Solution growth of silicon carbide using unary chromium solvent

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ABSTRACT

Solution growth of silicon carbide (SiC) using unary chromium (Cr) solvent was studied because the system enables a high solubility difference and a low degree of supersaturation, which would lead to rapid growth with a stabilized growth interface. The liquidus composition at SiC saturation in a quasi-binary Cr–SiC system was studied at 1823–2173 K. The measured carbon (C) contents are in good agreement with the thermodynamic evaluation using the sub-regular solution model. In addition, growth experiments using a unary Cr solvent were performed by the bottom-seeded travelling solvent method. The obtained growth rates at 1803–1923 K with a temperature difference of 15–70 K were proportional to the solubility difference between the seed and source temperatures, indicating that the growth was controlled by the mass transfer of C in the solution. The maximum growth rate of 720 μm/h at 1803 K was much higher than the growth rate by Si-rich solvents, suggesting that the Cr-rich solvent is suitable for the rapid growth at a low temperature.

1. Introduction

Silicon carbide (SiC) is a prominent semiconductor for power devices because of its attractive properties such as high breakdown field and high thermal conductivity [1]. The physical vapor transport (PVT) is a major method for producing bulk SiC crystals which are used as substrates for device fabrication. Although the crystal quality of SiC grown by the PVT method has been improved to obtain zero-micropipe crystals [2,3], many dislocations (generally 10^2–10^4 cm^{-2}) still exist in the crystals [4], which degrade the performance of the device.

Solution growth of SiC has the advantage of producing high quality crystals because the state of the growth interface is close to thermal equilibrium [5]. Various solvent systems, such as Si [5], Si–Cr [6–8], Si–Ti [9,10], Si–Sc [11], Fe–Si [12] and so forth, have been studied to obtain rapid growth and/or high quality SiC crystals. Here, the rapid growth can be obtained by using the solvent that exhibits a large temperature dependence of C solubility because the growth rate is generally limited by the mass transfer of solute elements at the boundary layer in the solution. However, the growth rate and stability of the growth front are generally in a trade-off relationship. Hence, the increase of the growth rate with an increasing temperature difference deteriorates the crystal quality owing to the formation of the other polytypes and the entrapment of solution in the grown layer. To solve

these problems, the large C solubility would also have an important role to suppress the two-dimensional (2D) nucleation of the other polytypes and to attain uniform solute incorporation because of the low degree of supersaturation. Recently, rapid growth as high as 2000 μm/h [7] and high quality crystals with ultra-low dislocation density [8] have been reported by using a Si–40 mol% Cr-based solvent at approximately 2273 K. In the experiments, a high operation temperature was needed to increase the C solubility in the solvent. To attain rapid growth with a stable growth front at lower temperature, the optimization of the solvent (system and composition) is indispensable.

In our previous study, the thermodynamic evaluation of the C–Cr–Si system was performed and the liquid phase saturated with SiC was confirmed even in a Cr-rich composition because of the relatively high activity coefficient of Si in the liquid phase of the Cr–Si system [13]. In addition, the activity coefficient of C in the liquid phase of the C–Cr system is significantly low, leading to a high C solubility in the liquid phase. Therefore, a Cr-rich Cr–Si solvent was considered to possess the advantages of both rapid growth and stability of the growth interface. In this study, unary Cr was selected as a solvent to achieve rapid growth, that is, equimolar C and Si existing in the solution as solute elements. SiC solubility in a Cr–SiC quasi-binary system was investigated to quantitatively evaluate the solubility and its temperature dependence. The equilibrium phase relation between SiC and the

liquid was also thermodynamically assessed. Then, growth experiments were performed at 1803–1923 K to reveal the potential of the unary Cr solvent for the rapid growth. The rate-limiting step was discussed and the obtained growth rates were compared with other studies [7,9,12–14].

2. SiC solubility in a Cr–(SiC)$_{0.5}$ quasi-binary system

2.1. Method

Solubility measurements were performed by using an induction furnace (280 kHz). A piece of Cr (0.1 g, 99.9%) was placed on a polycrystalline SiC substrate (10×10×t1 mm, > 99.5%), which was fixed inside the graphite container. After the evacuation under 0.5 Pa, the sample assembly was heated to 1823–2173 K and kept for 5–20 min under an Ar atmosphere. Here, the temperature of the back side of the SiC substrate was measured and controlled by a single-color pyrometer with an emissivity of 0.9 [15]. During holding, SiC dissolved into molten Cr to reach SiC saturation, where a time of 5 min was preliminary confirmed to be sufficient to reach the solid–liquid equilibrium. A droplet at SiC saturation was then sucked up using a rolled piece of Mo or Ta foil, and the C content was analyzed by the combustion-IR absorption method.

The equilibrium phase relation was also investigated by thermodynamic assessment. The excess molar Gibbs energy of the liquid phase was assumed to behave as a sub-regular solution with a Redlich–Kister-type polynomial and the ternary interaction was ignored. All the thermodynamic data used for the calculations were the same as those used in our previous study [13]. The equilibrium phase relation of SiC and the liquid phase in the quasi-binary Cr–(SiC)$_{0.5}$ system was evaluated by using the thermodynamic calculation software, FactSage 6.4.

2.2. Results

Fig. 1 shows the temperature dependence of the measured C contents at SiC saturation together with the thermodynamic evaluation and the reported values in the Si–40 mol% Cr alloy [16]. The C contents at the SiC saturation were measured to be 21–24 mol% at 1823–2173 K. The obtained values increased with an increasing temperature and were much higher than those in Si–40 mol% Cr alloy [16]. In addition, the measured values were in good agreement with the estimation, although we recently reported that the liquidus compositions along SiC saturation at the low C content region cannot be expressed by the sub-regular solution model but can be well repro-
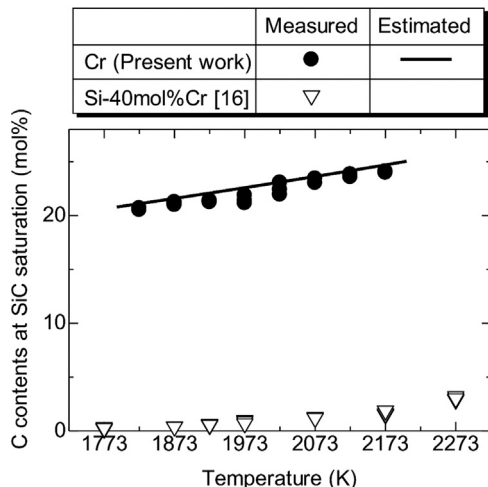

Fig. 1. Temperature dependence of the measured and estimated C contents at SiC saturation in Cr and in Si–40 mol% Cr alloy [16].
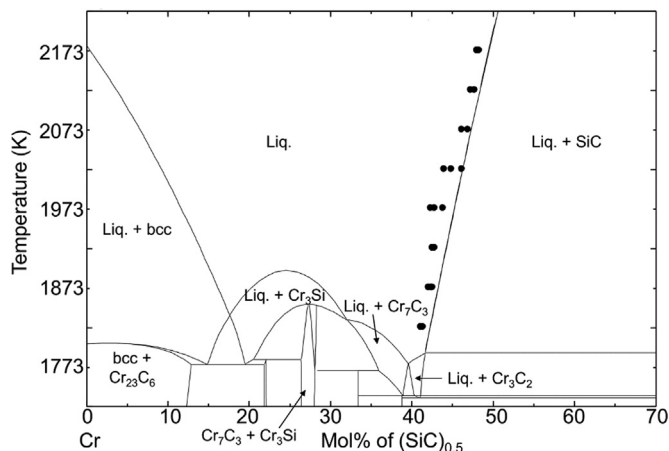

Fig. 2. Quasi-binary phase diagram for the Cr–(SiC)$_{0.5}$ system with the measured values. Descriptions of three-phase equilibrium regions are omitted.

duced by the quasi-chemical model, where C exists at the interstitial sites [16]. Fig. 2 shows the quasi-binary phase diagram for the Cr–(SiC)$_{0.5}$ system with the measured values. Here, the concentration of (SiC)$_{0.5}$ for the quasi-binary Cr–(SiC)$_{0.5}$ system can be written by:

$$\text{Mol\% of (SiC)}_{0.5} = 100 \times \frac{N_{Si} + N_C}{N_{Cr} + N_{Si} + N_C} \qquad (1)$$

where N_i is the molar amounts of component i in the liquid phase and N_{Si} is equivalent with N_C. Although the melting point of pure Cr is as high as 2176 K, the system forms the liquid phase at a much lower temperature owing to the dissolution of SiC. Therefore, low temperature solution growth of SiC using a unary Cr solvent is possible with an extremely high C content in the solution.

3. Solution growth of SiC using Cr solvent

3.1. Method

Growth experiments were carried out by the bottom-seeded travelling solvent method using an induction furnace (25–28 kHz), as schematically shown in Fig. 3 together with the heat pattern of the sample assembly. A seed substrate (10×10×t0.35 mm, on-axis, 4H-SiC (0001) Si face) faced a source substrate (φ10×t3 mm, poly-SiC, > 99.5%), both of which were fixed on graphite susceptors. A cubic Cr block (1.8 g, 99.9%) was placed between the substrates. After the evacuation inside the chamber to below 0.02 Pa, the sample assembly was heated in an Ar–10% H$_2$ atmosphere. The back-side temperature of the seed SiC was controlled and measured by a single-color pyrometer, while the top-side temperature of the source SiC was also monitored with a two-color pyrometer. When the Cr block was heated on the source poly-SiC substrate in the preliminary experiment, a liquid portion appeared at the contact part and showed spreading wetting on the substrate. Accordingly, the poly-SiC substrate was placed above the Cr block with contacting, and a droplet was formed, which was hanging from the substrate, by heating. After keeping the solution droplet at the growth temperature for 15 min to allow saturation with SiC, the droplet was moved downward to the seed substrate, which enabled the formation of a stable meniscus with suppression of the spreading wetting. The height of the liquid bridge was adjusted to 5 mm. The source temperature was then increased to the target temperature, while the seed temperature, namely the growth temperature (1803–1923 K), was kept constant. The sample assembly was held for an hour under the fixed temperature difference (ΔT=15–70 K) between the substrates, and then the substrates were separated to minimize the crystallization during the cooling process. After cooling the sample, the polytype of the grown layer was analyzed by micro-