View metadata, citation and similar papers at core.ac.uk

brought to you by CORE

provided by NASA Technical Reports Server

NASA/TM—2012-217708

Characterization of 4H <000-1> Silicon Carbide Films Grown by Solvent-Laser Heated Floating Zone

Andrew A. Woodworth
Glenn Research Center, Cleveland, Ohio

Ali Sayir and Philip G. Neudeck
Glenn Research Center, Cleveland, Ohio

Balaji Raghothamachar and Michael Dudley
Stony Brook University, Stony Brook, New York

September 2012

NASA STI Program . . . in Profile

Since its founding, NASA has been dedicated to the advancement of aeronautics and space science. The NASA Scientific and Technical Information (STI) program plays a key part in helping NASA maintain this important role.

The NASA STI Program operates under the auspices of the Agency Chief Information Officer. It collects, organizes, provides for archiving, and disseminates NASA's STI. The NASA STI program provides access to the NASA Aeronautics and Space Database and its public interface, the NASA Technical Reports Server, thus providing one of the largest collections of aeronautical and space science STI in the world. Results are published in both non-NASA channels and by NASA in the NASA STI Report Series, which includes the following report types:

- TECHNICAL PUBLICATION. Reports of completed research or a major significant phase of research that present the results of NASA programs and include extensive data or theoretical analysis. Includes compilations of significant scientific and technical data and information deemed to be of continuing reference value. NASA counterpart of peer-reviewed formal professional papers but has less stringent limitations on manuscript length and extent of graphic presentations.

- TECHNICAL MEMORANDUM. Scientific and technical findings that are preliminary or of specialized interest, e.g., quick release reports, working papers, and bibliographies that contain minimal annotation. Does not contain extensive analysis.

- CONTRACTOR REPORT. Scientific and technical findings by NASA-sponsored contractors and grantees.

- CONFERENCE PUBLICATION. Collected papers from scientific and technical conferences, symposia, seminars, or other meetings sponsored or cosponsored by NASA.

- SPECIAL PUBLICATION. Scientific, technical, or historical information from NASA programs, projects, and missions, often concerned with subjects having substantial public interest.

- TECHNICAL TRANSLATION. English-language translations of foreign scientific and technical material pertinent to NASA's mission.

Specialized services also include creating custom thesauri, building customized databases, organizing and publishing research results.

For more information about the NASA STI program, see the following:

- Access the NASA STI program home page at *http://www.sti.nasa.gov*

- E-mail your question to *help@sti.nasa.gov*

- Fax your question to the NASA STI Information Desk at 443–757–5803

- Phone the NASA STI Information Desk at 443–757–5802

- Write to:
  STI Information Desk
  NASA Center for AeroSpace Information
  7115 Standard Drive
  Hanover, MD 21076–1320

NASA/TM—2012-217708

Characterization of 4H <000-1> Silicon Carbide Films Grown by Solvent-Laser Heated Floating Zone

Andrew A. Woodworth
Glenn Research Center, Cleveland, Ohio

Ali Sayir and Philip G. Neudeck
Glenn Research Center, Cleveland, Ohio

Balaji Raghothamachar and Michael Dudley
Stony Brook University, Stony Brook, New York

Prepared for the
2012 Spring Meeting and Exhibit
sponsored by the Materials Research Society
San Francisco, California, April 9–13, 2012

National Aeronautics and
Space Administration

Glenn Research Center
Cleveland, Ohio 44135

September 2012

Acknowledgments

The NASA Postdoctoral Program, NASA Vehicle Systems Safety Technologies Project in the Aviation Safety Program, and the US Department of Energy Vehicle Technology Program via Space Act Agreement (NASA GRC SAA3-1048, DOE IA # DE-EE0001093/001) monitored by Susan Rogers provided funding for this work. Technical help from J. Anthony Powell, David Spry, Fredric Dynys, Thomas Sabo, Mark Dieringer, Michelle Mrdonovich-Hill, Francisco Solá-López, Beth Osborn and Charles Blaha is greatly appreciated. Use of the National Synchrotron Light Source, Brookhaven National Laboratory, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886.

Level of Review: This material has been technically reviewed by technical management.

Available from

NASA Center for Aerospace Information
7115 Standard Drive
Hanover, MD 21076–1320

National Technical Information Service
5301 Shawnee Road
Alexandria, VA 22312

Available electronically at http://www.sti.nasa.gov

Characterization of 4H <000-1> Silicon Carbide Films Grown by Solvent-Laser Heated Floating Zone

Andrew A. Woodworth[1]
National Aeronautics and Space Administration
Glenn Research Center
Cleveland, Ohio 44135

Ali Sayir and Philip G. Neudeck
National Aeronautics and Space Administration
Glenn Research Center
Cleveland, Ohio 44135

Balaji Raghothamachar and Michael Dudley
Stony Brook University
Stony Brook, New York 11794

Abstract

Commercially available bulk silicon carbide (SiC) has a high number (>2000/cm^2) of screw dislocations (SD) that have been linked to degradation of high-field power device electrical performance properties. Researchers at the NASA Glenn Research Center have proposed a method to mass-produce significantly higher quality bulk SiC. In order for this bulk growth method to become reality, growth of long single crystal SiC fibers must first be achieved. Therefore, a new growth method, Solvent-Laser Heated Floating Zone (Solvent-LHFZ), has been implemented. While some of the initial Solvent-LHFZ results have recently been reported, this paper focuses on further characterization of grown crystals and their growth fronts. To this end, secondary ion mass spectroscopy (SIMS) depth profiles, cross section analysis by focused ion beam (FIB) milling and mechanical polishing, and orientation and structural characterization by x-ray transmission Laue diffraction patterns and x-ray topography were used. Results paint a picture of a chaotic growth front, with Fe incorporation dependant on C concentration.

Introduction

The use of silicon carbide (SiC) power electronics are widely accepted to be capable of enabling systems that are significantly lighter, smaller, and electrically more efficient than systems comprised of conventional silicon (Si) based electronics. Although some SiC devices (e.g., Schottky diodes and field-effect transistors (FETs)) have been developed, the performance of most SiC power devices are significantly degraded/limited because of a high density of crystal defects in all commercially-available SiC semiconductor wafers. Among the more serious defects in these SiC wafers is a defect known as a "closed-core" screw dislocation (SD), with densities typically greater than 2000 per cm^2 (Refs. 1 to 3). Eliminating these dislocation defects (i.e., reducing them to densities <1 per cm^2) would unlock more of SiC's enormous (as yet unfulfilled) promise to revolutionize nearly all high-power electronic systems.

Recently, SiC growth perpendicular to the c-axis has been shown to grow higher quality (lower defect density) bulk SiC (Ref. 4). Researchers at the NASA Glenn Research Center have proposed a method to mass-produce high quality bulk SiC (Ref. 5). This technique starts by growing a long continuous single

[1]NASA Glenn Research Center, NASA Postdoctoral Program Fellow.

crystal SiC fiber in the crystallographic c-direction, and then laterally (perpendicular to the c-direction) enlarging the fiber into a high quality boule via chemical vapor deposition growth. In order for this bulk SiC growth method to become a reality, growth of both long single crystal SiC fibers and lateral growth of the fiber by CVD must be achieved. Therefore, two parallel development tracks have been formed: SiC fiber growth and lateral CVD.

In order to create long single crystal SiC fibers, growth has been implemented that combines the advantages of two well known growth methods: Laser Heated Floating Zone (proven for oxide-based crystals) (Ref. 6) and Traveling Solvent Method (demonstrated for SiC) (Ref. 7). Solvent-Laser Heated Floating Zone (Solvent-LHFZ) (Ref. 8) couples the potential to grow long fibers with a solvent system capable of growing SiC.

Experiment

Characterization of the grown crystals and their growth fronts were carried out by depth profile, cross sectional analysis and x-ray techniques. Secondary ion mass spectroscopy (SIMS) was performed on the C-face (000-1) face of several samples with an analysis area of ~175×175 μm in order to create depth profiles of the metal solvents incorporated into the grown crystals. Focused ion beam (FIB) milling and mechanical polishing were used to make cross sections of the crystals, which were then examined by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS), and orientation and structural characterization studies were carried out by x-ray transmission Laue diffraction and white beam x-ray topography at the Stony Brook Synchrotron Topography Station, Beamline X19C at the National Synchrotron Light Source, Brookhaven National Laboratory.

Experiments were carried out in a custom vacuum system under 15 slm flow of argon at 115 torr, using a CO_2 laser as the heat source. A more detailed description of the system can be found elsewhere (Ref. 8). At the heart of the system, a 0.5 by 0.5 by 15 mm 4H-SiC crystal (long axis parallel to the <0001> direction) is mounted so that the carbon face (000-1) of the crystal is facing down. The growth surface varied from on axis to roughly 10° from the (000-1). Directly below the crystal, a ~2 mm diameter feed rod (composed of the source material for crystal growth) is mounted vertically. The laser heats and melts the top end of the feed rod creating a melt (liquid) composed of the crystal growth materials. The seed crystal is then brought into contact with the melt allowing the liquid to wet the seed crystal. The melting and wetting processes are critical to the success of the experiments; if the feed rod fails to melt into a stable liquid, or wet the seed crystal, then no crystal growth can occur.

For these experiments Fe was chosen as the metal solvent based upon its well known ability to dissolve both C and Si. Exact compositions were derived from examining the Fe-Si-C (1150 °C) ternary diagram (Ref. 9), which indicated that there are two ranges of compositions that would produce a liquid + SiC phase. With this knowledge, a high Fe composition (Fe/Si ~ 1.9, C = 8 at.%), and a high Si composition (Fe/Si ~ 0.35, C = 8 percent) were chosen. While studying the effects of Fe/Si concentration is important, the effects of different C concentrations may be even more important. Therefore, a third composition was chosen at the high Si (Fe/Si ~ 0.35) composition with double the C (16 at.%). Specific seed crystal, feed rod preparation, and post experiment crystal processing information can be found elsewhere (Ref. 8).

Since significant transport of material starts once a melt is formed, growth temperatures are given relative to the observed melting point (M.P.) of the source material (e.g., growth temperature = total observed temperature – M.P.). Also, due to the possible wide range of emissivity (ε_{Fe} = 0.3 (Ref. 10) to $\varepsilon_{graphite}$ = 0.9 (Ref. 11)) and small size (~2 mm^2) heated zone, none of the listed optical pyrometer-measured temperatures are corrected for emissivity.

Discussion

As has been previously reported (Ref. 8) (summarized in Table 1), experimental runs using source materials with high Fe content failed to produce a stable melt, and were abandoned. The high Si source material easily formed a stable melt and predictably melted at 1170 °C (Table 1). Both the 8 and 16 at.% (high Si) compositions melted at similar temperatures (ΔM.P. = 25 °C or < 2 percent absolute temperature). Growth is found to increase with an increase in C present in the source material and also with temperature. These results indicate that temperature did have an effect on the amount of C transported from the source material to the growing crystal.

X-ray transmission Laue diffraction pattern (Fig. 1(a)) recorded using the synchrotron white beam on selected grown crystals matches exactly with (1-100)-oriented 4H-SiC x-ray transmission Laue diffraction pattern (Fig. 1(b)) simulated using the LauePt software (Ref. 12). The grown crystal retained both the orientation and polytype of the seed crystal and is therefore considered single crystal and epitaxial. The x-ray topographs (not shown) from the grown crystals are highly distorted indicating that it is under significant inhomogeneous strain.

TABLE 1.—SUMMARY OF RESULTS. M.P.= TEMPERATURE AT WHICH THE FEED ROD FORMED A MELT, (at.% = ATOMIC PERCENT). TEMPERATURES ARE NOT CORRECTED FOR EMISSIVITY APPROXIMATE FE CONCENTRATIONS IN THE SiC CRYSTAL LAYERS ARE LISTED

			Fe Concentration (atom/cm^3)	
Fe/Si (atomic ratio)	C (at.%)	M.P. (°C)	M.P.+90 °C	M.P.+190 °C
High-Si (Fe/Si~0.35)	8	1170	~10^{17}	~10^{17}
	16	1195	~10^{18}	~10^{18}
High-Fe (Fe/Si~1.9)	8	N/A	No Growth	

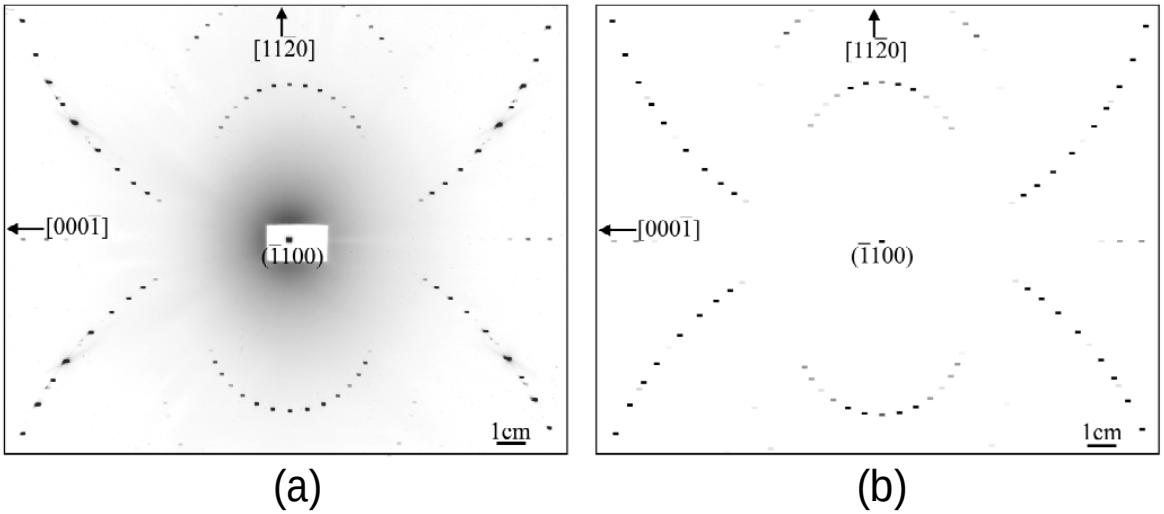

Figure 1.—X-ray transmission Laue diffraction pattern (a) recorded from the LHFZ layer portion of fiber sample matches exactly with a (1-100)-oriented 4H-SiC x-ray transmission Laue diffraction pattern (b) simulated using the LauePt software (Ref. 12).

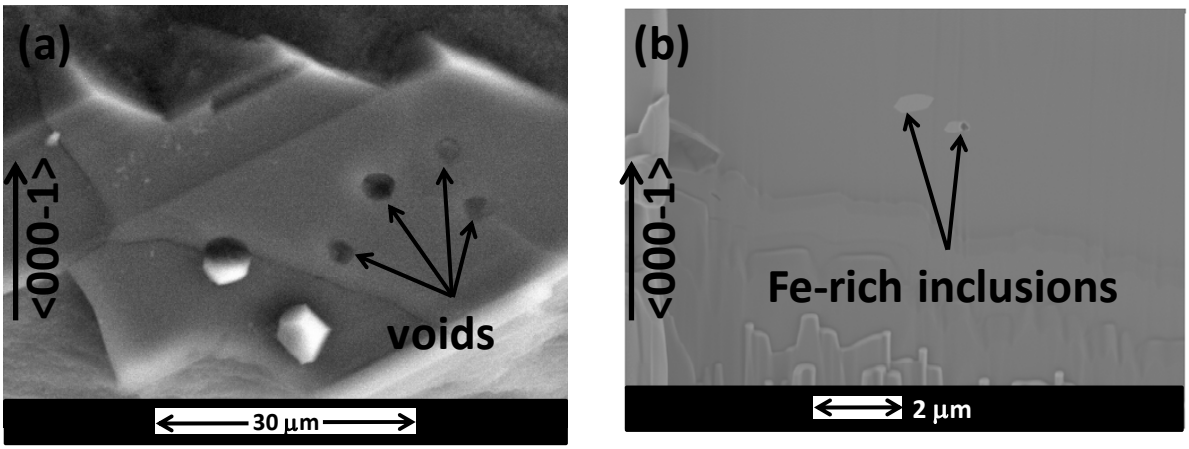

Figure 2.—(a) Interior of a cross-section of a growth front exposed by mechanical polishing (b) FIB of cross section of a grown crystal.

SEM images reveal two different morphologies (shown elsewhere (Ref. 8)), a platelet-like morphology (present on ~75 percent growth fronts examined) and a step flow like growth front (present on about 25 percent of the grown surfaces examined). One important note is that the occurrence of either type of growth front did not correspond to a specific growth condition, and in a couple of cases both morphologies were produced in different regions of a single sample surface. Cross-sectional analysis reveals many voids (Fig. 2(a)) and Si-Fe rich pockets (confirmed with EDS, Fig. 2(b)) sealed in the grown crystal layer. These voids and inclusions are very possibly the source of the stress detected by the topography measurements.

One possible explanation for the formation of the Fe rich inclusions is that each platelet of the platelet-like growth front is actually many competing individual growth fronts that eventually collide to form new defects as the SiC closes over the trapped solvent. The crystal then continues growing using the newly formed defect. A similar process has been reported by Dudley et al. (Ref. 13) in the physical vapor transport method of SiC crystal growth.

SIMS results (Fig. 3) shows that the concentration of Fe in the grown crystals varies in three significant ways. First, “bumps” in the SIMS profile are believed to arise from the Fe rich inclusions seen by FIB cross sectional analysis, as indicated by the arrows in Figure 3. With an analysis area much larger than the inclusions, the “bump” width and magnitude is an average over the entire SIMS analysis area. This explains why the “bumps” visible by SIMS are also visible by SEM/EDS. Second, these results also indicate that for both high and low C concentration source materials the Fe concentration decreases more than an order of magnitude from the surface. This decrease may indicate a change in melt composition as a function of growth time. Please note that for crystals grown with low C concentration source material, the Fe concentration drops almost two orders of magnitude in the first
0.25 μm. The reason for this large change is unknown, but is possibly either an artifact of the post-growth etch, which removes excess source material/solvent, and/or the cooling of the crystal/solvent system at the end of a growth or the SIMS process. Third and also indicated in Table 1, the crystals grown with source material containing a higher C concentration incorporated an order of magnitude more Fe than did crystals grown from melts containing less C at either growth temperature. Further SIMS analysis reveals that Fe incorporation into grown crystals exhibits the same correlation to C concentration in the source material independent of growth rate. Therefore C concentration in the source material seems to dictate the amount of Fe solvent incorporated into the matrix of the grown crystal, and that the Fe concentration is considerably less sensitive to growth temperature.

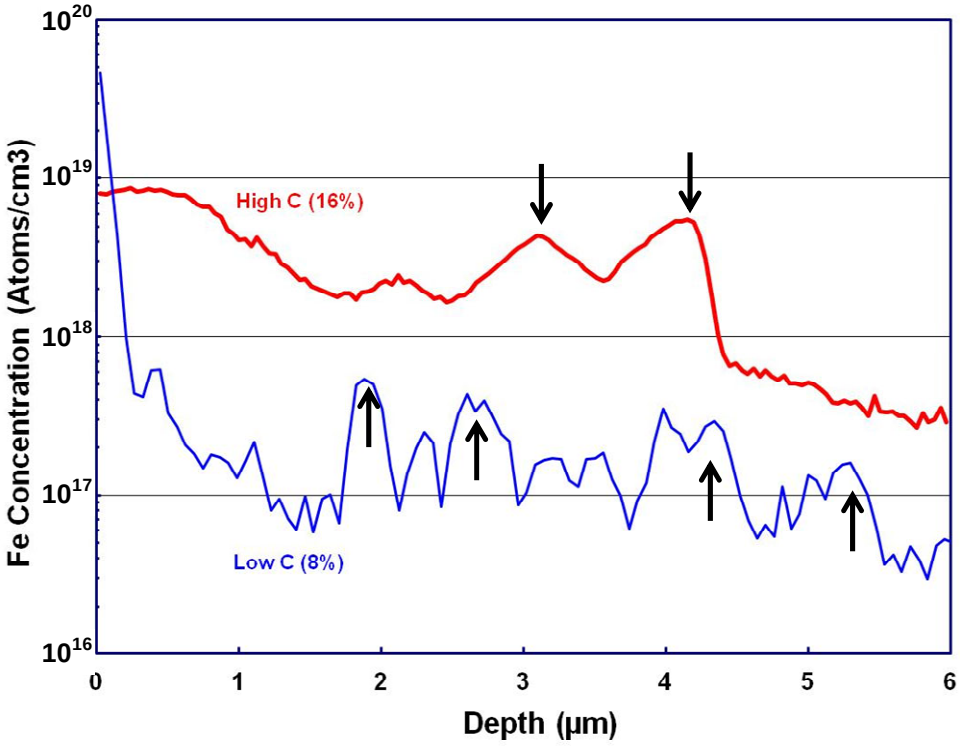

Figure 3.—SIMS analysis of a high C (at.% = 16, growth rate = 40 μm/hour) and low C (at.% = 8, growth rate = 4 μm/hour) grown at M.P.+90 °C. The arrows indicate Fe rich areas in the grown crystals. Note Fe/Si = 0.35 in the feed rod.

Conclusions

This paper has reported further characterization of 4H-SiC crystal layers grown by the recently implemented Solvent-LHFZ technique. X-ray diffraction and topography confirmed that the grown crystals were single crystal in nature (replicating polytypic and crystallographic direction of the seed), but under significant amount of inhomogeneous strain. Cross sectional analysis by mechanical polishing and FIB, and along with SIMS analysis revealed voids and Fe rich inclusions throughout the grown crystals and is most likely the source of the strain. These voids and Fe rich areas are possibly created by growth fronts colliding and sealing off pockets and then creating defects which help propagate the growth front. SIMS analysis also revealed that Fe inclusion into the grown crystal seems to be a function of the C content of the grown crystal and not growth temperature or growth rate. These results lead us to believe that in order to grow a long, high-quality 4H-SiC single crystal fiber, the growing crystal must be reduced to a single growth font and that the C content of the source material will have to be tuned both with consideration to growth rate and also to Fe incorporation into the grown crystal.

References

1. P.G. Neudeck W. Huang and M. Dudley., *Solid-State Elec.*, 42, 1257 (1998).
2. J. Zhang, G. Chung, E. Sanchez, M.J. Loboda, S. Sundaresan and R. Singh International Conference on Silicon Carbide and Related Materials, Cleveland, OH, September 11-16 (2011) (to be published).
3. R. Berechman, S. chung, S. Soloviev and M. Skowronski, International Conference on Silicon Carbide and Related Materials, Cleveland, OH, September 11-16 (2011) (to be published).
4. Y. Urakami, I. Gunjishima, S. Yamaguchi, H. Kondo, F. Hirose, A. Adachi and S. Onda, International Conference on Silicon Carbide and Related Materials, Cleveland, OH, September 11-16, 2011 (to be published).
5. J.A. Powell, P.G. Neudeck, A.J. Trunek and D.J. Spry, U.S. Patent 7,449,065 issued November 11, 2008.
6. C.A. Burrus and J Stone, *App. Phys. Lett.*, 26, 318-320 (1975).
7. L.B. Griffiths and A.I. Mlavsky, Electrochem. Soc., 111, 805 (1964).
8. A.A. Woodworth, et al., International Conference on Silicon Carbide and Related Materials, Cleveland, OH, September 11-16, 2011 (to be published).
9. T. Yoshikawa, S. Kawanishi, and T. Tanaka, Int. Conf. on Adv. Structure and Funct. Mater. Des., 2008, J. Phys.: Conf. Series 165 (2009) 012022.
10. H.B. Wahlin and H.W. Knop, *Phys. Rev.*, 74 (1948) 687.
11. M.R. Null and W.W. Lozier, *J. Appl. Phys.*, 29 (1958) 1605.
12. X.R. Huang, *J. Appl. Cryst.*, 43, 926 (2010).
13. M. Dudley, X.R. Huang, W. Huang, A. Powell, S. Wang, P.G. Neudeck and M. Skowronski, Appl. Phys. Lett., 75, 784, (1999).

REPORT DOCUMENTATION PAGE	Form Approved OMB No. 0704-0188

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.
PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
01-09-2012	Technical Memorandum	

4. TITLE AND SUBTITLE
Characterization of 4H <000-1> Silicon Carbide Films Grown by Solvent-Laser Heated Floating Zone

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Woodworth, Andrew, A.; Sayir, Ali; Neudeck, Philip, G.; Raghothamachar, Balaji; Dudley, Michael

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER
WBS 031102.02.03.0781.12

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
National Aeronautics and Space Administration
John H. Glenn Research Center at Lewis Field
Cleveland, Ohio 44135-3191

8. PERFORMING ORGANIZATION REPORT NUMBER
E-18413

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
National Aeronautics and Space Administration
Washington, DC 20546-0001

10. SPONSORING/MONITOR'S ACRONYM(S)
NASA

11. SPONSORING/MONITORING REPORT NUMBER
NASA/TM-2012-217708

12. DISTRIBUTION/AVAILABILITY STATEMENT
Unclassified-Unlimited
Subject Categories: 33, 23, and 76
Available electronically at http://www.sti.nasa.gov
This publication is available from the NASA Center for AeroSpace Information, 443-757-5802

13. SUPPLEMENTARY NOTES
Andrew A. Woodworth, NASA Glenn Research Center, NASA Postdoctoral Program Fellow. Alternate report number DOI: 10.1557/opl.2012.1149.

14. ABSTRACT
Commercially available bulk silicon carbide (SiC) has a high number (>2000/cm^2) of screw dislocations (SD) that have been linked to degradation of high-field power device electrical performance properties. Researchers at the NASA Glenn Research Center have proposed a method to mass-produce significantly higher quality bulk SiC. In order for this bulk growth method to become reality, growth of long single crystal SiC fibers must first be achieved. Therefore, a new growth method, Solvent-Laser Heated Floating Zone (Solvent-LHFZ), has been implemented. While some of the initial Solvent-LHFZ results have recently been reported, this paper focuses on further characterization of grown crystals and their growth fronts. To this end, secondary ion mass spectroscopy (SIMS) depth profiles, cross section analysis by focused ion beam (FIB) milling and mechanical polishing, and orientation and structural characterization by x-ray transmission Laue diffraction patterns and x-ray topography were used. Results paint a picture of a chaotic growth front, with Fe incorporation dependant on C concentration.

15. SUBJECT TERMS
Silicon carbides; Crystal growth; Melts; Single crystals

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			STI Help Desk (email:help@sti.nasa.gov)
U	U	U	UU	14	19b. TELEPHONE NUMBER *(include area code)* 443-757-5802