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Restraint of nucleation of SiC polycrystals surrounding the seed during SiC single crystal growth

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Abstract The nucleation and growth of SiC polycrystals around seed crystals restrain the growth of SiC single crystals in the radial direction fabricated by physical vapor transport method in which the ordinary graphite is used as the crucible lid. Therefore, it is necessary to reduce the nucleation and growth of SiC polycrystals around the seed crystals. In order to effectively enlarge SiC single crystals, the authors propose the use of a graphite paper instead of graphite as the lid to restrain the nucleation of SiC polycrystals on the lid. The micrographs of SiC polycrystals on the graphite paper and graphite at the different growth stages show that the nucleation of SiC polycrystals on the graphite paper is more difficult than that on graphite. X-ray diffraction and scanning electron microscope investigations show that the graphite paper possesses high-macroscopic anisotropy, which induced that polycrystals can only grow on the surface of graphite paper and be easily removed.

Introduction

Silicon carbide is currently under intensive investigations because of the potential applications as an enabling material for a variety of high-power, high-frequency, high-temperature, and high-radiation devices [1]. The size and quality of single-crystalline substrates are among the main factors determining the applications of SiC-based epitaxial structures for high-power LEDs, DVD players, SiC sensors, and high-power devices [2]. Among the different preparation methods, physical vapor transport (PVT) is widely investigated and a successful technique for the growth of bulk SiC crystals [3–5]. In this method the vapor species will deposit on the seed rather than on the crucible lid when a large radial thermal gradient exists across the crucible lid. The seed diameter will increase with an increase in (crucible lid) length [6]. The growth rate of SiC single crystals and polycrystals can be controlled by the supersaturation of vapors in the growth chamber [7].

Although the considerable progress in the fabrication of bulk SiC crystals has been achieved, there are many factors that hinder the realization of the commercial SiC-based electronic devices such as the enlargement of SiC single crystals. In the literature there are many papers proposing various materials used as the crucible lids for investigating the enlargement of SiC single crystals on them such as the nucleation of SiC polycrystals on the graphite lid with a truncated cone [8] and on TaC [9]. However, it is difficult to enlarge SiC single crystals because of the nucleation and growth of SiC polycrystals on the graphite lid. The surrounding polycrystals prevent SiC single crystals from expanding sideward and induce large stresses in the growth of SiC single crystals [10–12].

In order to effectively restrain the nucleation of SiC polycrystals around seed crystals, the graphite paper was used as the crucible lid to prepare SiC single crystals. The results demonstrate that the graphite paper is unfavorable to the nucleation of SiC polycrystals.

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Experimental section

The SiC growth system was set up in the lab, which consists of an induction power supply, a radio-frequency (RF) fistulous copper coil, carbon insulation, graphite crucible, and a high vacuum system. The copper coil is entwined by a hollow copper tube to allow the flow of cooling water. This special design allows for the differential thermal expansion between the graphite crucible and the copper coil and also can withstand the high temperature when the graphite crucible is heated up to 2300 °C.

The starting material used in this experiment was commercial SiC powders (Zaozhuang Liyuan SiC Co., Ltd., Zaozhuang, China, Averaege size: 120 μm, Purity: 99.9%). The polycrystalline growth on the graphite paper lid (GP-lid) and graphite lid (G-lid) were investigated by the PVT technique. SiC powders were placed in two graphite crucibles with two different lids, respectively. The distance between the lid and the source material was equal to 30 mm. An RF induction power was used to generate the heat in the graphite crucible, and SiC powders were then heated by the crucible. A mass flow meter was used to control the argon gas pressure in the growth chamber. Two infrared (IR) pyrometers were used to measure the temperature at the top and bottom of the crucible.

The growth process consists of the following steps. At the vacuum degassing stage, a low gas pressure (10^{-3} Pa) and an evacuation temperature (800–1000 °C) were applied to reduce the nitrogen contamination of furnace; At the preheating stage, the temperature was gradually increased to the growth temperature and stabilized to achieve an optimum ΔT between the source and the lid in a high purity argon atmosphere of 5×10^4 Pa; At the growth stage, the temperature gradient was about 30 °C/cm. The difference of temperature between the charge and lid depends on the system configuration, and is critical to the growth rate of crystals. The bottom temperature of crucible was set to 2300 °C, and it was 90 °C higher than that of the lid. When the system pressure of the argon gas was 4×10^3 Pa, the crystal growth occurred; at the cooling stage, the temperature is gradually reduced after the growth was finished. The graphitization degrees of G-lid and GP-lid were measured by XRD. In addition, SEM coupled with electron dispersive X-ray analysis (EDXA) was used to investigate the polycrystals/lid interfaces.

Results and discussion

Figure 1 shows the microstructure of SiC polycrystals grown on G-lid and GP-lid for half an hour and 6 h, respectively. It was observed that the crystal nuclei formed on G-lid were much more than that on GP-lid at the initial stage of the growth process for half an hour in Fig. 1a, b. Few crystal nucleus on GP-lid give larger space for its growth in the radial direction than that on G-lid, thus larger crystal grains were grown on GP-lid and smaller on G-lid, as shown in Fig. 1c, d. The main vapor species in the growth chamber are Si, SiC_2, and Si_2C using PVT method [13]. The silicon-carrying gas species can react with or deposit on the lid, which leads to the growth of SiC polycrystalline. Thus, the results suggest that G-lid is favorable to the reactions of silicon-carrying gas species with the lid.

Figure 2 shows the XRD patterns of G- and GP-lid. The diffraction peaks of the latter are sharper and higher than that of the former. It suggests that the degree of graphitization of the GP-lid is higher than G-lid. The crystallinity of graphite will increase and the disordered structures and active carbon atoms will decrease gradually with the increase of graphitization degree, which results in the decreasing of activity of graphite. Figure 2 also shows that diffraction peaks in (100) and (101) faces of G-lid were not observed for GP-lid, which implies that the surface texture of GP-lid is different from that of G-lid. The SEM images in Fig. 3 show the surface micrograph of primary G-lid and GP-lid. It was observed that G-lid has a porous and disordered structure, while GP-lid has a laminated structure. According to Ref. [14], graphite is a special brittle material with inconsistent polycrystal microstructure. It has many interior micro-defects such as micropores and microcracks, while the graphite paper possesses of high macroscopic anisotropy since they were made by laminating the graphite wafers from the expanded natural graphite. The graphite wafers with (002) in Fig. 2b, are all similarly orientated. Therefore, the specific surface area of GP-lid is far less than that of G-lid, which results in the much lower activity and less crystal nuclei on GP-lid than G-lid.

It was also observed in the investigations that the polycrystals formed on the lid were more easily removed from GP-lid than that from G-lid. In order to explain this phenomenon, GP- and G-lid with SiC polycrystals grown for 6 h were then cleaved open along the growth direction and the microstructures were observed by SEM/EDXA.

Figure 4 is SEM images and their corresponding EDXA images of polished cross section of the lids with the lid/polycrystals interfaces. It showed that there were some pores with diameter about 200 μm near the interface in G-lid in Fig. 4a and they were filled with SiC polycrystals in Fig. 4c. The transport of vapor in a standard PVT system is driven by an axial temperature gradient in the growth chamber. The temperature gradient will lead to the diffusion of the silicon-carrying gas species into the pores of the G-lid and formed SiC. Thus, the bond between the G-lid and polycrystals was relatively strong, and leads to hardly remove the polycrystals from the G-lid.

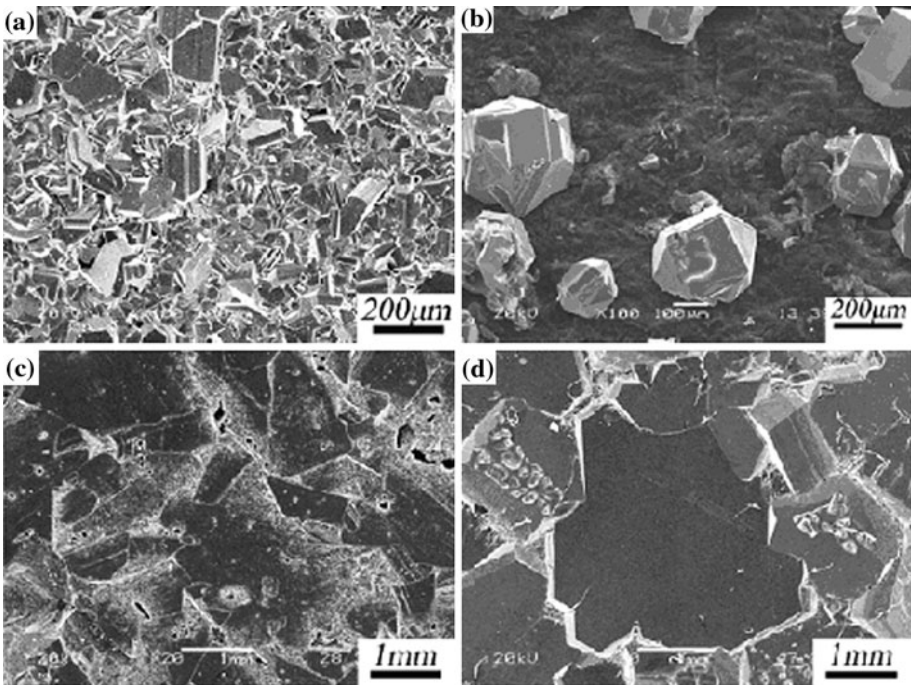

Fig. 1 Scanning electron microscopy (SEM) images of polycrystals grown on G-lid and GP-lid **a** on G-lid for half an hour **b** on GP-lid for half an hour **c** on G-lid for 6 h **d** on GP-lid for 6 h

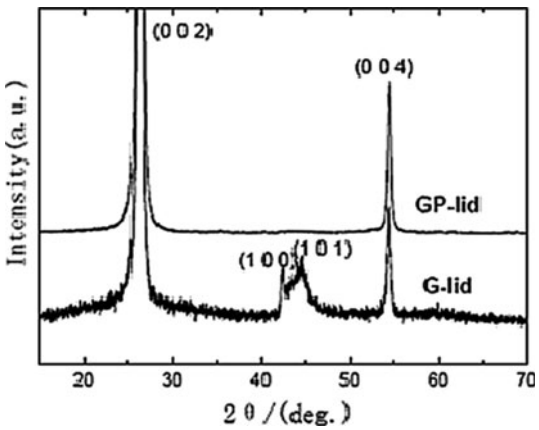

Fig. 2 XRD patterns of G- and GP-lid

The graphite paper is made up of the laminating and imperforate natural graphite wafers, which are almost planar orientation. There are no pores in the graphite wafers of GP-lid for the diffusion of silicon-carrying gas species under temperature gradient. The EDXA image in Fig. 4d confirmed that there was no silicon carbide formed in the GP-lid. The big crack in the GP-lid, shown in Fig. 4b, was engendered by the cutting and polishing. The polycrystals on the GP-lid can be easily removed from its surface for the weak Van der Waals force between the graphite wafers, which is beneficial to the enlargement of SiC crystal in the next growth process.

Conclusion

The nucleation of SiC polycrystals surrounding the seed crystals during the growth of SiC single crystal via PVT was investigated in this study. Two different carbonous materials, the graphite paper and graphite, were used as the crucible lids to investigate their effects on the inhibition of the growth of SiC polycrystals. XRD and SEM/EDXA were used to examine the structure and morphology of

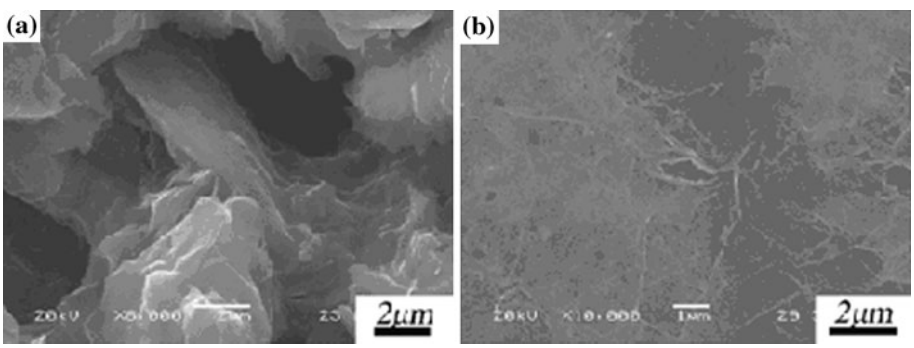

Fig. 3 The surface micrograph of the lids before used **a** G-lid **b** GP-lid

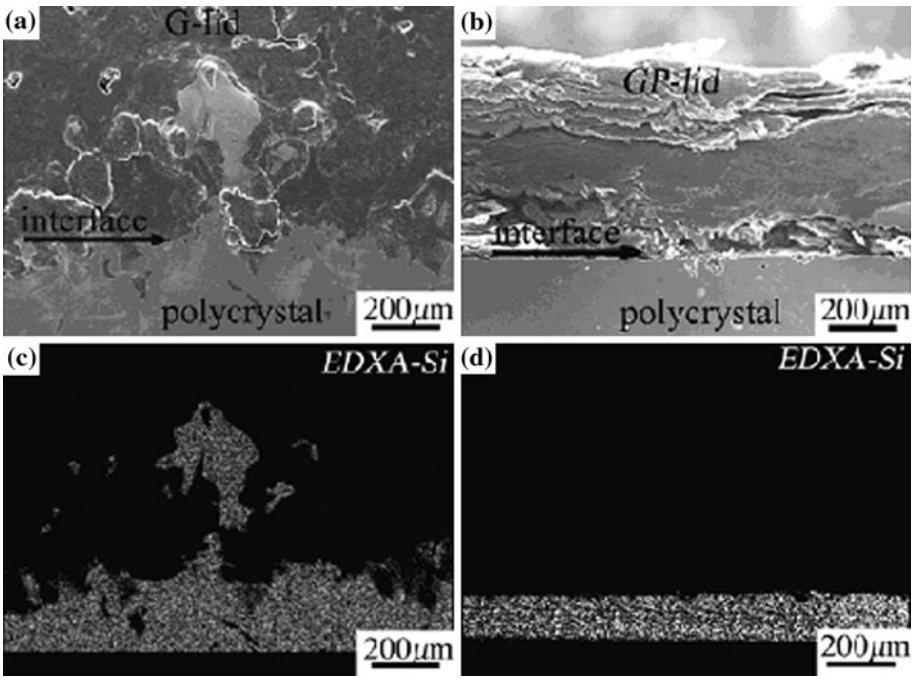

Fig. 4 SEM images of the cross section of the interfaces between polycrystals and different lids (**a, b**) and the corresponding EDXA (**c, d**)

sample. XRD revealed that the graphitization degree of GP-lid is higher than that of G-lid and the surface texture of GP-lid is different from G-lid. SEM micrographs showed that G-lid has a porous and disordered structure and SiC polycrystals are favorable to nucleate and grow on G-lid. The GP-lid has a laminated structure and the nucleation of SiC polycrystals can be well restrained. The polycrystals formed on the lid were more easily removed from GP-lid than that from G-lid because of the weak Van der Waals force between the graphite wafers, which is of great benefits to the further enlargement of SiC crystals.

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