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Thermal Decomposition Cavities in Physical Vapor Transport Grown SiC

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Abstract: The relationship between the formation of thermal decomposition cavities and seed mounting in physical vapor transport grown silicon carbide was investigated. Experimental results indicate that voids exist in the attachment layer between the single crystal seed and graphite crucible lid. These voids lead to the formation of cavities in the seed and grown boule by local decomposition of the seed, transport of silicon bearing species across the void and the deposition of silicon on, and diffusion into, the porous graphite lid. The application of a diffusion barrier on the seed crystal backside is shown to suppress the formation of thermal decomposition cavities.

Introduction

It is well known that hollow tubes form along the c-axis of SiC crystals during physical vapor transport (PVT) growth [1,2]. These defects intersect the surface of (0001) oriented wafers sliced from such boules and limit the usable area of the substrate. It has been argued by the authors that these defects can be divided in two separate classes, micropipes and thermal decomposition cavities (TDC) [3]. The TDCs, also called macrodefects, have been observed by several authors [4-6]. They have noted that thermal decomposition cavities originate at the interface between the SiC seed and the graphite seed holder. Vodakov *et al.* [5] proposed that thermal decomposition cavities form through a recrystallization process, in which SiC is transported across small gaps or liquid droplets at the holder/SiC interface. Similarly, Anikin *et al.* [6] suggested that they form by localized sublimation from the back of the relatively hot seed to a relatively cool graphite seed holder. More recently several authors have stated that voids in the carbonized sucrose attachment layer at the seed crystal/crucible lid interface are responsible for thermal decomposition cavities [7,8]. Tuominen *et al.* [7] have suggested that backside evaporation can be diminished by maintaining the system near the equilibrium silicon vapor pressure. Chourou et. al. [8] have stated that TDCs can be removed by using a mechanical mount instead of carbonized sucrose. They have also observed that the depth of TDCs can be decreased by reducing the growth temperature. This paper has two goals. First it provides evidence for the mechanism by which voids in the attachment layer create cavities. Second, it demonstrates that cavity formation can be suppressed by controlling the homogeneity of the attachment layer.

Experimental

On-axis (0001) 6H-SiC plates, produced by the Lely method [9], were used as seeds for all of the growth experiments. The experiments were carried out in a PVT growth apparatus similar to those described in the literature [2]. The source powder, 1-2 mm grain size high purity Acheson powder, was produced by Elektroschmelzwerk Delfzijl, Netherlands. Two different techniques were used for seed mounting; attachment with carbonized sucrose and a mechanical mount. For the first method sucrose is placed on a graphite crucible lid and melted at a temperature of 200°C . The Lely seed is then placed on top of the melted sucrose, and a small force is applied to it. The attachment layer is baked to 400 °C while the seed is still under load. This results in a carbonized attachment layer. The second method is accomplished by pressing the seed crystal against the lid with a graphite disk and support sleeve.

During each growth run the system is heated in stages to about 1200 °C at a pressure below 3×10^{-4} torr. The system is then backfilled with ultra high purity argon to a pressure of 650 torr. The temperature is gradually increased to the growth temperature of 2300 °C, at a rate of 24°C/min. The duration of individual growth experiments ranged from 15 minutes to 14 hours. The pressure in the growth chamber was maintained at 650 torr during short growth runs to minimize transport of the vapor species. This resulted in slow growth rates of approximately 0.05 mm/hr. For longer growth runs, the pressure is lowered to between 10 to 20 torr. Here, the growth rates were between 0.2 mm/hr and 6mm/hr.

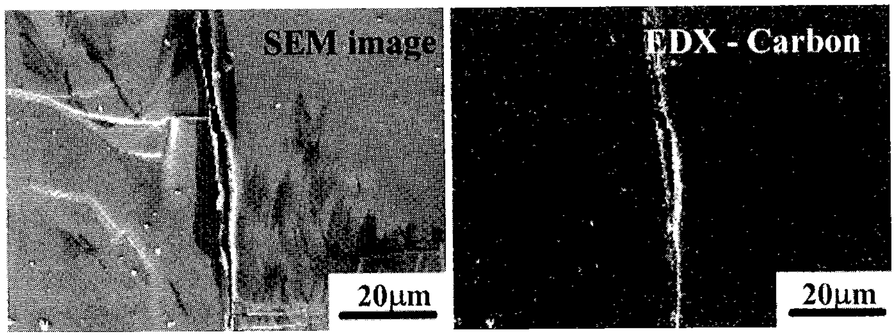

Fig. 1 Cross-sectional image of a thermal decomposition cavity in a 6H SiC crystal grown by physical vapor transport.

Samples for energy dispersive x-ray (EDX) and Auger electron spectroscopy (AES) were cleaved open in order to avoid chemical contamination due to cutting and polishing. Scanning electron microscopy (SEM) and EDX images were obtained at an accelerating voltage of 25 kV on a Philips XL-30 microscope. AES was performed on a scanning Auger spectrometer at an accelerating voltage of 3 kV. Optical transmission images of axial slices from PVT grown SiC were obtained by cutting boules along the c-axis and polishing with diamond paste.

Results and Discussion

Fig. 1 shows a SEM and EDX image of a cleaved surface of a PVT boule grown at 2300 °C and a pressure of 10 torr. The section of the seed was located approximately 4 mm from the seed/crucible lid interface. A tubular void running almost vertically is apparent in both images. The bright areas in the carbon EDX image indicate that the cavity walls have a higher carbon concentration than the SiC matrix. The silicon EDX image (not shown) was in agreement. This result was additionally supported by Auger spectroscopy on the same cleaved sample. The Auger spectrum inside the cavity revealed only carbon while the spectrum taken outside the cavity indicated the presence of silicon, carbon and oxygen. One possible explanation for the observed concentration of carbon in the cavities is local sublimation of the SiC matrix. During PVT growth, SiC sublimes and releases mainly Si, Si_2C and SiC_2 as vapor. Since the vapor is silicon rich, carbon is left behind [10]:

$$SiC(s) \rightarrow Si(g) + Si_2C(g) + SiC_2(g) + C(s) \qquad (1)$$

Due to the axial temperature gradient in PVT growth, it is expected that material from the hot seed will transport across voids in the carbonized attachment layer to the cooler lid. An estimate of this transport rate was obtained by growing on a seed with an intentional gap between the seed crystal and the graphite lid. The lower limit for the transport rate across the intentional gap was 0.5 mm/hour [3]. This is on the same order of magnitude as the typical crystal growth rates in PVT.

In the fashion described above, a Lely seed was mounted on the lid with sucrose. It was then annealed at 2300 °C, 10K/cm, 10 torr, for 15 minutes. Following growth, the seed was removed from the crucible lid, and the backside inspected. Fig. 2(a), an optical image taken in reflection, shows a section of the backside of the seed, and Fig. 2(b), the corresponding area on the graphite crucible (mirrored). There is a one to one relationship between the dark, topographically lower areas on the seed, and the bright, topographically higher areas on the cap. The crucible lid was analyzed with powder x-ray diffraction. Indexing the resulting peaks indicated the presence of graphite and SiC. Based on these observations, it can be concluded that the bright portions on the seed backside are areas where the attachment layer created a bond between the lid and seed. The dark areas on the seed backside show signs of sublimation and correspond to the voids which existed in the attachment layer. Here the seed has locally sublimed, vapor has been transported across the void and deposited on the lid as polycrystalline SiC.

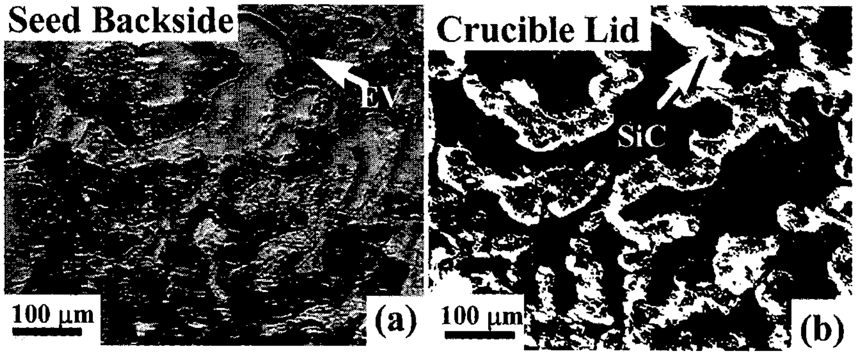

Fig. 2 Optical images of (a) the backside of the seed crystal and (b) the corresponding area of the graphite lid. Dark regions in both images are topographically lower then light regions. The arrow shows where SiC has been deposited on the lid directly under the evaporated region of the seed, EV.

The lid shown in Fig. 2 was fractured along the growth direction and analyzed with EDX. The EDX results indicate the presence of silicon in the graphite lid, up to 200 µm from the mounting surface. The intensity of this silicon signal is comparable to that of SiC. If cavities are to form at voids in the attachment layer then the silicon rich vapor has to be dissipated into the growth system. It is possible that the silicon species diffuses through the porous graphite lid.

The above observations provide an insight to how the formation of TDCs can be suppressed. It suggests that the key to the prevention of TDCs is the existence of a continuous diffusion barrier on the seed backside. To test this, a Lely platelet was cut in half. One half had the backside painted with photoresist of approximately 15 µm thickness and cured at 120°C for 5 min. It was then heated in vacuum ($<3\times10^{-4}$ torr) to a temperature of 1200°C, utilizing a temperature ramp rate of 400°C/h [11]. The resulting carbon layer was smooth and contained no visible cracks or voids. Using the carbonized sucrose method, this seed and an unprotected seed crystal were mounted side by side on the same crucible lid. Both crystals were overgrown simultaneously in the same PVT growth experiment (2300°C, 10 K/cm, 20 torr) for 14 hours. An axial slice parallel to the growth direction was cut from the boule revealing both seed crystals.

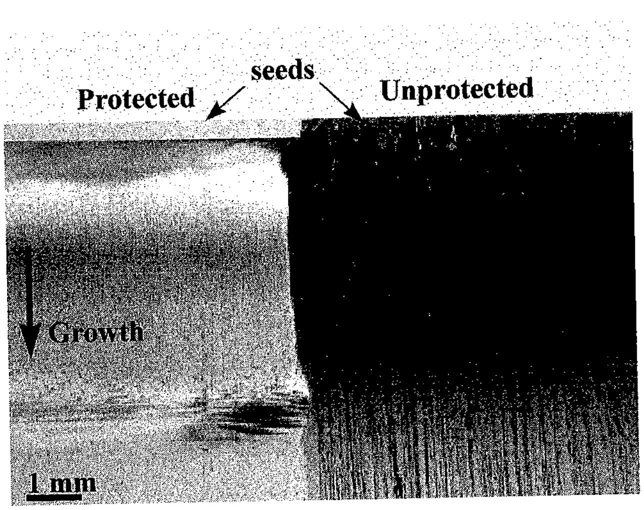

Fig. 3 Transmission optical microscopy image of a cross sectional slice along the c-axis of a dual seed growth. The seed crystal on the left has been protected by the application of a thin continuous film of graphite on the seed backside.

An optical image of the slice in transmitted light is shown in Fig. 3. The protected seed is transparent with no signs of backside decomposition. The seed crystal that was not protected contains thermal decomposition cavities propagating though it. It is apparent that the continuous graphite film on the backside of the protected seed has suppressed the local evaporation, while the TDCs in the unprotected seed are seen to originate at the seed/lid boundary. Further work on optimization of this method is in progress.

Conclusions

Experimental observations support the proposed mechanism for the formation of thermal decomposition cavities during the PVT growth of SiC. Voids in the sucrose attachment layer have been shown to cause local evaporation of the seed crystal backside. Energy dispersive x-ray analysis and Auger electron spectroscopy support this by indicating that the walls of these cavities are decorated with carbon. The vapor released during sublimation was transported across the cavities and along the axial temperature gradient. The vapor either recrystallized on the exposed graphite surface of the lid, or partially diffused into it. A continuous, void-free carbon protection layer applied to the backside of the seed crystal helped to suppress the formation of thermal decomposition cavities at the interface between the seed crystal and the graphite lid.

Acknowledgments

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