401, ring element 407, and seals 409 and 411, is press fit within a thin-wall graphite cylinder 415 (step 307), thereby preventing reactive gases such as Si, SiC, and/or SiC_2 from reaching the non-growth surfaces of seed crystal 401.

A source 417 is placed within a growth chamber 419. (Step 309). Seed crystal 401, the multi-element sealing system and graphite cylinder 415 are then located within the growth chamber. (Step 311) Growth chamber 419 is fabricated from Ta_xC_y, Nb_xC_y, or graphite. If graphite is used for growth chamber 419, the inner surfaces of the chamber are coated with either Ta_xC_y or Nb_xC_y. Preferably the distance between the seed crystal growth surface and the top of the source material 417 is less than 30 percent of the diameter of source 417, thus allowing quasi-equilibrium vapor phase conditions to be maintained.

Source 417 is fabricated in such a manner as to suppress the formation of source particles in the gas phase during crystal growth. In the preferred embodiment of the invention, this goal is achieved by annealing electronic grade SiC powder or a mixture of Si and C powders at a temperature of between about 2100 and 2500° C. for approximately 1 hour. As a result of the annealing process, a dense deposit is formed that eliminates particle formation

during crystal growth. In order to obtain doped SiC crystals using the invention, the desired dopants and/or impurities (e.g., nitrogen, boron, aluminum, indium, vanadium, molybdenum, scandium, chromium, iron, magnesium, tin, and zirconium) are included in source 417.

Growth chamber 419 is placed within a two-piece graphite crucible 421 (step 313), the shape (e.g., the tapered portions) of which is designed to provide the temperature gradients described in further detail below. In order to prevent graphitization, a requirement of the present invention, the stoichiometry of the vapor within the growth chamber, i.e., the ratio of silicon to carbon, must remain relatively constant during crystal growth. One method of realizing this objective is to minimize material losses. Accordingly, in the preferred embodiment of the invention, the rate of material loss during the growth process is maintained at a level of less than 0.5 percent of the initial source weight per hour. In particular this rate loss is achieved by first locating graphite crucible 421 within a high temperature furnace 423, preferably an RF induction furnace as shown. (Step 315) Graphite foam 425 is used to suppress heat losses from the furnace. The furnace, along with the growth chamber, is next evacuated down to a pressure of 10^{-5} torr or less (step 317) and then heated to a temperature of approximately 1500° C. (step 319). Chamber 419 is then sealed, preferably using different types of graphite with different coefficients of thermal expansion, in order to prevent graphitization. (Step 321)

After chamber sealing, the furnace is filled with pure argon or argon with traces of nitrogen. (Step 323) To obtain the desired resistivity within the grown crystal, the partial pressure of the gas filled furnace is maintained within a range of 10^{-1} to 10^{-4} torr. Crucible 421 and chamber 419 are then heated to a temperature of between 1900 and 2400° C. at a rate of between 6 and 20° C. per minute. (Step 325)

During crystal growth, crucible 421 is axially rotated at a rate of approximately 1 to 5 revolutions per minute. (Step 327) As the crystal grows, the required temperature gradients are achieved, at least in part, by altering the relative positions of crucible 421 and furnace 423. (Step 329) Typically the rate of movement is approximately equivalent to the rate of crystal growth, i.e., between 0.1 and 1.5 millimeters per hour.

Preferred Crystal Growth Methodology

In addition to the method and apparatus described above, the inventors have found that certain growth methodologies are preferred. As previously noted, free-space expansion of the crystal during growth is critical to achieving defect free SiC. Accordingly, it is important to prevent the formation of polycrystalline deposits on all surfaces that surround seed 401, such surfaces including ring element 407, seed holder 405, graphite cylinder 415, and growth chamber 419. Insuring that the temperature of the surface in question is higher than that of the seed is the preferred technique for preventing polycrystalline deposits. At the same time, however, it is important that the temperature differential between the seed and the adjacent surfaces not be too great, otherwise lateral crystal growth may be deterred. Accordingly, the inventors have found that the temperature differential between the crystallization front and the adjacent surface before the crystallization front should be in the range of 1 to 5° C.

The inventors have found that during the period of time in which the crystal is undergoing lateral expansion, a temperature drop of between 5 and 25° C., and preferably between 5 and 10° C., should be maintained between seed 401 and source 417. This temperature differential aids in the suppression of normal (i.e., non-lateral) crystal growth.

Preferably there is a lateral dependence to the temperature differential such that the smallest temperature differential occurs at the center of the seed, increasing with lateral distance. As a result, a convex crystallization growth front is formed which aids in the elimination of micropipe propagation.

As previously described, preferably the angle between the normal crystal growth and the lateral crystal growth (e.g., angle 107 of FIG. 1) is greater than 25 degrees. If the angle is less than 25 degrees, the defects of seed crystal 401 and any defects that may be generated during the initial crystal growth will continue to propagate throughout the newly grown crystal. If the angle is greater than 45 degrees, as in the preferred embodiment of the invention, typically all of the defects will move towards the lateral surface and, once the lateral surface is reached, not participate further in the growth process. In those cases in which not all of the defects are eliminated from participation in the growth process, the defect density in the laterally grown material is typically on the order of 10^2 per square centimeter or less, and more typically on the order of 10 per square centimeter or less. In the intermediate situation in which the angle is between 25 and 45 degrees, the expansion of defects into the laterally growing crystal body is typically observed. If seed crystal 401 is of a high quality, however, angles within this range may yield crystals of sufficiently low defect density.

Initially, lateral crystal growth dominates (step 331), the laterally grown crystal being free of micropipes and having a defect (e.g., dislocations, micropipes) density less than 10^4 per square centimeter, preferably less than 10^3 per square centimeter, more preferably less than 10^2 per square centimeter, still more preferably less than 10 per square centimeter, and still more preferably with zero defects per square centimeter. As observed, this material is free of any graphite inclusions. Crystal growth, dominated by lateral crystal growth, continues until the desired crystal diameter is reached, this crystal diameter being defined by the growth chamber in general, and for the embodiment illustrated in FIG. 5, by ring element 407. Once the crystal reaches the desired diameter (step 333), the vertical temperature gradient is changed to promote normal, i.e., vertical, crystal growth (step 335). In order to achieve the desired change in the temperature gradient, the relative positions of furnace 423 and crucible 421 are changed. In the preferred embodiment of the invention, furnace 423 is an inductive furnace and the coils of the furnace are moved relative to crucible 421. Alternately, or in addition to changing the relative positions of the furnace and the crucible, the temperature within portions of the furnace may be changed. Preferably the axial temperature gradient, i.e., the gradient between the source and the growth surface, is in the range of 10to 50° C. per centimeter, yielding the desired normal growth rate of between 0.4 and 1.5 millimeters per hour.

During the last stage of crystal growth it is important to prevent considerable lateral crystal expansion. It is also important, as previously described, to prevent SiC deposits from forming on the crucible side walls (e.g., the side walls of ring element 407, graphite cylinder 415, and growth chamber 419). Accordingly, a higher side wall temperature is maintained relative to the temperature of the seed crystal, preferably the temperature difference being at least 10° C., more preferably between 10 and 30° C., and still more preferably between 10 and 15° C. The higher side wall temperature radiatively heats the sides of the growing crystal, thereby achieving hotter crystal side walls than the normal growth surface of the crystal. As a result, all of the vapor species are consumed at the normal growth surface of

the crystal and growth on the crucible side walls is suppressed. Additionally, this temperature difference insures that the growing crystal does not come into contact with the crucible side walls, such contact being a major source of defects.

The inventors have also found that the temperature gradient in the growing crystal must be maintained at a relatively low number, preferably on the order of 5° C. per centimeter or less. If the temperature gradient becomes too large, strain is created within the growing crystal, resulting in the formation of dislocations or other defects.

Detailed Growth Region

FIG. 5 is a cross-sectional view of the critical growth region in the preferred embodiment of the invention. In this embodiment the SiC seed crystal **501** is held within a portion of ring element **503**. A graphite foil ring **505** is interposed between ring element **503** and the growth surface of crystal **501**, foil ring **505** sealing the seed crystal to the ring element. The side and back surfaces of crystal **501** are covered with a graphite foil **507**. A graphite disk **509** is coupled to seed crystal **501** via graphite foil **507**. The primary purpose of disk **509** and interposed graphite foil **507** is to aid in the removal of heat from crystal **501**. Additionally, disk **509** provides a support surface for crystal **501** as well as a means for conveniently applying pressure to the crystal with graphite ring **511**, thereby achieving a seal between the crystal and element **503**. Graphite foils **505** and **507** are typically between 0.25 and 0.80 millimeters thick.

Ring element **503** is preferably press fit within a graphite cylinder **513**. Graphite foil **515**, typically between 0.25 and 0.80 millimeters thick, is preferably interposed between the outer wall of ring element **503** and the inner wall of cylinder **513**, thus helping to achieve a good pressure seal. Graphite foam **517** is used to suppress heat losses from the furnace.

In this embodiment of the invention, ring element **503** is fabricated from graphite with inner surfaces **519** coated with Ta_xC_y or Nb_xC_y. Diameter D, the largest inner diameter of element **503**, is 30 millimeters although there are no major limitations to increasing this diameter, thereby yielding a larger grown crystal. Diameter d, the smallest inner diameter of element **503** is selected such that the ratio D/d is greater than 3. Angle **521** is selected, as previously disclosed, to be greater than 25 degrees and preferably less than 90 degrees.

Thermal Analysis

FIGS. **6–10** provide calculated temperature distributions within the growth cell and in the growing crystal for a specific embodiment of the invention. In FIGS. **6–9** the seed crystal is indicated as substrate **601**, the crystal growth interface is indicated as surface **603**, and the ring element is indicated as element **605**. For purposes of this analysis, ring element **605** is comprised of a single conical surface rather than a pair of conical surfaces as shown in the ring elements of FIGS. **4** and **5**.

FIGS. **6** and **7** illustrate the temperature distribution after approximately 4 hours of growth while FIGS. **8** and **9** illustrate the temperature distribution after approximately 22 hours of growth. The cone angle for the ring element in FIGS. **6** and **8** is 45 degrees while the cone angle for the ring element in FIGS. **7** and **9** is 70 degrees.

FIG. **10** illustrates a one dimensional temperature distribution over the ring element cell wall, i.e., line **1001**, and the crystal interface, i.e., line **1003**. The ring element wall locations and the crystal interface locations that correspond to the data points shown on lines **1001** and **1003**, respectively, are shown in FIG. **11**.

Thermal Elastic Stress Distribution

As disclosed above, the temperature gradient within the growing crystal must be maintained at a relatively low number, preferably 5° C. per centimeter or less. FIGS. **12** and **13** illustrate the distribution of the principal component of the thermal elastic stress tensor σ_{rz} given in Pascals, as computed for the temperature distributions shown in FIGS. **6** and **8**. The illustrated thermal elastic stress component is responsible for gliding of dislocations.

The computed results indicate that the σ_{rz} value does not exceed the SiC plasticity threshold in the major portion of the crystal. Accordingly, the probability of generating dislocations within the growing crystal is negligible.

As will be understood by those familiar with the art, the present invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. Accordingly, the disclosures and descriptions herein are intended to be illustrative, but not limiting, of the scope of the invention which is set forth in the following claims.

What is claimed is:

1. A silicon carbide material, comprising:

a single crystal silicon carbide seed crystal, said single crystal silicon carbide seed crystal having a first density of defects, said defects comprised of micropipes and dislocations;

an axial region of re-crystallized silicon carbide, said axial region grown off of said single crystal silicon carbide seed crystal, said axial region having a second density of defects, said defects comprised of micropipes and dislocations; and

a lateral region of re-crystallized silicon carbide, said lateral region grown off of said single crystal silicon carbide seed crystal, said lateral region having a third density of defects, said defects comprised of micropipes and dislocations, wherein said third defect density is less than said first defect density and less than said second defect density, and wherein said third defect density is less than 10^4 per square centimeter.

2. The silicon carbide material of claim **1**, wherein said third density of defects is less than 10^3 per square centimeter.

3. The silicon carbide material of claim **1**, wherein said third density of defects is less than 10^2 per square centimeter.

4. The silicon carbide material of claim **1**, wherein said third density of defects is less than 10 per square centimeter.

5. The silicon carbide material of claim **1**, wherein said axial region of re-crystaized silicon carbide has a first thickness and said lateral region of re-crystallized silicon carbide has a second thickness substantially equivalent to said first thickness, and wherein said first thickness is at least 1 millimeter thick.

6. The silicon carbide material of claim **1**, wherein said axial region of re-crystallized silicon carbide has a first thickness and said lateral region of re-crystallized silicon carbide has a second thickness substantially equivalent to said first thickness, and wherein said first thickness is at least 1 centimeter thick.

7. A silicon carbide material, comprising:

a single crystal silicon carbide seed crystal, said single crystal silicon carbide seed crystal having a first density of defects, said defects comprised of micropipes and dislocations, said single crystal silicon carbide seed crystal having a growth surface;

a first region of re-crystallized silicon carbide, said first region of re-crystallized silicon carbide initiating at said growth surface of said single crystal silicon carbide seed crystal, wherein a first portion of a crystallization growth front corresponding to said first region

of re-crystallized silicon carbide follows an axial growth path, said first region of re-crystallized silicon carbide having a second density of defects, said defects comprised of micropipes and dislocations; and

a second region of re-crystallized silicon carbide, said second region of re-crystallized silicon carbide initiating at said growth surface of said single crystal silicon carbide seed crystal, wherein a second portion of said crystallization growth front corresponding to said second region of re-crystallized silicon carbide follows a laterally expanding growth path, wherein an outermost edge of said second portion of said crystallization growth front is at an angle of greater than 25 degrees as measured from a normal growth axis, said second region of re-crystallized silicon carbide having a third density of defects, said defects comprised of micropipes and dislocations, wherein said third density of defects is less than said first density of defects and less than said second density of defects, and wherein said third density of defects is less than 10^4 per square centimeter.

8. The silicon carbide material of claim 7, wherein said second density of defects is greater than 10^5 per square centimeter.

9. The silicon carbide material of claim 7, wherein said third density of defects is less than 10^3 per square centimeter.

10. The silicon carbide material of claim 7, wherein said third density of defects is less than 10^2 per square centimeter.

11. The silicon carbide material of claim 7, wherein said third density of defects is less than 10 per square centimeter.

12. The silicon carbide material of claim 7, wherein said first and second regions of re-crystallized silicon carbide are at least 1 millimeter thick.

13. The silicon carbide material of claim 7, wherein said first and second regions of re-crystallized silicon carbide are at least 1 centimeter thick.

14. The silicon carbide material of claim 7, wherein said angle is greater than 45 degrees.

* * * * *

EXHIBIT E

Claim Chart of Dow Corning's Infringement of U.S. Patent No. 6,534,026:

Claims	
1. A silicon carbide material, comprising: a single crystal silicon carbide seed crystal, said single crystal silicon carbide seed crystal having a first density of defects, said defects comprised of micropipes and dislocations;	Fox understands from Dow Corning's public statements that Dow Corning is using physical vapor transport to grow the infringing material on a SiC seed crystal, which has a first density of defects, these defects include micropipes and dislocations.
an axial region of re-crystallized silicon carbide, said axial region grown off of said single crystal silicon carbide seed crystal, said axial region having a second density of defects, said defects comprised of micropipes and dislocations; and	Fox understands from Dow Corning's public statements that Dow Corning's process produces an axial region of recrystallized silicon carbide grown off a single crystal silicon carbide seed and that this axial region has a second density of defects comprising micropipes and dislocations.
a lateral region of re-crystallized silicon carbide, said lateral region grown off of said single crystal silicon carbide seed crystal, said lateral region having a third density of defects, said defects comprised of micropipes and dislocations,	Fox understands from Dow Corning's public statements that Dow Corning's process produces a lateral region of re-crystallized silicon carbide grown off the single crystal silicon carbide seed and that this lateral region has a third density of defects comprising micropipes and dislocations.
wherein said third defect density is less than said first defect density and less than said second defect density, and wherein said third defect density is less than 10^4 per square centimeter.	Fox understands from Dow Corning's public statements that the third defect density in Dow Corning's accused materials is less than the first defect density and less than the second defect density, and that the third defect density is less than 10^4 per square centimeter.

EXHIBIT F

US006562130B2

(12) **United States Patent**
Vodakov et al.

(10) **Patent No.: US 6,562,130 B2**
(45) **Date of Patent: *May 13, 2003**

(54) **LOW DEFECT AXIALLY GROWN SINGLE CRYSTAL SILICON CARBIDE**

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(73) Assignee: **The Fox Group, Inc.**, Livermore, CA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **09/849,615**

(22) Filed: **May 4, 2001**

(65) **Prior Publication Data**

US 2002/0059901 A1 May 23, 2002

Related U.S. Application Data

(63) Continuation-in-part of application No. 09/355,561, filed as application No. PCT/RU97/00005 on Jan. 22, 1997, now Pat. No. 6,261,363.

(51) **Int. Cl.**[7] **C30B 23/06**
(52) **U.S. Cl.** **117/109**; 117/107; 117/200; 117/201; 117/900; 423/345
(58) **Field of Search** 117/109, 107, 117/200; 423/345

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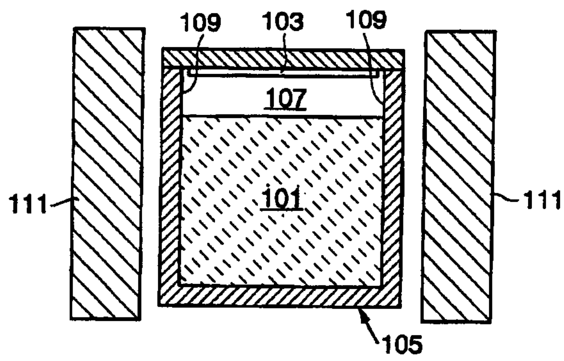
Primary Examiner—Robert Kunemund
(74) *Attorney, Agent, or Firm*—Bingham, McCutchen, LLP; David G. Beck

(57) **ABSTRACT**

A method and apparatus for axially growing single crystal silicon carbide is provided. Utilizing the system, silicon carbide can be grown with a dislocation density of less than 10^4 per square centimeter, a micropipe density of less than 10 per square centimeter, and a secondary phase inclusion density of less than 10 per cubic centimeter. As disclosed, a SiC source and a SiC seed crystal of the desired polytype are co-located within a crucible, the growth zone being defined by the substantially parallel surfaces of the source and the seed in combination with the sidewalls of the crucible. Prior to reaching the growth temperature, the crucible is evacuated and sealed, either directly or through the use of a secondary container housing the crucible. The crucible is comprised of tantalum or niobium that has been specially treated. As a result of the treatment, the inner surfaces of the crucible exhibit a depth variable composition of Ta—Si—C or Nb—Si—C that is no longer capable of absorbing SiC vapors, thus allowing the vapor-phase composition within the crucible to be close to the SiC—Si system with the partial pressure of Si-vapor slightly higher than that in the SiC—Si system.

26 Claims, 1 Drawing Sheet



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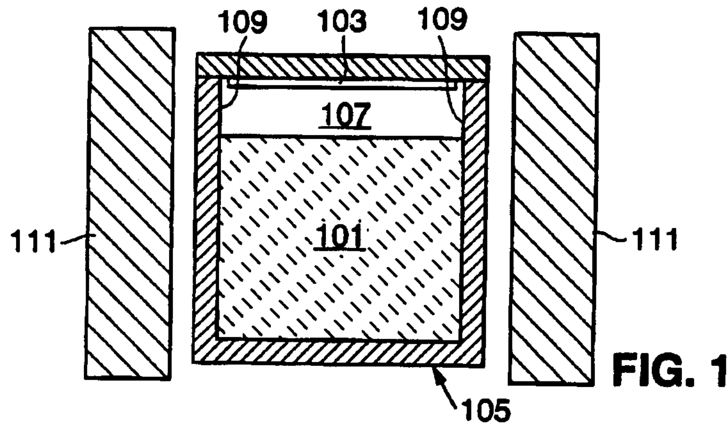

FIG. 1

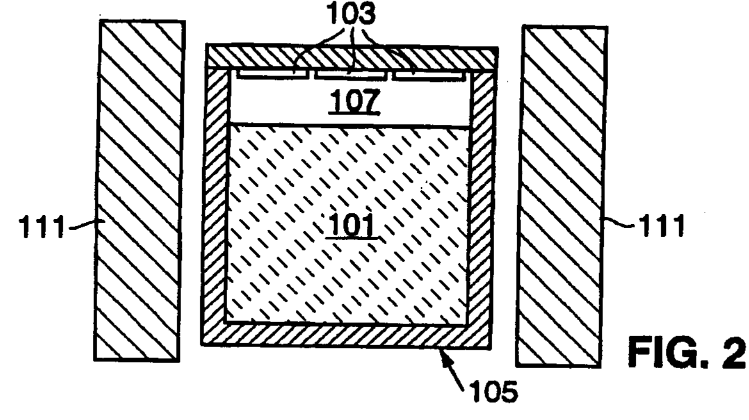

FIG. 2

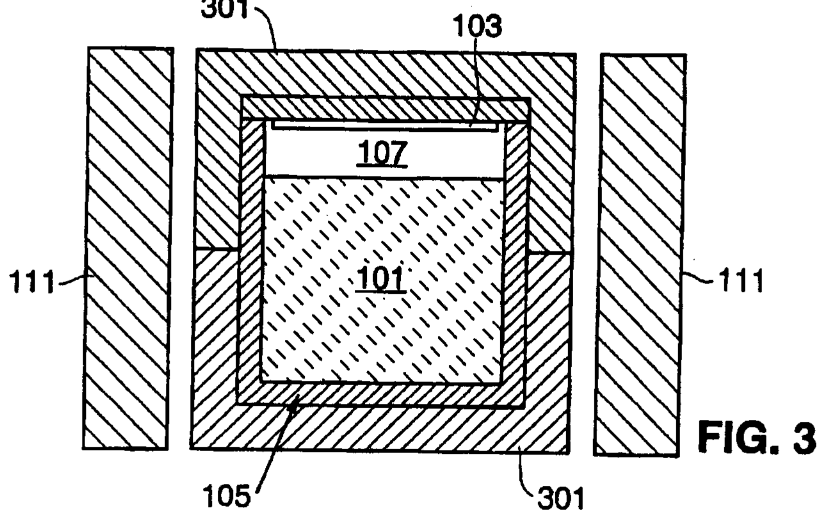

FIG. 3

LOW DEFECT AXIALLY GROWN SINGLE CRYSTAL SILICON CARBIDE

CROSS-REFERENCES TO RELATED APPLICATIONS

This application is a continuation-in-part of U.S. patent application Ser. No. 09/355,561, filed Jul. 20, 1999 now U.S. Pat. No. 6,261,363, which is a 371, and claims priority from PCT Application Serial No. PCT/RU97/00005, filed Jan. 22, 1997.

FIELD OF THE INVENTION

The present invention relates generally to the generation of monocrystalline materials and, more particularly, to a method and apparatus for growing monocrystalline silicon carbide.

BACKGROUND OF THE INVENTION

Silicon carbide (SiC) is wide-band-gap semiconductor material that has a number of characteristics that make it an ideal candidate for a variety of semiconductor applications including, but not limited to, light sources, power diodes, field-effect transistors, and photodiodes. The ability to realize the benefits offered by SiC is largely controlled by the purity of the material as well as its structural characteristics.

The methods most commonly used in producing SiC single crystals are sublimation techniques based on the Lely method, this method utilizing vapor-phase crystallization of evaporated solid silicon carbide. (See, for example, U.S. Pat. Ser. Nos. 2,854,364 and 4,866,005). As shown by Karpov et al. in an article entitled Excess Phase Formation During Sublimation Growth of Silicon Carbide, 6th Int. Conf. on Silicon Carbide, Kyoto, Japan, 74–75 (September 1995), in order to achieve SiC monocrystalline growth from vapor without forming secondary-phase inclusions, the external silicon (Si) flux on the growing surface must exceed the carbon (C) flux. The ability to achieve the desired excess silicon flux depends on the temperature of the growing surface and, in the case of sublimation techniques, the composition of the vapor adjacent to the growth surface.

As silicon molecules have the maximum concentration in the gaseous phase, any drift of the substance from the growth zone will result in the vapor phase within the growth zone being depleted of silicon and enriched with carbon. Excessive carbon in the growth zone leads to source graphitization, crystal quality degradation, and eventually the discontinuation of the growth process. On the other hand, excessive silicon in the growth zone may result both in the formation of defects on the growing surface of the SiC crystal, primarily due to the precipitation of excess silicon drops, and in the generation of polytypes differing from the seed polytype. Accordingly, it has been established that the best characteristics for the as-grown SiC single crystal are achieved when the vapor composition in the growth zone is shifted the towards the vapor phase corresponding to the SiC—Si system.

U.S. Pat. Ser. No. 2,854,364 discloses locating SiC powder with a mass of more than three times the mass of the single crystal to be grown in the growth zone in order to maintain a relatively constant vapor phase composition, the powder serving as a source of silicon carbide vapors. As disclosed, the drift of SiC vapors into the space outside the growth zone is balanced by the generation of SiC vapors from the SiC powder. The duration of the stable growth process is limited by the quantity of SiC powder located in the growth zone. Once the source of SiC vapors becomes depleted, the vapor composition shifts to the non-advantageous SiC—C system.

In U.S. Pat. Ser. No. 4,866,005 a technique is disclosed that continuously feeds small portions of SiC powder into a temperature zone of the growth chamber. Although this technique does allow a SiC—Si system to be maintained indefinitely, it is an inefficient process due to the SiC material consumed in addition to the SiC source as well as the growth zone geometry. As disclosed, the evaporating surface of the SiC vapor source is approximately 10 centimeters from the growing surface of the seed crystal, a distance that far exceeds the Si, Si_2C, SiC_2 molecular track length at the working pressure in the growth zone.

U.S. Pat. Ser. No. 4,147,572 discloses a growth technique in which the evaporating surface of the SiC source and the growth surface of the SiC seed crystal are arranged in parallel at a distance that is less than 20 percent of the maximum linear dimension of the source. The single crystals are grown in a graphite crucible in an inert gas atmosphere at temperatures of 1600 to 2000° C. with an axial thermal gradient of 5 to 200° C. per centimeter. This technique is limited to relatively small crystals, typically less than 1 millimeter thick, due to a sharp drop in the growth rate as the crystallization time increases. The change in growth rate is due to the silicon at the edge of the growth zone being volatilized, thereby causing excessive carbon to be released from the evaporating surface of the SiC source and the growing surface of the grown crystal. Single crystals obtained by this technique show defects such as secondary-phase inclusions (predominantly, graphite), micropipes with a density of more than 100 per square centimeter, and dislocations of at least 10^4 per square centimeter. These crystals also have relatively high concentrations of residual impurities such as boron, oxygen, etc.

In an article by D. Hofmann et al. entitled The Use of Tantalum Container Material for Quality Improvement of SiC Crystals Grown by the Sublimation Technique, 6th Int. Conf. on Silicon Carbide, Kyoto, Japan, 15 (September 1995), it was shown that the inclusion of tantalum (Ta) during the sublimation growth of monocrystalline SiC resulted in the vapor medium produced in the growth zone being close to the SiC—Si system. The favorable aspects were found to occur both in an inert gas atmosphere and in vacuum. Unfortunately it was also found that during the early stages of growth, secondary-phase inclusions of tantalum or its compounds were formed. An increased concentration of dissolved tantalum in the monocrystalline SiC was also noted. Lastly, due to the carbon enrichment of the vapor phase that results from silicon drifting outside of the growth zone, carbon dust was embedded into the growing crystal, further reducing the quality of the growing crystal while simultaneously decreasing the transferal efficiency of source material to the growing crystal.

Another problem associated with the use of a Ta container as disclosed in the previously cited article arises during the initial stage of the growth process when the silicon vapors formed by the evaporating SiC source interact with the material of the tantalum container. As a result of this interaction, a low-melting-point tantalum silicon alloy is formed which can lead to the destruction of the container at the normal growth temperature.

In known sublimation techniques for growing SiC single crystals, the vapor source may be either a pre-synthesized SiC powder of the specified dispersity or a polycrystalline or monocrystalline SiC wafer produced, for example, by the

Lely method. Although the use of SiC powder is more economical than the use of wafers, providing a continuous supply of powder into the growth zone, as required to grow large single crystals, is quite complicated. Additionally, SiC powder often includes impurities such as graphite or other dust that are transported to the growth surface along with the SiC molecules. These impurities lead to a high density of micropipes and dislocations in the growing crystal, thus substantially impacting the crystal quality.

Accordingly, what is needed in the art is a method and system that allows high quality SiC single crystals to be grown. The present invention provides such a method and system.

SUMMARY OF THE INVENTION

The present invention provides a method and apparatus for growing low dislocation density single crystal silicon carbide. Utilizing the system of the invention, silicon carbide can be grown with a dislocation density of less than 10^4 per square centimeter, preferably less than 10^3 per square centimeter, and more preferably less than 10^2 per square centimeter. The density of micropipes in the as-grown material is less than 10 per square centimeter. The density of secondary phase inclusions is less than 10 per cubic centimeter and preferably less than 1 per cubic centimeter. Depending upon the construction of the crucible, the concentration of tantalum or niobium impurities is less than 10^{17} per cubic centimeter.

In accordance with the invention, a SiC source and a SiC seed crystal of the desired polytype are co-located within a crucible with the distance separating the source evaporating surface from the growing surface being comparable to the track length of a SiC molecule. The growth zone is defined by the substantially parallel surfaces of the source and the seed in combination with the sidewalls of the crucible. Prior to reaching the growth temperature, the crucible is evacuated and sealed, either directly or through the use of a secondary container housing the crucible.

In further accordance with the invention, the crucible is comprised of tantalum or niobium that has been specially treated. As a result of the treatment, the inner surfaces of the crucible exhibit a depth variable composition of Ta—Si—C or Nb—Si—C that is no longer capable of absorbing SiC vapors as the monocrystalline silicon carbide is grown. Accordingly, during crystal growth the vapor-phase composition within the crucible is close to the SiC—Si system with the partial pressure of Si-vapor slightly higher than that in the SiC—Si system. Additionally, the resultant Ta—Si—C or Nb—Si—C material is refractory, thus allowing it to withstand the operating temperatures required to grow the silicon carbide.

The crucible is initially fabricated from tantalum or niobium that is preferably at least 99.9 percent pure. Once the crucible is shaped, it undergoes a series of processing steps to clean the surfaces and remove surface contaminants. A thin, near-surface layer of Ta—C or Nb—C is then formed and annealed, resulting in a surface that will not interact with carbon particles. Lastly the crucible is annealed in silicon containing vapor that is diluted by an inert gas, preferably argon, resulting in the formation of a depth variable composition of Ta—Si—C or Nb—Si—C on the crucible surfaces.

A further understanding of the nature and advantages of the present invention may be realized by reference to the remaining portions of the specification and the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view of a crucible according to the invention;

FIG. 2 is a cross-sectional view of a crucible similar to that shown in FIG. 1 with multiple silicon carbide seeds contained therein; and

FIG. 3 is a cross-sectional view of a crucible similar to that shown in FIG. 1 with a separate, sealable container.

DESCRIPTION OF THE SPECIFIC EMBODIMENTS

Growth Process

According to the invention and as illustrated in FIG. 1, a silicon carbide (SiC) source **101** and a SiC seed crystal **103** of the desired polytype (e.g., 4H, 6H, 3C, etc.) are co-located within a crucible **105**. An axial growth zone **107** is defined by the substantially parallel surfaces of source **101** and seed **103** in combination with sidewalls **109** of crucible **105**. If multiple seed crystals **103** are used as illustrated in FIG. 2, their growth surfaces are located within the same plane and parallel to the evaporating surface of source **101**.

The distance between the evaporating surface of source **101** and the growing surface of seed crystal **103** is preferably not much in excess of the track length of a SiC molecule. This configuration enhances the crystal growth rate as the precipitation of source vapors outside of the seed crystal growth surface is minimized.

In the preferred embodiment, source **101** is comprised of SiC ceramics that are produced from SiC powder that has been sintered at a temperature that permits partial oversublimation of the SiC grains. The sintering process is preferably carried out in an inert gas environment (e.g., argon) within a temperature range of 1500 to 2300° C. In addition to achieving partial binding of the powder, during the sintering process basic background impurities and dust are removed from the powder, thus preventing the dust composition from being transferred from the evaporating surface of source **101** in the vapor phase. The SiC ceramics used for source **101** can also be fabricated by compressing SiC powder.

Additionally, during the fabrication of the SiC ceramics, a doping agent can be deliberately introduced. By using SiC ceramics in which the dopant has been uniformly distributed throughout the entire volume, a uniformly doped single crystal can be grown.

In another embodiment of the invention, a SiC polycrystal or mono-crystal source is used.

As shown in FIG. 1, in the preferred embodiment SiC source **101** is located on the bottom of crucible **105** and seed crystal **103** is mounted to the top surface of the crucible. Alternately, source **101** can be mounted on the top surface of the crucible with seed crystal **103** mounted to the crucible's bottom surface. In order to prevent the loss of SiC source material due to precipitation of SiC vapors outside the growth surface, preferably the inner dimensions of crucible **105** in general, and crucible sidewalls **109** in particular, do not exceed the dimensions of growth zone **107**. Accordingly, in this embodiment of the invention, sidewalls **109** define the periphery of growth zone **107**. If the inner dimensions of sidewalls **109** do exceed the dimensions of growth zone **107**, preferably it is by a minor amount.

As described in further detail below, crucible **105** is comprised of tantalum (Ta) or niobium (Nb) that has been specially treated. It has been established by the inventors that as a result of such treatment, the crucible exhibits a depth-variable composition of Ta—Si—C or Nb—Si—C that is no longer capable of absorbing SiC vapors as the monocrystalline silicon carbide is grown. Consequently, during crystal growth the vapor-phase composition within crucible **105** is close to the SiC—Si system with the partial

pressure of Si-vapor slightly higher than that in the SiC—Si system. Additionally, the resultant variable composition Ta—Si—C or Nb—Si—C is a refractory material that can withstand the operating temperatures required to grow the SiC single crystal.

Preferably crucible **105** is capable of being evacuated and sealed, either directly or indirectly through the use of an external container **301** as illustrated in FIG. 3. In one embodiment of the invention, after crucible **105** is loaded with source **101** and seed **103**, it is placed within a high temperature oven **111**. Oven **111** provides an axial temperature gradient from seed **103** to source **101**, resulting in the evaporation of the SiC of source **101** and vapor phase crystallization of SiC on the growing surface of seed **103**. In this embodiment crucible **105** (or container **301**) is sealed before the final operating temperature is reached, sealing being accomplished using any of a variety of sealing systems (e.g., vacuum welding, graphite or other based sealants, etc.). In an alternate embodiment, crucible **105** (or container **301**) is evacuated and hermetically sealed prior to placement within high temperature furnace **111**.

If the crystal growing process is run for an extended time period, for example as required to grow an exceptionally large crystal, the gradually increasing thickness of the grown crystal is accompanied by a corresponding decrease in the thickness of source **101**. Accordingly, in order to maintain the growth process, a large source must be used, for example, a source rod of SiC that can be continuously fed into growth zone **107**.

In the illustrated embodiment, furnace **111** provides the required thermal gradient, either through the use of multiple temperature zones (e.g., one zone for source **101** and one zone for seed crystal **103**) or other means. During crystal growth, a stable temperature profile must be maintained throughout the entire growth period. Preferably this is achieved by altering the relative positions of crucible **105** and furnace **111**, for example by moving crucible **105** within furnace **111** at a rate that is substantially equivalent to the growth rate.

As previously disclosed, preferably growth zone **107** is evacuated and sealed prior to initiation of the sublimation process. As a result, material losses from source **101** are substantially reduced. Additionally, sealing crucible **105**, either directly or through the use of separate container **301**, prevents foreign impurities from the environment from entering into growth zone **107**.

By isolating the growth zone from the environment and using a crucible exhibiting a depth-variable composition of Ta—Si—C or Nb—Si—C, the vapor phase in the growth zone shifts from the SiC—C system to the SiC—Si system. Furthermore, as the depth-variable composition of Ta—Si—C or Nb—Si—C remains relatively unchanged for an extended period of time, a stable composition of the vapor phase within growth zone **107** can be achieved, thereby resulting in improvements in both crystal quality and size. For example, the present invention allows SiC single crystals to be grown with a dislocation density of less than 10^4 per square centimeter, preferably less than 10^3 per square centimeter, and more preferably less than 10^2 per square centimeter. The density of micropipes in the as-grown material is less than 10^2 per square centimeter. The density of secondary phase inclusions is less than 10 per cubic centimeter and preferably less than 1 per cubic centimeter. Depending upon the construction of the crucible, the concentration of tantalum or niobium impurities is less than 10^{17} per cubic centimeter and typically in the range of 10^{16} to 10^{17} per cubic centimeter.

In order to grow a SiC crystal of the 4H polytype, a 4H polytype single crystal is used as seed **103** and the growth process is carried out in the presence of tin vapors that have been introduced into the crucible prior to its sealing.

Crucible Preparation

As previously disclosed, crucible **105** is preferably fabricated from tantalum or niobium, thereby allowing the vapor composition during growth to remain close to equilibrium thus reducing crystal graphitization. The tantalum or niobium must be pre-treated, however, to prevent the metals from interacting with the Si—C vapor and forming low-temperature eutectics. The pre-treatment consists of two stages. First, tantalum or niobium carbide layers are formed on the surface. During SiC crystal growth, binding of carbon vapor leads to deeper diffusion of carbon atoms into the pure metal. Second, tantalum or niobium silicide surface layers are formed, the existence of which increases silicon containing species partial pressure.

Initially crucible **105** is fabricated from metallic tantalum or niobium, the metal being at least 99.9 percent pure and of any suitable shape (e.g., rod, rolled, etc.). It is understood that the shape of crucible **105** is not limited to the shape shown in FIGS. 1–3. Once the crucible has been shaped, for example using standard machining processes, it is initially cleaned with standard organic solvents. The crucible is then boiled for 30 minutes in a pre-heated acid solution comprised of a 3:1 mixture of HCl and HNO_3, the acid solution removing metallic remnants left on the surface after crucible shaping. The crucible is then etched in a room temperature 1:1 mixture of HNO_3 and HF for approximately 20 to 30 seconds. This etching step must be short to insure that the etchant does not damage the surface finish quality of the crucible. After etching, the crucible is washed in distilled or deionized boiling water for 10 minutes, the water being changed three times during the process. Lastly, the crucible is dried.

After the crucible has been fabricated and the surfaces cleaned, preferably following the above-described process, the crucible is processed in carbon containing vapor in order to form a thin, near-surface layer of Ta—C or Nb—C. After further temperature processing, this layer protects the crucible's surfaces from interaction with carbon particles.

During carbon vapor processing, the crucible is placed within a furnace and annealed at a pressure of at least 10^{-3} Torr in graphite that is at least 99.99 percent pure. Alternately, the crucible is annealed at a pressure of at least 10^{-1} Torr in vapor that contains carbon species. Preferably a step-wise annealing process is used, such that the crucible is annealed at 800° ±50° C. for one hour, followed by a 1500° ±50° C. anneal for one hour, and ending with a 2000° ±50° C. anneal for two hours. As a result of this annealing process, a thin near-surface layer comprised of Ta—C or Nb—C carbides is formed on the entire surface of the crucible. The depth of carbon penetration for crucibles in which the material is prepared by vacuum melting or metal rolling is approximately 5 to 30 microns while the penetration depth for crucibles formed of materials prepared by powder metallurgy is approximately 100 to 500 microns, the greater penetration depth due to accelerated diffusion along grain boundaries. Quality of the layer as well as the boundary between the metal and the carbide is governed by the technique used to fabricate the metal (e.g., powder metallurgy, rolled metal, vacuum melting, etc.).

After formation of the carbide layer, the crucible is subjected to further temperature processing, thus assuring that the layer protects the surface of the crucible from interaction with carbon particles. During this processing step

the crucible is placed in graphite powder in an argon atmosphere, the graphite powder being at least 99.99 percent pure with a grain size of less than 100 microns and the argon being at least 99.999 percent pure. If the crucible is formed of tantalum it is annealed at a temperature of between 2200 and 2500° C. If the crucible is formed of niobium it is annealed at a temperature of between 2000 and 2300° C. The annealing time for either material is at least 2 hours, the final annealing time being governed by the thickness of the crucible.

Lastly the crucible is annealed for at least 2 hours in silicon containing vapor (i.e., SiC or Si vapor) that is diluted by purified argon. The annealing temperature for a crucible formed of tantalum is between 2200 and 2500° C. while the annealing temperature for a crucible formed of niobium is between 2000 and 2300° C. During annealing, the source of Si-vapor should not come into contact with the crucible. Thus, for example, SiC powder is located in a higher temperature zone than the crucible with a temperature difference of between 10 and 20° C.

After completion of each of the annealing steps outlined above, the crucible is cooled to room temperature at a cooling rate less than 20° C. per minute. Additionally, during each annealing step the temperature variation across the surface of the crucible should be less than 20° C. After all stages of annealing are complete, the amount of carbon that has penetrated into the tantalum or niobium crucible surfaces should be more than 0.02 grams per square centimeter while the amount of silicon that has penetrated into the tantalum or niobium crucible surfaces should be more than 0.0005 grams per square centimeter.

EXAMPLES

SiC crystals have been grown using the disclosed processes, examples of which are provided below. A pretreated tantalum crucible was used. During growth, the evaporating surface of source **101** was separated from the growing surface of seed **103** by approximately 3 to 18 millimeters. An operating temperature of between 1800–2500° C. was used with an axial temperature gradient of between 20 and 25 degrees per centimeter, yielding a growth rate of between 0.7 and 1.2 millimeters per hour.

Seed crystal polytypes included 6H SiC growing in direction [0001] Si; 4H SiC growing in direction [0001] C.; and 6H SiC growing in a direction lying at an angle of 5 degrees to direction [0001].

The as-grown single crystals were approximately 10 millimeters thick with diameters ranging between 20 and 75 millimeters. The density of dislocations was in the range of 10^2 and 10^4 per square centimeter, the density being dependent upon the doping. The density of micropipes was less than 10 per square centimeter while the density of secondary-phase inclusions (i.e., carbon and silicon) was 10 per cubic centimeter. The measured concentration of background impurities was 10^{16} per cubic centimeter for nitrogen; 10^{16} per cubic centimeter for boron; and 10^{16} to 10^{17} per cubic centimeter for tantalum. There was no measurable graphitization of the source or the growing surface during a 10 hour growth procedure which was performed at a temperature of 2000° C. and at a pressure of 10^{-5} Torr. The seed polytype reproducibility was 80 percent for a 6H SiC seed growing in direction [0001] Si; 70 percent for a 4H SiC seed growing in direction [0001] C; and 100 percent for a 6H SiC seed growing in a direction lying at an angle of 5 degrees to direction [0001].

As will be understood by those familiar with the art, the present invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. Accordingly, the disclosures and descriptions herein are intended to be illustrative, but not limiting, of the scope of the invention which is set forth in the following claims.

What is claimed is:

1. A silicon carbide material comprising an axial region of re-crystallized single crystal silicon carbide with a density of dislocations of less than 10^4 per square centimeter, a density of micropipes of less than 10 per square centimeter, and a density of secondary phase inclusions of less than 10 per cubic centimeter.

2. The silicon carbide material of claim **1**, wherein said axial region of re-crystallized single crystal silicon carbide has a tantalum impurity concentration of less than 10^{17} per cubic centimeter, said tantalum impurity concentration uniformly distributed throughout the re-crystallized single crystal silicon carbide material.

3. The silicon carbide material of claim **1**, wherein said axial region of re-crystallized single crystal silicon carbide has a tantalum impurity concentration of between 10^{16} and 10^{17} per cubic centimeter, said tantalum impurity concentration uniformly distributed throughout the re-crystallized single crystal silicon carbide material.

4. The silicon carbide material of claim **1**, wherein said axial region of re-crystallized single crystal silicon carbide has a niobium impurity concentration of less than 10^{17} per cubic centimeter, said niobium impurity concentration uniformly distributed throughout the re-crystallized single crystal silicon carbide material.

5. The silicon carbide material of claim **1**, wherein said axial region of re-crystallized single crystal silicon carbide has a niobium impurity concentration of between 10^{16} and 10^{17} per cubic centimeter, said niobium impurity concentration uniformly distributed throughout the re-crystallized single crystal silicon carbide material.

6. The silicon carbide material of claim **1**, wherein said density of secondary phase inclusions is less than 1 per cubic centimeter.

7. A silicon carbide material comprising an axial region of re-crystallized single crystal silicon carbide with a density of dislocations of less than 10^3 per square centimeter, a density of micropipes of less than 10 per square centimeter, and a density of secondary phase inclusions of less than 10 per cubic centimeter.

8. The silicon carbide material of claim **7**, wherein said axial region of re-crystallized single crystal silicon carbide has a tantalum impurity concentration of less than 10^{17} per cubic centimeter, said tantalum impurity concentration uniformly distributed throughout the re-crystallized single crystal silicon carbide material.

9. The silicon carbide material of claim **7**, wherein said axial region of re-crystallized single crystal silicon carbide has a tantalum impurity concentration of between 10^{16} and 10^{17} per cubic centimeter, said tantalum impurity concentration uniformly distributed throughout the re-crystallized single crystal silicon carbide material.

10. The silicon carbide material of claim **7**, wherein said axial region of re-crystallized single crystal silicon carbide has a niobium impurity concentration of less than 10^{17} per cubic centimeter, said niobium impurity concentration uniformly distributed throughout the re-crystallized single crystal silicon carbide material.

11. The silicon carbide material of claim **7**, wherein said axial region of re-crystallized single crystal silicon carbide has a niobium impurity concentration of between 10^{16} and 10^{17} per cubic centimeter, said niobium impurity concentration uniformly distributed throughout the re-crystallized single crystal silicon carbide material.

12. The silicon carbide material of claim 7, wherein said density of secondary phase inclusions is less than 1 per cubic centimeter.

13. A silicon carbide material comprising an axial region of re-crystallized single crystal silicon carbide with a density of dislocations of less than 10^2 per square centimeter, a density of micropipes of less than 10 per square centimeter, and a density of secondary phase inclusions of less than 10 per cubic centimeter.

14. The silicon carbide material of claim 13, wherein said axial region of re-crystallized single crystal silicon carbide has a tantalum impurity concentration of less than 10^{17} per cubic centimeter, said tantalum impurity concentration uniformly distributed throughout the re-crystallized single crystal silicon carbide material.

15. The silicon carbide material of claim 13, wherein said axial region of re-crystallized single crystal silicon carbide has a tantalum impurity concentration of between 10^{16} and 10^{17} per cubic centimeter, said tantalum impurity concentration uniformly distributed throughout the re-crystallized single crystal silicon carbide material.

16. The silicon carbide material of claim 13, wherein said axial region of re-crystallized single crystal silicon carbide has a niobium impurity concentration of less than 10^{17} per cubic centimeter, said niobium impurity concentration uniformly distributed throughout the re-crystallized single crystal silicon carbide material.

17. The silicon carbide material of claim 13, wherein said axial region of re-crystallized single crystal silicon carbide has a niobium impurity concentration of between 10^{16} and 10^{17} per cubic centimeter, said niobium impurity concentration uniformly distributed throughout the re-crystallized single crystal silicon carbide material.

18. The silicon carbide material of claim 13, wherein said density of secondary phase inclusions is less than 1 per cubic centimeter.

19. A silicon carbide material, comprising:

a single crystal silicon carbide seed crystal, said single crystal silicon carbide seed crystal having a growth surface; and

a region of axially re-crystallized silicon carbide, said region of axially re-crystallized silicon carbide initiating at said growth surface of said single crystal silicon carbide seed crystal, said region of axially re-crystallized silicon carbide having a density of dislocations of less than 10^4 per square centimeter, a density of micropipes of less than 10 per square centimeter, and a density of secondary phase inclusions of less than 10 per cubic centimeter.

20. The silicon carbide material of claim 19, wherein said density of dislocations in said region of axially re-crystallized silicon carbide is less than 10^3 per square centimeter.

21. The silicon carbide material of claim 19, wherein said density of dislocations in said region of axially re-crystallized silicon carbide is less than 10^2 per square centimeter.

22. The silicon carbide material of claim 19, wherein said axial region of re-crystallized single crystal silicon carbide has a tantalum impurity concentration of less than 10^{17} per cubic centimeter, said tantalum impurity concentration uniformly distributed throughout the re-crystallized single crystal silicon carbide material.

23. The silicon carbide material of claim 19, wherein said axial region of re-crystallized single crystal silicon carbide has a tantalum impurity concentration of between 10^{16} and 10^{17} per cubic centimeter, said tantalum impurity concentration uniformly distributed throughout the re-crystallized single crystal silicon carbide material.

24. The silicon carbide material of claim 19, wherein said axial region of re-crystallized single crystal silicon carbide has a niobium impurity concentration of less than 10^{17} per cubic centimeter, said niobium impurity concentration uniformly distributed throughout the re-crystallized single crystal silicon carbide material.

25. The silicon carbide material of claim 19, wherein said axial region of re-crystallized single crystal silicon carbide has a niobium impurity concentration of between 10^{16} and 10^{17} per cubic centimeter, said niobium impurity concentration uniformly distributed throughout the re-crystallized single crystal silicon carbide material.

26. The silicon carbide material of claim 19, wherein said density of secondary phase inclusions is less than 1 per cubic centimeter.

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EXHIBIT G

Claim Chart of Dow Corning's Infringement of U.S. Patent No. 6,562,130:

Claim	
1. A silicon carbide material comprising an axial region of recrystallized single crystal silicon carbide	Fox understands from Dow Corning's public statements that Dow Corning is using physical vapor transport to grow the infringing material on a SiC seed, which sublimates a crystalline SiC source and produces an axial region of re-crystallized single crystal silicon carbide.
with a density of dislocations of less than 10^4 per square centimeter,	Fox understands Dow Corning's public statements that Dow Corning's silicon carbide material has a density of dislocations less than 10^4 per square centimeter.
a density of micropipes of less than 10 per square centimeter,	Fox understands Dow Corning's public statements that Dow Corning's silicon carbide material has a density of micropipes of less than 10 per square centimeter.
and a density of secondary phase inclusions of less than 10 per cubic centimeter.	Fox understands Dow Corning's public statements that Dow Corning's silicon carbide material has a density of secondary phase inclusions of less than 10 per cubic centimeter.