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A New Method to Grow SiC: Solvent-Laser Heated Floating Zone

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Abstract

The solvent-laser heated floating zone (solvent-LHFZ) growth method is being developed to grow long single crystal SiC fibers. The technique combines the single crystal fiber growth ability of laser heated floating zone with solvent based growth techniques' (e.g. traveling solvent method) ability to grow SiC from the liquid phase. Initial investigations reported in this paper show that the solvent-LHFZ method readily grows single crystal SiC (retains polytype and orientation), but has a significant amount of inhomogeneous strain and solvent rich inclusions.

Introduction

Recently researchers at the NASA Glenn Research Center patented a new approach to growing high quality bulk silicon carbide (SiC) [1]. The concept, known as the Large Tapered Crystal (LTC) Growth Method, uses a long (> 1 cm) single crystal fiber grown in the <000-1> direction as a seed crystal for lateral (perpendicular to the <000-1> direction) bulk vapor-phase growth. However, to date a method of growing single crystal SiC fibers does not exist. To this end, solvent-laser heated floating zone (solvent-LHFZ) is being developed.

The roots of solvent-LHFZ growth lay in SiC solvent based growth methods and laser heated floating zone (LHFZ) crystal growth methods. LHFZ growth methods are a subset of the floating zone techniques that have long been used to grow single crystal fibers [2]. This technique uses a laser (heat source) to melt a feed rod composed of crystal growth source materials. Once a melt (liquid) is established on top of the feed rod, a seed crystal is lowered into contact with the melt (Fig.1(a)). Once in contact, the melt wets to the seed crystal and growth begins (Fig.1(b)). As the crystal grows, the crystal is pulled upward keeping the growth front at a constant position in the heated zone. The feed rod is also moved upward as it is consumed by the growing crystal. Unfortunately, SiC melts incongruently and therefore LHFZ as it had been utilized previously for other materials cannot grow single crystal SiC.

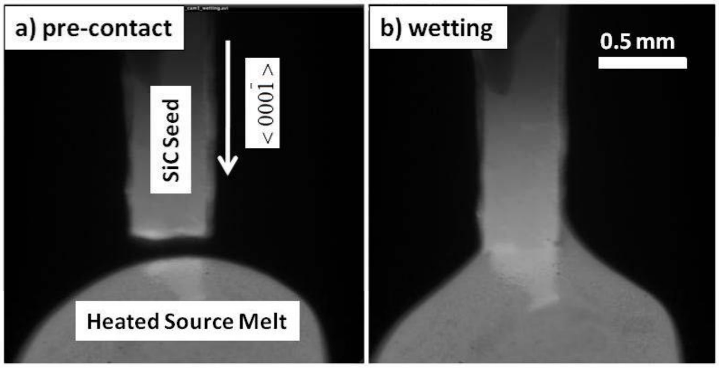

Fig. 1. Long range optical micrographs of the seed crystal/melt system (a) pre-contact and (b) after wetting.

There are many techniques, such as the traveling solvent method [3], that have grown single-crystal SiC from the liquid phase. In these techniques a solvent is used that can dissolve both Si and C and transport those species to the growth surface without significant solvent incorporation into the crystal. Therefore, a metal solvent has been added to the LHFZ feed rod in order to facilitate fiber growth.

Experiment

In order to carry out solvent-LHFZ, a custom growth system had to be developed. Fig. 2 shows a top down schematic of the system, which consists of a vacuum chamber, long range optical microscope, optical pyrometer and specialized opposing ZnSe windows that allow the CO_2 laser's beam to enter the chamber. The CO_2 laser was chosen because the beam wavelength of 10.6 µm couples well with the crystal growth materials. The beam creates a heated area, roughly in the center of the chamber approximately 2 mm x 4 mm. The beam enters the chamber from opposing sides in order to create even heating on both sides of the feed rod. Experiments are performed at 115 Torr of Ar flowing through the chamber at a rate of 15 slm. Ar is brought in through the top of the chamber and around the windows in order to keep sensitive parts clean.

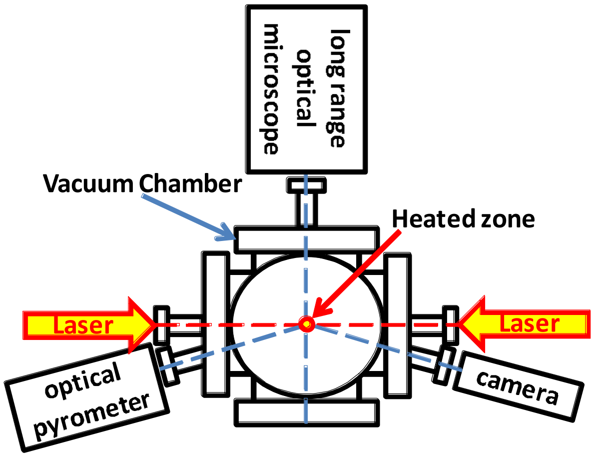

Fig. 2. Top down Solvent- LHFZ system schematic [4]

Feed rods are formed by pressing source powders into rods by cold isostatic press, and then rods are sintered under a hydrogen atmosphere at 1150 °C. Sintering increases the density by ~50% and, gives structural strength to the feed rod for handling. Iron metal (Fe) was chosen as the solvent due its ability to dissolve C and Si and also a significant amount of work has been already been done to understand SiC growth using Fe as a solvent [5, 6]. In particular Yoshikawa *et al* published a ternary diagram [5] of the Fe-Si-C system at 1250 °C, showing two regions where SiC alone exists with liquid. These regions roughly correspond to Fe/Si~0.35 (high Si) and Fe/Si~1.9 (high Fe). Yoshikawa *et al* also indicated that the Fe/Si content would affect the ability of the melt to dissolve C, and therefore limit growth. Therefore, three feed rod compositions were chosen for initial experiments. The first composition had high Fe concentration and the second had high Si concentration, with both compositions contain ~8 atomic % (at.%) C (low C). The third composition was chosen with Fe/Si~35 (high Si) 16% C (high C) in order to study the effects of increased C content in the feed rod on the growth process.

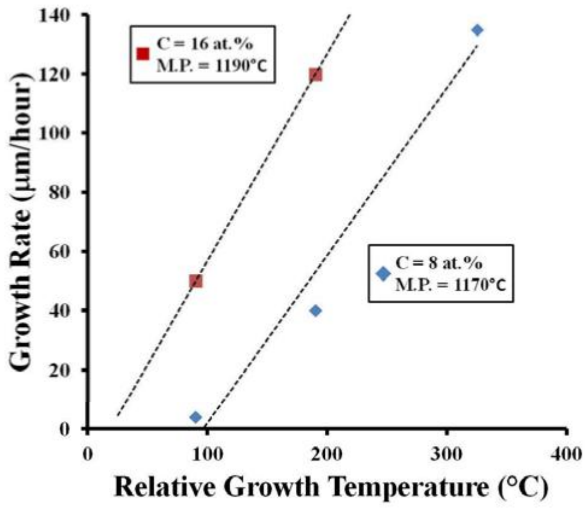

Fig. 3. Growth rates for high Si (Fe/Si=0.35) feed rod experiments where relative growth temperature (°C) $T_{growth}=T_{observed}-T_{MP}$. Note: trend lines are added only as a visual aid.

4H-SiC seed crystals (0.5 mm x 0.5 mm x 15 mm, long axis parallel to the <0001> direction) were cut from SiC wafers and mounted so that the carbon face (000-1) of the crystal is facing down and used as the growth face. The (000-1) face of the seed crystal varied from on axis to 10° off axis. More information about the mounting and preparation of the seed crystal can be found elsewhere [4].

Growth temperatures were monitored by a single color optical pyrometer. The super heated growth temperatures reported here are given relative to the melting point (MP) of the feed rod because significant transport of growth material to the growth front does not occur before a melt is formed (e.g. $T_{growth}=T_{observed}-T_{MP}$). Also, because the emissivity of the melt is relatively unknown ($\varepsilon_{Fe}=0.3$ [7] to $\varepsilon_{graphite}=0.9$ [8]) the temperatures are reported uncorrected.

Before post-growth analysis was carried out, excess growth materials not incorporated into the crystal were removed by etching using a HNO_3:HF:2HCl bath for 4 hours. Post-growth analysis consisted of scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and cross sectional analysis by focused ion beam (FIB). Depth profiles were carried out on selected samples by secondary ion mass spectroscopy (SIMS) with an analysis of area ~175µm x 175µm. X-ray transmission Laue diffraction patterns and synchrotron white beam x-ray topography (SWBXT) images were collected at the Stony Brook Synchrotron Topography Station, Beamline X19C at the National Synchrotron Light Source, Brookhaven National Laboratory.

Results/Discussion

All but one of the experiments involving feed rods with high Fe content (Fe/Si~1.9, C~8 at. %) failed to form a stable melt that could wet to the crystal. In the one case where a stable melt was formed, the melt quickly dissolved the SiC seed crystal. Therefore, no crystals were grown using the high Fe concentration feed rods.

High Si (Fe/Si ~ 0.35) feed rods did form stable melts that wetted to the seed crystal as shown in Fig. 1 (a) and (b). The feed rods reproducibly melted at 1170°C and 1195°C for the high Si feed rods with C = 8 at.% (low C) and C = 16 at.% (high C), respectively. Melts for high and low C feed rods were stable to temperatures of MP +190 °C. At a temperature of MP + 325 °C the low C melt was stable (wetted to the seed and did not detach) long enough (a few minutes) to conduct experiments, but the high C feed rod melt behaved erratically and produced un-reportable results. Growths rates (measured crystal growth/ growth time) for both high and low C feed rods are shown in Fig.3. There are two important trends to note in the growth rate. First, growth rates for both high and low C feed rods did increase with temperature indicating increased mobility of growth species through the melt to the growth face. Second, growth rates also increased with C concentration in the initial feed rod, indicating that growth with the low C feed rods is C limited.

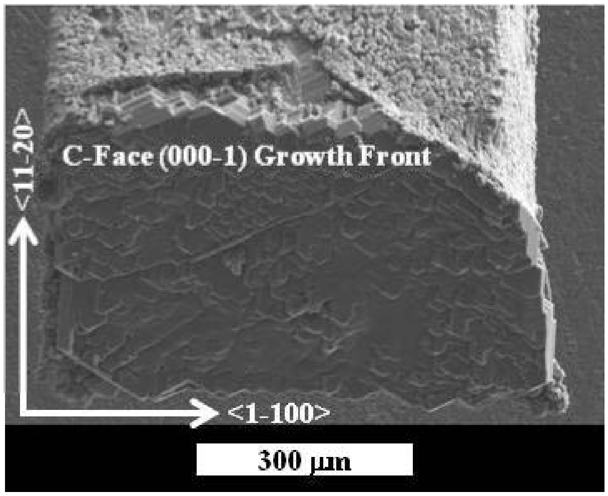

Fig. 4. C face (000-1) growth front of a crystal grown at MP + 90°C with High Si (Fe/Si ~ 0.35) high C (C = 16 at.%) feed rod

X-ray transmission Laue diffraction

patterns (shown elsewhere [9]) indicate that the crystals grown with this method are single crystal and retain the orientation (<000-1>) and 4H polytype of the seed crystal. However, SWBXT images (not shown) indicate significant inhomogeneous strain is present. When examined by SEM two different growth fronts were observed. The predominant growth front shown in Fig. 4 is the "platelet" like growth front. This growth front is composed of many small competing hexagonal growth fronts. When cross sectioned by FIB (shown elsewhere [9]) small Fe-rich pockets were observed (confirmed by EDS). These pockets were also observed at many depths by SIMS analysis. Therefore, we propose that many small competing growth fronts (Fig. 4) are likely to converge, forming small pockets that trap Fe rich growth materials. When these pockets close over the Fe rich growth materials, they are likely to form defects [10]. Both of these defects likely help propagate SiC growth in the <000-1> direction and are the source of the inhomogeneous strain visible in the SWBXT images.

Conclusions

Solvent-LHFZ has been shown to grow single crystal SiC and the effects of C concentration in the initial feed rod on the growth process have been observed. Growth rate has been shown to increase with temperature and with C concentration in the initial feed rod. This result suggests that growth with low C (8 at. %) is feed rods is C limited. Not enough data currently exist to determine if the high C feed is also C limited. The crystals grown by this method have a significant amount of inhomogeneous strain as a result of many competing growth fronts. In order to grow a long single crystal fiber suitable as a seed crystal for the LTC process a much more uniform growth front must be formed and maintained.

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