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The role of an SiC interlayer at a graphite–silicon liquid interface in the solution growth of SiC crystals

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ABSTRACT

SiC crystal growth using the top seeded solution growth (TSSG) method involves the precipitation of solid SiC from carbon that is dissolved in a silicon melt. The growth rate of SiC is strongly influenced by the solubility of C in liquid Si, which is quite low. In this study, the dissolution of C from graphite to the Si melt was explored by observing the formation of an SiC interlayer at a graphite – Si liquid interface. The SiC interlayer was observed to become thickened during the several hours needed to reach a certain thickness at 1500 °C. Assuming that the SiC interlayer is a direct C source, a pre-formed SiC layer was coated on the graphite crucible to evaluate its effect on the concentration of C in the Si melt. As a result, the concentration of C in the Si melt increased within a short time, especially at low temperatures. By applying the SiC coated crucible to the TSSG process for SiC crystal growth, we confirmed that the development of a pre-formed SiC layer enhanced the growth rate of SiC crystals, especially at the initial stage of crystal growth at low temperatures.

1. Introduction

Power devices for the conversion, control and processing of electric power have conventionally used Si-based semiconductors. However, Si device technology is approaching its material limitations, so that next generation substrate materials are needed for the circuit integration and to improve the performance of such electronic devices. Compared to Si semiconductors, wide bandgap (WBG) semiconductors such as SiC [1,2], AlN [3,4] and GaN [5,6] represent potential substrates for power devices. Since these materials are smaller sized and perform better, they could be operated at higher voltages and higher temperatures with better energy conversion efficiencies. Among these materials, SiC appears to be the most feasible substrate for use in the near future [7,8] because the scale-up of SiC wafers has already reached diameters of 6 in. in commercialized products [9–13].

Conventional crystal growth for the commercialized SiC substrate involve the use of the physical vapor transport (PVT) method [14, 15]. In this method, high purity SiC powder, the starting material, is sublimed and recrystallized in an induction heated furnace. The high temperature chemical vapor deposition (HTCVD) method was proposed as an alternative growing technique for SiC substrates, in which a continuously fed source gas is condensed on the seed crystals located at the top of the induction heated furnace [16–21].

While both the PVT method and HTCVD method are based on the vapor phase growth of SiC, solution growth methods of SiC are based on the liquid phase growth of SiC from an incongruent melt composed of Si and C. In the top seeded solution growth (TSSG) method for SiC, the crystal growth on seed crystals is accomplished by the precipitation of solid SiC from C dissolved the Si melt on a seed crystal located at the top of the liquid. Because of the low solubility of C in liquid Si [22, 23], SiC crystal growth on seed crystals using conventional TSSG involves the use of a silicon-rich Si–C solution and the supply of C to the growth front governs the growth rate of SiC. In recent reports, the growth rate of SiC has been improved from few tens μm/h in Si–C solution to hundreds μm/h by adding transition metals to the solution such as Ti [24], Cr [25], or by using force convection technique such as accelerated crucible rotation technique (ACRT) [26].

Generally, a graphite crucible in the TSSG method for producing

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SiC has three functions: containing the Si–C solution, heating by an rf induction to the crucible and supplying C source. However, studies directed at the TSSG method for SiC growth have focused less on the graphite crucible in spite of its importance. We assumed that the graphite crucible in the TSSG method could be optimized based on a more complete understanding of the above three functions. In this study, therefore, we explored the dissolution of C from the graphite to the Si melt to develop an alternative crucible design that would be more applicable for use in the TSSG method. The proposed crucible was then verified by the crystal growth of SiC via the TSSG method.

2. Experimental

The dissolution of C in the Si melt was first evaluated using an induction heating furnace (Takeuchi electric Co. Ltd., Japan). The graphite crucible containing Si powder (99.999%, Kojundo Chemical Laboratory Co. Ltd., Japan) was located inside a graphite fixture, as shown in Fig. 1(a). The inner diameter, the inner depth and the thickness of the graphite crucible were 30 mm, 40 mm and 10 mm, respectively. Si powder (24.0 g) was placed in the graphite crucible for each experiment. The graphite fixture located in a quartz tube was heated by RF induction and was thermally insulated by graphite felt (Morgan Korea, Co. Ltd., Korea). The temperature was measured beneath the graphite fixture using a pyrometer. The evaluation of C dissolution in the Si melt was conducted at temperatures of 1500 °C, 1700 °C and 1900 °C for 1∼4 h under an Ar atmosphere. To analyze the effect of an SiC reactive layer formed at the Si–C interface, SiC coated graphite crucibles were used in evaluating C dissolution in the Si melt under identical conditions as were used for normal graphite crucibles. The SiC coated graphite crucibles were fabricated with an SiC layer of ∼60 μm thickness (Dicera Tech, Korea), which is confirmed by FE-SEM (field emission scanning electron microscope, SU-70, HITACHI, Japan) equipped with energy dispersive spectroscopy (EDS) (Fig. S1). After every experiment, cross-sectional samples were polished to produce a mirror face to be evaluated by optical microscopy (ME600, Nikon, Japan). The characterization of the formed crystallite in the Si melt was conducted by micro-Raman spectroscopy (NRS-3100, JASCO, Japan) with a wavelength of 532 nm as its beam source.

Next, the crystal growth of SiC was conducted using another induction heating furnace (Takeuchi electric Co. Ltd., Japan) by the TSSG method shown in Fig. 1(b). The inner diameter, the inner depth and the thickness for the crucibles used for the TSSG were 40 mm, 48 mm and 10 mm, respectively. The graphite crucible containing Si powder was located inside the outer graphite crucible that was thermally insulated by graphite felt. The inner diameter, the inner depth and the thickness of the outer graphite crucible were 100 mm, 90 mm and 15 mm, respectively. Si powder (62.0 g) was placed in the graphite crucible for each experiment. The crystal was grown on the C-face of a 4° off-axis 4H-SiC crystal fixed at the graphite shaft rotating clockwise at a speed of 10 rpm, for 1 h at 1500 °C and 1700 °C. The temperature was measured beneath the graphite fixture and on the surface of the melt using pyrometers. According to pyrometer data, the bottom melt temperature is higher than the surface temperature and vertical temperature gradient between surface and bottom in Si melt is about 23 °C/cm. After the growing tests, Si melts that had solidified on the grown crystal were removed by chemical etching with a HF/HNO_3 solution. The grown crystals were then investigated by optical microscopy (OM) and micro-Raman spectroscopy following the same procedures as described above. The crystal quality of the grown crystal was analyzed using high resolution X-ray diffraction (HRXRD, X'Pert Pro MRD, PANalytical, Netherlands).

3. Results and discussion

3.1. Distribution of SiC in the solution

As mentioned in the introduction, the crystal growth of SiC using the TSSG method is accomplished by the precipitation of solid SiC from the supersaturated C in the Si–C solution on a seed crystal located at the top of the liquid. The dissolved C in the Si–C solution is definitely from graphite, through the reaction between liquid Si and the graphite crucible. The reaction between C and liquid Si is used for reaction bonded silicon carbide (RBSC) or C/SiC composites, so that this topic has been extensively studied due to interests for applications [27–34]. As a general rule, the reactive interface can be categorized into two layers [27,28,30-33]. One layer close to the graphite is believed to be formed by a carbon dissolution process followed by the precipitation of small

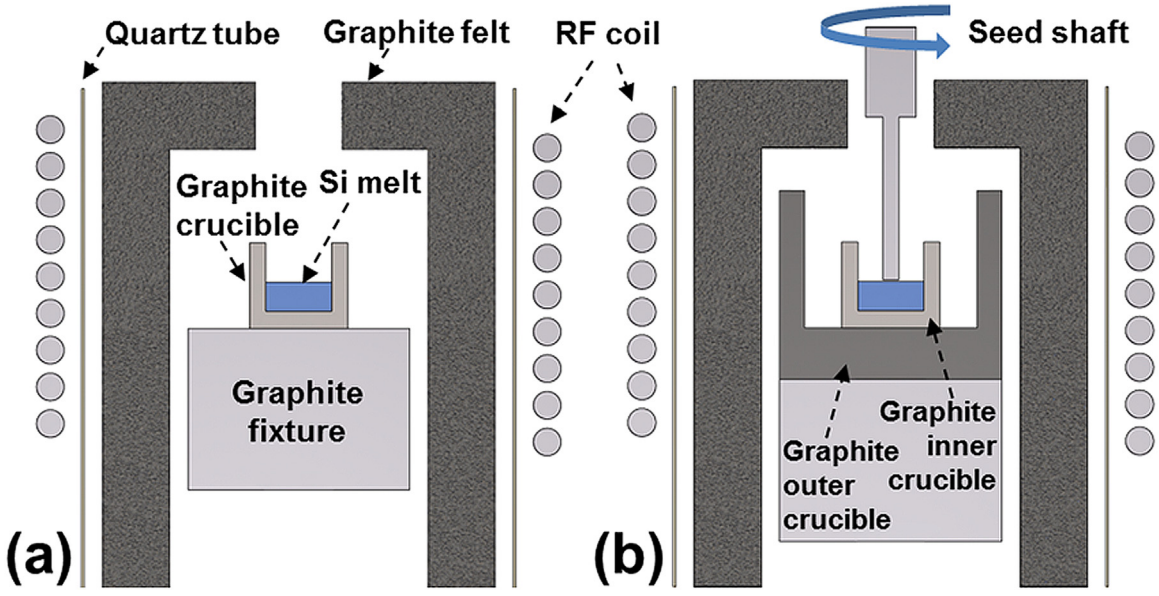

Fig. 1. The layout of experiments of (a) Si melting test and (b) SiC crystal growth by the TSSG method.